Spectroscopic and Structural Insight into the Size-Dependent Behavior of the Nanophase

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Editorial

Spectroscopic and Structural Insight into the Size-Dependent Behavior of the Nanophase

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Nanoscience and nanotechnology demand high-quality spectroscopic characterization and an in-depth understanding of spectral characteristics of nanomaterials. Several methodologies combining microscopy and spectroscopy are adapted to explain the special characteristics of the nanomaterials. In this special issue, it is aimed to bring the recent research papers which explain the special features in spectroscopic data and its analyses in case of nanostructures. Here, we have selected six papers, limited to few spectroscopic techniques. This is of course not the state of the art of total spectroscopic studies in this field. The selected papers in this topic are merely representing the type and trend of work in this area and are not really depicting a complete picture. We thank the authors for their excellent contributions to this issue. The critical reviews and comments by the reviewers are very helpful in improving some of the papers, and their contributions are gratefully acknowledged.

This special issue contains six papers, where five papers deal with vibrational spectroscopy and one paper deals with the electron spectroscopy of nanostructured materials.

The first paper entitled “Phonon spectra of small colloidal II-VI semiconductor nanocrystals” by V. Dzhagan et al. explores the first- and higher-order phonon spectra of several kinds of II-VI nanocrystals using resonant Raman spectroscopy to have a unified view onto the vibrational spectrum of semiconductor nanocrystals. The combinational modes consisting either of longitudinal and transverse or surface optical modes is accounted for the lineshape of the spectrum of the first-order modes. The paper shows that the Electron-phonon coupling-mediated strong Fröhlich interaction in II-VI compounds prohibits observation of second-order transverse and surface optical modes. A broad surface optical mode is found to dominate the resonant phonon Raman spectrum of nanocrystals smaller than 2 nm.

The second paper entitled “Size-dependent non-fret photoluminescence quenching in nanocomposites based on semiconductor quantum dots CdSe/ZnS and functionalized porphyrin ligands” by E. I. Zenkevich et al. shows strong quenching of quantum dots (QDs) photoluminescence (PL) in “QD-Porphyrin” nanocomposites based on colloidal CdSe/ZnS and CdSe QDs surface modified with tetra-meso-pyridyl substituted porphyrin molecules, and its possible origin is reported from steady-state and picosecond time-resolved measurements. QD PL quenching rate constants are found inversely proportional to QD diameter. The comparative study of experimental data and quantum mechanical calculations lead to the inference of QD PL quenching as an effect of tunneling of the electron of the excited electron-hole pair followed by a self-localization of the electron or formation of trap states. The calculated quantum-confined exciton wave function at the QD surface is thought to be the major contributing factor to PL quenching. It has been highlighted in the study that a single functionalized molecule is good enough to be one of the probes for the complex interface physics and dynamics of colloidal semiconductor QDs.
The third paper entitled “Analysis on binding energy and Auger parameter for estimating size and stoichiometry of ZnO nanorods” by S. Bera et al. relates the features of photoelectron spectra with the nanosize tips of ZnO nanorods. The SEM picture of the nanorods shows the rod ends composed of nanosize tips which significantly change the binding energy of Zn 2p photoelectron peaks. The paper explains the shift in binding energy in terms of the change in relaxation energy of the photoelectrons coming out of the nanotips of the oxide.

The fourth paper entitled “Raman spectra of quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals embedded in borosilicate glass” by Azhniuk et al. reports about a set of samples with quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals grown in a borosilicate glass matrix by the diffusion-limited growth technique with three types of cations distributed over nanocrystal lattice sites. The Raman spectra confirm the three-mode compositional behavior of phonon modes in these crystals. The compositional dependence of the longitudinal optical phonon frequencies has been studied for a set of nanocrystalline samples having composition with nearly equal stoichiometry of Se and Te.

The fifth paper entitled “Vibrational spectroscopy of chemical species in silicon and silicon-rich nitride thin films” by K. O. Bugaev et al. reports vibrational properties of hydrogenated silicon-rich nitride of various stoichiometry and hydrogenated amorphous silicon (a-Si:H) films using Raman and Fourier transform infrared (FTIR) spectroscopic techniques. FTIR analyses show formation of Si-H bonds in the thermally and laser-annealed samples of partial crystallized silicon nitride with near stoichiometric composition. On the other hand, Raman spectroscopic analyses show presence of Si-H bonds for a-Si:H films with hydrogen concentration $\leq 15\%$ and existence of Si-H$_2$ bonds for hydrogen concentration of 30–35%. Nanosecond-pulsed laser treatments show crystallization of these films and its dehydrogenization.

The sixth paper entitled “Room temperature synthesis and catalytic properties of surfactant-modified Ag nanoparticles” by W. Li et al. mostly concentrates on the preparation of uniform size nano-Ag particle through wet chemistry route at room temperature. Regular spectral features observed in FTIR and UV absorption spectra along with TEM analyses have been coordinated to understand the character of the nanoparticle. Suspended nano-Ag of size 20–30 nm showed extremely good catalytic property. However, less importance is given in correlating the spectral features observed in FTIR or UV absorption spectra with the size of the nanoparticle, and this is mostly because the sizes are of the order of 20–30 nm.

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Research Article

Phonon Spectra of Small Colloidal II-VI Semiconductor Nanocrystals

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Resonant Raman spectroscopy has been employed to explore the first- and higher-order phonon spectra of several kinds of II-VI nanocrystals (NCs), with the aim of better understanding of the nature of phonon modes and forming a unified view onto the vibrational spectrum of semiconductor NCs. Particularly, besides the previously discussed TO, SO, LO, and 2LO modes, the combinational modes of TO+LO and SO+LO can be assumed to account for the lineshape of the spectrum below 2LO band. No trace of 2TO or 2SO band was detected, what can be the result of the dominance of Fröhlich mechanism in electron-phonon coupling in II-VI compounds. The resonant phonon Raman spectrum of NCs smaller than 2 nm is shown to be dominated by a broad feature similar to the SO mode of larger NCs or phonon density of states of a bulk crystal.

The understanding of the phonon spectrum of semiconductor nanocrystals (NCs), electron-phonon coupling (EPC), dependence of the phonon spectra on the NC size, surface-bound moieties, and extended environment is of a large fundamental and application significance [1–11] due to the determinant role phonons play in the optical and electrical properties of semiconductor nanostructures [12, 13]. Though a number of in-depth studies have addressed the phonon spectra of colloidal [14–20], glass-embedded [21–23] NCs, and epitaxial nanostructures [24–26], a significant divergence of the results exists concerning both the nature of the modes and their response to such factors as size, surface conditions, properties of the hosting medium and so forth. In particular, the apparently similar Raman spectra of a wide range of compounds (e.g., II-VI, III-V, and IV) and NC morphologies (dots, rods, tetrapods, wires, and discs) have been assigned differently.

Recently, attempts were made to build a general picture of the phonon spectrum of various semiconductor NCs, based on analysis of the experimental Raman data and appropriate models [14, 27, 28]. This paper further explores the first- and higher-order phonon spectra of several kinds of II-VI NCs, as well as their similarity to other compounds, with the aim of better understanding of the vibrational spectrum of small NCs. High-quality NC samples were selected for this study in order to resolve Raman features, which are usually smeared by size dispersion, structural disorder, or low signal-to-noise ratio.

The NC samples studied in this work have been prepared by means of colloidal chemistry according to protocols
reported elsewhere [29–32], and CdSe, CdS, and CdTe NC samples of the same mean diameter (~4 nm) were selected. Another sort of NCs studied were ultrasmall NCs of about 1.8 nm mean diameter, which revealed distinct Raman spectra. The attempts to measure the size and shape of these NCs directly by electron microscopy were unsuccessful [19], obviously due to ultrasmall NC size and charging of the stabilizing polymer. The broad X-ray features of these ultrasmall NCs [3] indicated their small size or/and noticeable structural deformations due to dominance of the surface atoms. Therefore, the size of the latter ultrasmall NCs has been estimated from the energy of the first excitonic maximum [19].

The main features observed in resonant Raman scattering spectra of II-VI NCs are the longitudinal optical (LO) phonon mode (fundamental) and its overtones (Figures 1 and 2), which are shifted to lower frequencies and broadened compared to the bulk crystal. The nature of a low-frequency shoulder of the LO peak, commonly observed for different kinds of semiconductor NCs, is still under discussion. It is related either with phonons at $k \neq 0$ [33], surface optical (SO) [23], zone-edge (ZE) [22] phonons, or quantized optical phonons (vibrons) with a quantum number $n > 1$ [17, 34, 35]. Fitting the Raman spectrum in the range of LO mode with two Lorentzians, corresponding to SO (or ZE) and LO phonon or to vibrons with different quantum numbers, is widely applicable for II-VI NCs [15, 18, 23, 36]. However, the similar shoulder has been observed in bulk alloys [37]. The alloys, even defect free, are known to possess a kind of disorder caused by the fluctuation of the electrostatic potential due to the inhomogeneous spatial distribution of the counterpart ions. This kind of disorder, along with the structural disorder, can lead to activation of some vibrational modes (disorder-activated ZE phonons) [37]. Investigation of the surface-related (SO) vibrations in NCs is important not only due to its potential in probing the NC-environment interaction [4], but also because they may take part in the optical transitions in NCs [38].

In a majority of experimental studies, the low-frequency shoulder being not resolved as a separate peak may lead to large errors in determination of its frequency position and widths. In addition, the LO phonon peak possesses in many cases a noticeable high-frequency shoulder (HFS, Figures 1(a) and 1(b)), which probably originates from vibrations...

Figure 1: First-order Raman spectra of CdTe (a), CdSe (b), and CdS (c) NCs in the range of LO phonon with multi-Lorentzian fitting. Indicated is the assignment of the phonon modes.
of tellurium (selenium) on the CdTe (CdSe) NC surface or coupled optical-acoustical phonon modes [28, 29, 32]. Trying to satisfactory fit the whole spectrum in the range of the LO peak without taking into account the HFS can lead to overestimation of the frequency and bandwidth of the SO mode and affect the width of the LO peak and its ratio to overtones.

Our recent study of high-quality and monodispersed CdTe NCs revealed that the fitting of the lower-frequency asymmetry of the LO peak requires at least two components, attributed to TO and SO modes, correspondingly [28]. Here we extend this approach to fitting of the RRS spectra of CdSe and CdS NCs (Figure 1), as well as their overtones (Figure 2). According to this approach [28], the lowest frequency component, peaked at 145 cm$^{-1}$ for CdTe NCs, 177 cm$^{-1}$ for CdSe NCs, and 250 cm$^{-1}$ for CdS NCs, may be assigned to TO mode, because of its frequency proximity to the frequencies for the corresponding bulk crystals. The broad component between this mode and LO may be naturally assigned to the SO mode(s), as predicted by theory [39]. Quantitatively, the SO mode frequency is calculated using the same formalism as in previous works [18, 23, 31]—$\approx 200$ cm$^{-1}$ for CdSe NCs, $\approx 280$ cm$^{-1}$ for CdS, and $\approx 160$ cm$^{-1}$ for CdTe NCs—being in good correlation with the position of the component marked as “SO” in our experimental spectra in Figure 1, as well as with other reports [18, 23, 31].

The general appearance of the first-order resonant Raman spectrum of II-VI NCs studied here (Figure 1) is well reproduced by the model of quantized optical vibrations of spherical NC [34, 35], with the ($l_p = 0$, $n = 1$) vibron corresponding to (fundamental) LO mode. However, as the experimental $\nu_{SO}$ does not vary noticeably with NC size [32], it is unlikely to be related with the ($l_p = 2$, $n = 1$) vibron mode revealing a strong size dependence of its frequency [34, 35]. Instead, the experimentally observed SO mode may be related to the density of $l_p = 2$ vibron modes, centered around 180 cm$^{-1}$ for CdSe and 240–255 cm$^{-1}$ for CdS [34].

Based on a simple qualitative argument of the SO mode intensity, $I_{SO}$, being proportional to the NC surface-to-volume ($S/V$) ratio, the $I_{SO}/I_{LO}$ is expected to increase with NC size decrease. However, this approach may be...
oversimplified and prone to be offset by other factors, for example, by the saturation of the SO vibration intensity below a certain NC size at which the SO mode field extends over the whole NC volume. As a result, no noticeable dependence of $I_{SO}/I_{LO}$ on NC size will take place below certain critical NC diameter, as can be seen in Figure 3 for NC diameter $d$ decreasing from 4 down to 2 nm, with the corresponding $S/V$ increasing almost twice (from about 35 up to 60%). Furthermore, the analysis of the literature shows that the relative intensity of the SO mode can be very close for different NC morphologies and dimensions (dots, rods, tetrapods, and wires) with various $S/V$.

The nonsystematic sensitivity of the SO peak parameters to capping of the CdSe core with a ZnS (or CdS) shell [40] introduces further ambiguity in understanding of the nature of this mode. Based on similarity of the SO mode parameters for different NC morphologies, as well as existence of similar low-frequency asymmetry for bulk alloys [37]; one may assume it to be induced by the presence of atoms with coordination differing from the rest of (bulk) atoms. In NCs, these are the surface atoms with undercoordinated bonds, while in alloys these can be the atoms adjacent to the “impurity” atom or a structural defect. This kind of disorder can lead to activation in Raman scattering of vibrational modes forbidden for perfect crystal, particularly ZE phonons [22].

The ZE phonons, that is, phonons from the boundary of the Brillouin zone, where TO and LO branches approach each other, are forbidden in Raman spectra due to their large $k$ (compared to that of the probing light). However, they can be activated in Raman by a certain degree of disorder in the lattice. The surface of the NC is a case of such a disorder, with the spatial dimension of 1-2 lattice constants—the same length where ZE phonons exist. The probability of the appearance of the surface-related modes in Raman spectrum may be higher in smaller NCs not only due to a larger surface-to-volume ratio but also due to a larger overlap of the carrier’s wavefunction with surface. As to the role of the surface-trapped excitons, it may be not relevant, because the trapping times are usually much longer than the duration of the Raman scattering event.

Though the low-frequency shoulders of the LO overtones resemble strongly that of the fundamental peak, the fitting of the spectra shows that the former cannot be attributed to the nSO modes. The frequency position of the shoulder is much larger than the corresponding $n \times \nu_{SO}$. More viable is the assignment of these shoulders to the SO+nLO ($n = 1, 2$) sum modes (Figure 2). At least the frequency position fits well to such a combination. This assignment can reveal new aspects of coupling between the strongly confined optical phonons in small semiconductor NC. Nevertheless, the contribution of second-order scattering on ZE phonons cannot be excluded and needs further studying. The second-order spectrum is also featured by the high-frequency shoulder centered around 20–40 cm$^{-1}$ above the 2LO band (Figure 2), similar to the HFS in the first-order spectrum (Figure 1).

The structure of the Raman spectrum has been observed to change qualitatively for NC smaller than 2 nm. The first-order spectrum of CdSe NCs as small as 1.8 nm (Figure 4) reveals a broad feature between bulk TO and LO frequencies, thus in the region of the SO mode observed for larger NCs. Simple estimation shows that at $d$ as small as 1.8 nm, most of the atoms can be classified as surface ones and such NCs can therefore be an illustration of a limiting case of small NC which do not support the bulk-like LO (and TO) phonon modes. Their spectrum more likely resembles the phonon density of states (DOS) predicted for bulk CdSe and CdSe nanowires with a diameter of $d = 2$ nm [41] or the spectrum of molecular-like clusters [16, 42]. From the viewpoint of the model based on bulk dispersion curves, the strong spatial confinement along with lattice distortion due to the reconstruction induced by a domination of surface atoms can lead to the situation when only phonons (TO and LO) close to (bulk) zone boundary exist in NCs. These ZE phonons manifest themselves in Raman spectrum as a single broad feature because of a very small TO-LO splitting near
the zone boundary, as has been inferred previously for the description of IR phonon spectra of Cd56Te32 clusters [43].

In conclusion, the resonant Raman spectra of several kinds of II-VI NCs have been analyzed. It is shown that similar set of phonon modes can be derived from fitting the spectra of high enough quality. Particularly, besides the previously discussed TO, SO, and LO modes, the combinational modes of TO+LO and SO+LO can be assumed to account for the lineshape of the spectrum below 2LO band. No trace of 2TO or 2SO band was detected, what can be the result of the dominant Fröhlich mechanism in electron-phonon coupling in II-VI compounds. The resonant phonon Raman spectrum of NCs smaller than 2 nm is shown to be dominated by a broad feature similar to the SO mode of larger NCs or a DOS of a bulk crystal.

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References


Research Article

Size-Dependent Non-FRET Photoluminescence Quenching in Nanocomposites Based on Semiconductor Quantum Dots CdSe/ZnS and Functionalized Porphyrin Ligands

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We review recent experimental work to utilize the size dependence of the luminescence quenching of colloidal semiconductor quantum dots induced by functionalized porphyrin molecules attached to the surface to describe a photoluminescence (PL) quenching process which is different from usual models of charge transfer (CT) or Förster resonant energy transfer (FRET). Steady-state and picosecond time-resolved measurements were carried out for nanocomposites based on colloidal CdSe/ZnS and CdSe quantum dots (QDs) of various sizes and surfacely attached tetra-mesopyridyl-substituted porphyrin molecules (“Quantum Dot-Porphyrin” nanocomposites), in toluene at 295 K. It was found that the major part of the observed strong quenching of QD PL in “QD-Porphyrin” nanocomposites can neither be assigned to FRET nor to photoinduced charge transfer between the QD and the chromophore. This PL quenching depends on QD size and shell and is stronger for smaller quantum dots: QD PL quenching rate constants \( k_q \) scale inversely with the QD diameter. Based on the comparison of experimental data and quantum mechanical calculations, it has been concluded that QD PL quenching in “QD-Porphyrin” nanocomposites can be understood in terms of a tunneling of the electron (of the excited electron-hole pair) followed by a (self-) localization of the electron or formation of trap states. The major contribution to PL quenching is found to be proportional to the calculated quantum-confined exciton wave function at the QD surface. Our findings highlight that single functionalized molecules can be considered as one of the probes for the complex interface physics and dynamics of colloidal semiconductor QD.

1. Introduction

Semiconductor quantum dots (QD), also known as “nanocrystals,” are structures with electronic and optical properties that can be engineered through the size of the structure, not just the composition. During the past decade, colloidal QDs from II–VI semiconductor materials such as CdSe have gained considerable interest due to their physical properties originating from quantum confinement [1–4]. Quantum confinement of charge carriers leads to a wide range of intriguing physical and chemical phenomena and is a new degree of freedom in material design. For instance, advances in the synthesis of semiconductor QDs with controllable size, shape, and optical properties as well as the hybridization of QDs with functional organic ligands make them promising materials for a diverse range of applications including photovoltaics and light emitting devices [3, 5–7], quantum computing [8], biology [9–13], and medicine [14–18].

Several concepts for the realization of QD-dye assemblies have been reported such as blends [19], substitution of surfactant molecules by appropriate dyes [20], tailored polymer-dye shells [21–24], or nanoassemblies based on self-assembly...
processes [14, 25–27]. While quantum confinement is basically understood, the anchoring of functional organic molecules to tunable wide-gap semiconductor colloidal QDs using various approaches is still of considerable scientific and practical interest [9, 11, 15, 28–30], as the particular chemical composition of the surfactant shell decisively affects the photophysical properties of the assembly, especially the PL quantum yield. Colloidal QDs are bright emitters and characterized by a large absorption cross-section [2–4]. However, their photoluminescence (PL) quantum efficiency has shown to be sensitive to a number of influences that originate either from the ligand shell [22–24] or directly from the QD core [31], the QD surface [32–34], and the surrounding matrix [35].

In most cases, formation of QD-dye nanocomposites is followed by QD PL quenching, which is studied both on bulk solutions and single-particle detection level. Commonly, this PL quenching is interpreted as being due to photoinduced charge transfer (CT) [36–38] and/or the energy transfer processes QD → dye [39–48]. To date, though in most cases ample qualitative evidence for the presence of such quenching processes is given, only limited papers unravel quantitatively that the PL quenching (full or in some cases partly, at least) can uniquely be assigned to CT [49, 50] or Förster resonance energy transfer (FRET) for bulk solutions [15, 40, 41, 43, 51–53] and for single QD-dye nanocomposites [47, 48, 54]. From the other hand, PL quenching may be induced by other non-FRET processes [25, 26, 39, 42, 48, 55] as well as may be connected with the involvement of QD surface states [32–34] or the photoinduced self-trapping of charges in the dielectric medium of the environment of QDs [56]. Finally, the dynamical attachment process on QD PL efficiency in QD-dye nanocomposites may be also the reason of an additional PL quenching [57–65].

Correspondingly, from the above considerations, it turned out that in the FRET case for QD-dye nanocomposites, the direct quantitative verification of the energy transfer process as a real reason of QD PL quenching is the comparison of the experimental values of FRET efficiencies obtained, from one hand, via the donor (QD) PL quenching and, from the other hand, via the sensitization of the acceptor (dye or organic ligand) fluorescence. This is often missing in most publications resulting in incorrect assignments of processes and erroneous data evaluation. With these ideas in mind, here we present the detailed photophysical studies of excited states relaxation dynamics for “CdSe/ZnS QD-porphyrin” nanocomposites based on steady-state and PL picosecond time-resolved measurements. The aim of this study is devoted to the quantitative analysis of FRET and non-FRET PL quenching for semiconductor CdSe and/or CdSe/ZnS QDs of various sizes. Especially we claim that a unique and quantitative identification of FRET processes requires a detailed investigation of both the QD donor PL quenching and the dye acceptor fluorescence enhancement, since processes other than FRET and CT will cause QD photoluminescence quenching. In the result, we show that a third mechanism clearly distinct from CT or FRET may cause dye-induced PL quenching (non-FRET) and which is QD size-dependent [63] and related to the extension of the wave function of the excition to the outside of the QD [64].

Although experimental evidence for such QD PL quenching mechanisms causing PL quenching of QDs without a corresponding PL enhancement of the dye molecules attached to their surfaces was reported by Willard et al. for complexes of QDs and tetramethylrhodamine-labeled streptavidin (SA-TMR) already earlier [65], such mechanisms have not been quantitatively discussed in other publications.

2. Experimental Methods

Highly monodisperse CdSe and CdSe/ZnS nanocrystals (or quantum dots, QDs) capped with n-trietylphosphine oxide (TOPO) were used in order to form semiconductor CdSe-porphyrin heterostructures in toluene (or chloroform) at ambient temperature. The colloidal TOPO-capped CdSe and core/shell CdSe/ZnS quantum dots were obtained from Evident Technologies Inc, Troy, NY, USA. The diameters $d_{\text{CdSe}}$ of QD vary between 2.1 and 5.2 nm, while, in most cases, two capping ZnS monolayers were applied. The molar absorption coefficients and core diameters of QDs were calculated from the first exciton absorption peak on the basis of well-proven experimental dependences between the position of the first exciton maximum in absorption and the nanoparticle diameter [67–69]. The absorbance of the QD starting solutions was adjusted to be lower than 0.1 OD at excitation and emission wavelengths in order to avoid nonlinear absorption and reabsorption effects. The concentrations varied in the range $(1 \div 10) \times 10^{-7}$ M. Stability and purity of the QD solutions were checked by measuring the quantum yield stability at least over 3 hrs after preparation.

In our studies, $(5,10,15,20)$-tetra-meta-pyridyl-porphyrin $\text{H}_2\text{P}(\text{m-Pyr})_4$ was chosen as a probe molecule for CdSe QD and CdSe/ZnS core/shell QD covered with 2 ZnS monolayers (ML) [25, 26, 40, 43, 63, 64]. The reason was that among a series of pyridyl-substituted free-base porphyrins, $\text{H}_2\text{P}(\text{m-Pyr})_4$ was found to exhibit the most effective PL quenching of the CdSe QD upon titration. At ambient temperature in toluene solutions, the self-formation of “CdSe/ZnS QD-porphyrin” nanocomposites is realized via two-fold noncovalent ligating coordination Zn···N-Pyr of heteroatoms N (in two adjacent pyridyl rings of porphyrin molecule) with $\text{Zn}^{2+}$ ions (in ZnS core-shell QD), the same key-hole organization principle we have used earlier upon formation of self-assembled multiporphyrin complexes [70–73].

Controllable formation of “CdSe/ZnS QD-porphyrin” nanocomposites has been done via multi-step titration as well as one-step (quasistatic) mixing. Titration experiments were carried out by adding to the QD solution at relative molar ratios $x = [\text{porphyrin}] / [\text{QD}]$ in toluene, thus varying the number of porphyrin molecules on the QD surface. Figure 1 shows a schematic presentation of such a hetero nanoassembly consisting of a QD with the tri-$n$-octyl phosphate oxide (TOPO) surfactant layer and one $\text{H}_2\text{P}(\text{m-Pyr})_4$ molecule attached via its mesopyridyl rings nearly perpendicular to the QD surface.

The absorption spectra of QD and $\text{H}_2\text{P}(\text{m-Pyr})_4$ solutions were recorded with a Shimadzu 3001 UV/Vis and Cary-500 M Varian spectrometers, and emission spectra were
measured with a Shimadzu RF-5001PC spectrofluorophotometer. Time-resolved photoluminescence measurements were carried out in the time-correlated single-photon counting (TCSPC) mode under right-angle geometry using homemade experimental setup [70, 71] based on a cavity-dumped dye laser (Spectra-Physics Models 375B and 344S) synchronously pumped by a mode-locked argon-ion laser (Spectra-Physics Model 171) for the excitation and a Peltier-cooled R3809U microchannel-plate photomultiplier tube (MCP-PMT Hamamatsu) with necessary monochromator and computer photon counting board for the emission detection.

3. Results and Discussion

3.1. Spectral-Kinetic Experiments. Typically, the titration of CdSe/ZnS QD toluene solution by a comparable amount of mesopyridyl-substituted porphyrin molecules $H_2P(\text{Pyr})_n$ manifests itself in the QD PL quenching (the relative intensity decrease and decay shortening [25, 26, 40, 43, 63, 64]. This has been interpreted as being due to the formation of nanoassemblies via anchoring porphyrin ligating molecules on the ZnS surface. As mentioned above, the quenching efficiency and thus the probability to form “QD-porphyrin” nanocomposites scales with the number of pyridyl rings having access to the QD surfaces, being the strongest one in the case of tetrapyridyl substituted porphyrin $H_2P(\text{Pyr})_4$. Figure 2 shows typical transformations of absorption and PL spectra of the QD solution as a function of added monomeric tetra-mesopyridyl-substituted porphyrins $H_2P(\text{m-Pyr})_4$ at well-defined molar ratios $x = [H_2P]/[\text{QD}]$. It is seen that upon increase of the molar ratio $x$, a linear increase of the porphyrin absorption bands takes place, whereas, in all cases, the QD absorption ($\lambda_{\text{max}} = 556 \text{ nm}$) remains constant. On the contrary, the QD PL emission (at $\lambda_{\text{max}} = 585 \text{ nm}$) is
considerably quenched upon titration by H$_2$P(Pyr)$_4$ molecules. Time-resolved PL measurements show that the emission of pure QDs without porphyrin ligand is characterized by a nonexponential decay (Figure 3). The interaction with anchored porphyrin molecules manifests itself in the appearance and rise of two additional short-time components (∼7 ns and ∼700 ps).

All these facts indicate that in “QD-porphyrin” nanocomposites, PL quenching of CdSe counterpart is a dynamic process caused by the increased nonradiative relaxation channels in the excited states of a nanocrystal. The increase of the solvent polarity (an addition of 32 vol% of polar acetone to toluene) enhances an additional decrease of QD PL by more than one order of magnitude. From typical physical reasons (mentioned in Introduction), the observed QD PL quenching may be commonly interpreted as being due to photoinduced charge transfer (CT) [36–38] and/or FRET. The dihedral angles between the donor (QD) PL quenching and the sensitization of the acceptor (porphyrin) fluorescence. Correspondingly for every “QD-porphyrin” nanocomposites under study in this work, the direct comparison of quenching results for QD emission and sensitization data for porphyrin fluorescence was carried out using a complete set of titration points. Using the approach described in [22–24, 74], we estimated FRET efficiencies being obtained via sensitization [39–48].

Usually in the FRET case, the direct verification of the energy transfer process as a real reason of PL quenching is the comparison of the experimental values of FRET efficiencies via the donor (QD) PL quenching and the sensitization of the acceptor (porphyrin) fluorescence. Correspondingly for every “QD-porphyrin” nanocomposites under study in this work, the direct comparison of quenching results for QD emission and sensitization data for porphyrin fluorescence was carried out using a complete set of titration points. Using the approach described in [22–24, 74], we estimated FRET efficiencies being obtained via sensitization effect. This estimation is based on the comparison of the absorption spectra of the QD-H$_2$P mixture solution at every $x$ ratio with the fluorescence excitation spectra of mixed solutions and individual porphyrin (A) solutions at the same molar porphyrin concentration. QD PL quenching data as well as fluorescence excitation spectra (recorded at $\lambda_{em} = 720$ nm) have been obtained at every titration step. Thus, at every titration step, FRET efficiencies $\Phi_{FRET}$ have been calculated from the direct measurements of the corresponding intensities in fluorescence excitation spectra and optical densities (OD) in absorption spectra using the formula

$$\Phi_{FRET} = \frac{I_{DA}(\lambda = 465 \text{ nm}) - I_A(\lambda = 590 \text{ nm})}{I_A(\lambda = 590 \text{ nm})}$$

where $I_{DA}$ corresponds to the porphyrin fluorescence intensity at $\lambda_{em} = 651$ nm for “QD-porphyrin” nanocomposites (i.e., for mixed solutions in the presence of both QD and H$_2$P(m-Pyr)$_4$), whereas $I_A$ is the fluorescence intensity of individual porphyrin at the same molar ratio at two different excitation wavelengths (465 and 590 nm). OD are the corresponding optical densities of the solution at given molar ratio $x$. The difference $I_{DA}(\lambda = 465 \text{ nm}) - I_A(\lambda = 465 \text{ nm})$ reflects the increase of the acceptor emission due to FRET. $\lambda = 590$ nm corresponds to the wavelength, where the absorption of QD is negligible.

Figure 4 presents the comparison of QD PL quenching efficiencies $I(x)/I_0$ and $\Phi_{FRET}$ values estimated via the porphyrin sensitization effect (1) obtained for a given “QD-porphyrin” nanocomposites in all experimental range of molar ratios $x$. It is evidently seen that, at every molar ratio $x$, $\Phi_{FRET}$ values calculated from fluorescence enhancement (right scale) are significantly smaller than those estimated from QD PL quenching efficiency $[\Phi_{QUENCH} = 1 - I(x)/I_0]$. In all titration range, $\Phi_{FRET}$ values are of order 6–10% and do not exceed 14–17% even at high $x$ values. It should be mentioned also that, beginning from $x > 6$, there is a saturation tendency for experimental $\Phi_{FRET}$ values. noteworthy, the same differences between $\Phi_{FRET}$ values (sensitization effect) and $\Phi_{QUENCH}$ efficiencies (quenching effect) have been observed for all “QD-porphyrin” nanocomposites based on H$_2$P(m-Pyr)$_4$ porphyrin molecules and CdSe/ZnS QDs of various sizes.

**Figure 2:** Absorption (a) and emission ((b), $\lambda = 465$ nm) spectra of CdSe/ZnS QD (diameter of CdSe core $d = 3.8$ nm) and H$_2$P(m-Pyr)$_4$ molecules in toluene at 295 upon molar ratio $x$ increase: 0.0 (1); 1.15 (2); 2.3 (3); 4.5 (4); 9.1 (5); 13.5 (6); 17.8 (7).
The obtained results demonstrate clearly that FRET is not a dominant reason of QD PL quenching for “QD-porphyrin” nanocomposites. In addition, for CdSe/ZnS QD of a given size ($d_{\text{CdSe}} = 2.6$ nm and 2 ZnS monolayers), upon the replacement of H$_2$P(m-Pyr)$_4$ molecules by CuP(m-Pyr)$_4$ and tetrahydro-porphyrin, THP(m-Pyr)$_4$ derivatives (thus changing the overlap integral $J(v) = \int_0^\infty f_D(v)\varepsilon_A(v)(dv/v^4)$ values by factor of 2.5), the quenching efficiency of QD photoluminescence remains nearly the same [26, 40]. Thus, FRET QD - porphyrin in “QD-porphyrin” nanocomposites is not the only one mechanism of the total QD PL quenching.

Nevertheless, FRET serves as indicator for the formation of the “QD-porphyrin” nanoassemblies.

From the other hand, it follows that, in the case of moderately exergonic nonadiabatic photoinduced charge (hole or electron) transfer [75], the porphyrin ligand fluorescence in “QD-porphyrin” nanocomposites should be also diminished. Nevertheless, fluorescence parameters (efficiency $\Phi_{\text{FRET}}$ and decay $\tau$) for H$_2$P(m-Pyr)$_4$ molecules upon complexation with QDs remain the same practically with respect to those measured for individual ligands and the same conditions [40]. In addition, the comparative titrations of the same QD solutions by H$_2$P(m-Pyr)$_4$ and THP(m-Pyr)$_4$ (holes acceptor) ligands as well as by H$_2$P(m-Pyr)$_4$(Ph)$_2$ and electron acceptors, H$_2$P(m-Pyr)$_4$(5FPh)$_2$, or H$_2$P(m-Pyr)$_4$(Anthraquinone)$_2$ gives the same curves for QD photoluminescence quenching [26, 40]. Thus, nondependence of QD PL quenching efficiency on redox properties of porphyrin ligands and the absence of the porphyrin fluorescence quenching in “QD-porphyrin” nanocomposites rule out the dominant role of usual photoinduced charge transfer processes with participation of molecular orbitals of porphyrin macrocycle in QD PL quenching for the systems under study.

Following these conclusions in mind, we put our attention on the comparative studies of PL quenching for CdSe/ZnS QDs of various sizes by attached H$_2$P(m-Pyr)$_4$ molecules in all nanocomposites. It is clearly seen from Figure 5(a) that the QD relative integrated PL intensity $I/I_0$ decreases with increasing molar ratio $x = [H_2P(m-Pyr)_4]/[QD]$ in toluene at 295 K. In addition, at the same molar ratios $x$, the observed QD PL quenching is more effective for small QD than for larger ones. In Figure 5(b) these quenching data are depicted in Stern-Volmer presentation $I_0/I(x)$ versus the molar ratio $x$ which is necessary for the subsequent analysis. It is seen that Stern-Volmer plots $I_0/I(x)$ of these results
reveal a nearly linear behavior suggesting that the quenching effect per molecule is approximately constant upon variation of x value during the titration experiment. Correspondingly, we will restrict our following considerations to molar ratios x, where these dependences are linear. This is a concentration range in which on average only a few porphyrin molecules are attached to a QD surface.

As was discussed above, QD PL quenching “QD-porphyrin” nanocomposites is due to two contributions (minor FRET and strong non-FRET). The contribution of FRET to the total PL quenching is at most 10% and hence in most cases negligible. Nevertheless, in order to analyze the main properties on the non-FRET quenching process, we have evaluated the FRET contribution in every case. FRET efficiencies \( \Phi_{\text{FRET}} \) have been found using approach described in \([22–24, 74]\) (see (1) and Figure 4). The corresponding dependences of FRET efficiencies \( \Phi_{\text{FRET}} \) on the molar ratio x for all QDs are shown in Figure 6. Experimental results are presented for QDs of four different CdSe core diameters with 2 ZnS monolayers and one for uncapped CdSe, respectively.
3.2. Analysis of QD Photoluminescence Quenching in “QD-Porphyrin” Nanocomposites. For the analysis of QD PL quenching curves as a function of the number of porphyrin molecules per QD, the well known was modified. In fact more generally, PL quenching may be described in integrated form as

\[ \frac{I_0}{I} = 1 + \int_0^\infty K(x) \cdot dx. \]  

(2)

Here, \( I \) and \( I_0 \) represent the QD PL intensities in presence (\( I \)) and absence (\( I_0 \)) of the attached organic quencher, respectively. In this approach, the Stern-Volmer constant \( K(x) \) depends explicitly on the molar ratio \( x = [\text{H}_2\text{P(m-Pyr)}_4]/[\text{QD}] \) and may be estimated from the experiment at every titration step as the first derivative of the experimental data (numerical differentiation) plotted in Stern-Volmer representation. The corresponding procedure has been carried out for all “QD-porphyrin” nanocomposites under study. Further, the Stern-Volmer function \( K(x) \) is expressed by

\[ K(x) = k_q \cdot \tau_0, \]  

(3)

where the variable \( k_q \) corresponds to the total quenching rate constant induced by the attached quencher and \( \tau_0 \) to the intrinsic PL decay of alone QD in absence of porphyrin molecules. Because of nonexponential decays for QDs under study (what is typical for the most of these objects [2–4, 76]), we are operating with mean values (\( \tau \)). FRET part in QD PL quenching (even minor) has been subtracted in every case.

Table 1 collects information on structural and spectral-kinetic properties of CdSe and CdSe/ZnS QDs under study as well as FRET and PL quenching parameters for “QD-porphyrin H2P(m-Pyr)4” nanocomposites in toluene at 295 K. For better accuracy, the mean quenching rate constants (\( k_q \)) were summarized from up to four titration series for each QD size. It has been found that in the region of molar ratio of \( x = 0.5 \div 8 \), a nearly linear behavior of Stern-Volmer plots \( I_0/I(x) \) is observed for all QDs. Our calculations according to (3) show that in this region for every given “QD-porphyrin” nanocomposites with fixed QD size, the mean quenching (\( k_q \)) values remain constant but differ significantly upon CdSe core diameter \( d_{\text{CdSe}} \) changing or ZnS shell removing. As it is obvious from Table 1, the quenching rate constant \( k_q \) characterizing non-FRET and major contribution in QD PL quenching is monotonically decreasing with the QD core diameter increase. For comparison, the CdSe QD without ZnS shell (Snapdragon Orange) shows a much stronger quenching with respect to ZnS core/shell QD (Hops Yellow).

As was discussed above, in case of “QD-porphyrin” nanocomposites, an effective photoinduced charge transfer leading to QD PL quenching could be excluded. For this reason, we will concentrate in the following discussion on the development of a microscopic model for that kind of PL quenching which is—with respect to attached porphyrin molecules—different from FRET or charge transfer. We have shown recently that for this QD PL specific quenching, the detailed nature of the electronic structure of the porphyrins is negligible [26, 40, 77]. Thus, we will pay our attention presumably to those aspects which are related directly to the outer interface of a QD as a function of CdSe core size and ZnS shell thickness.

It is known from previous experiments [26, 40, 66] that the porphyrin molecule attaches via two lone-pair nitrogen orbitals of the pyridyl ring to the QD surface in a presumably perpendicular geometry shown in Figure 1(a) Nitrogen lone-pair orbital is considered to form a coordinating bond with Zn or Cd atoms at the QD surface. Noteworthy, the attachment of pyridine molecule via one nitrogen orbital to QD at the same molar ratio does not manifest in a noticeable PL quenching with respect to pyridyl substituted porphyrins [40]. We apt to believe that the inductive and mesomeric effects (leading to the bond polarization and electronic density shifts [78]) are characteristic, namely, for pyridyl substituted porphyrin macrocycles (discussed in [40]) and may lead to the formation of specific sites on QD surface at interface [79]. This distortion of the charge distribution corresponds to the creation of an “effective” charge seen by the exciton and will enhance the nonradiative decay of excitons, showing up as PL quenching or a reduced quantum efficiency. We borrow from currently accepted blinking models [80] the idea that a charging of a QD (or molecule) is the major source of both PL intermittency and PL quenching. In the result, at the outer interface of “QD-porphyrin” nanocomposites, two contributions seem to be important: (i) the presence of specific “binding” sites with a distortion of the charge distribution capable to trap exciton and (ii) the evanescent wave function of the confined exciton “leaking” out of the core (and the ZnS shell) of the QD.

With respect to QDs, it is well known [2, 4, 81, 82] that quantum confinement of the excitonic wave function in its most simple version confines the wave function of the exciton (electron-hole pair) to a spherical box. As in any related quantum mechanical problem, the wave function may extend beyond the imposed barrier or, in other words, the corresponding particle may tunnel through the barrier. Considering hole and electron independently, as the confinement for the latter is much smaller due to its lower effective mass, we may safely assume that the tunneling probability for the electron is higher as compared to the hole. Thus, the following considerations are limited to the behavior of the electron wave function, especially, at the interface between the QD and the functional mesopyridyl group of the attached porphyrin macrocycle.

The general ideas of our model and calculation results are depicted in Figure 7(a). In addition to the coordination of a mesopyrold ring to the surface, the electron wave function at the QD outer interface is schematically shown. Imposed by the porphyrin attached to the surface, the electron wave function is locally perturbed due to the specific attachment of mesopyridyl-substituted porphyrin (i.e., the presence of the nitrogen lone-pair orbital forming a surface state subsequently trapping the electron of the photogenerated exciton). It is assumed that the particular influence of the nitrogen lone-pair to be independent of the QD size.

It follows from above considerations that all observed size dependence of the PL quenching (as expressed by the
Table 1: Structural and spectral-kinetic properties of CdSe and CdSe/ZnS QDs as well as FRET and PL quenching parameters for “QD-porphyrin H_2P(m-Pyr)_4” nanocomposites in toluene at 295 K.

<table>
<thead>
<tr>
<th>Quantum dots (Evident Technologies Nomenclature)</th>
<th>λ\text{max}^{a}, nm</th>
<th>CdSe core diameter\text{b} d, nm</th>
<th>ZnS ML number\text{c} \text{n} \text{l}</th>
<th>QD PL decay\text{d} \langle \tau_0 \rangle \text{ns}</th>
<th>Stern-Volmer constant\text{e} \langle K_{SV}(x) \rangle</th>
<th>QD PL total quenching rate constant\text{f} \text{k}_q \text{ns}^{-1}</th>
<th>FRET “QD-porphyrin” rate constant\text{g} \text{k}_{\text{FRET}} \text{ns}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Snapdragon Orange</td>
<td>568</td>
<td>3.5</td>
<td>—</td>
<td>3.5</td>
<td>20 ± 5</td>
<td>0.80 ± 0.12</td>
<td>0.041 ± 0.016</td>
</tr>
<tr>
<td>Lake Placid Blue</td>
<td>476</td>
<td>2.1</td>
<td>2</td>
<td>4.3</td>
<td>35 ± 6</td>
<td>0.65 ± 0.10</td>
<td>0.018 ± 0.010</td>
</tr>
<tr>
<td>Hops Yellow</td>
<td>548</td>
<td>3.0</td>
<td>2</td>
<td>5.2</td>
<td>25 ± 6</td>
<td>0.115 ± 0.015</td>
<td>0.0057 ± 0.0023</td>
</tr>
<tr>
<td>Fort Orange</td>
<td>587</td>
<td>4.1</td>
<td>2</td>
<td>6.3</td>
<td>20 ± 5</td>
<td>0.055±0.007</td>
<td>0.0027±0.0016</td>
</tr>
<tr>
<td>Maple Red</td>
<td>613</td>
<td>5.2</td>
<td>2</td>
<td>7.3</td>
<td>13 ± 4</td>
<td>0.020 ± 0.003</td>
<td>0.0015 ± 0.0009</td>
</tr>
</tbody>
</table>

\(^{a}\)Maximum of the first excitonic band in absorption (λ_{\text{max}}).

\(^{b}\)Found from the first exciton absorption peak on the basis of well-proven experimental dependences between the position of the first excitonic maximum in absorption and the nanoparticle diameter [60–62].

\(^{c}\)Number of ZnS monolayers were known from the producer (Evident Technologies), thickness of ZnS shell at \text{n} = 2 \text{ ML} is \text{l} = 10 \text{ Å}.

\(^{d}\)Mean PL decay was calculated as \langle \tau \rangle = \sum_i A_i \tau_i^2 / \sum_i A_i \tau_i.

\(^{e}\)Estimated from experimental Stern-Volmer plots (2).

\(^{f}\)Calculated from (3).

\(^{g}\)Found from experimental data presented in Figure 6(b).
respectively. Solutions were obtained by applying continuity relations for the single-carrier wave functions at the interfaces between the CdSe core \((i = 1)\), ZnS shell \((i, j = 2)\), and matrix \((j = 2)\), respectively, by assuming
\[
\psi_i(r_{ji}) = \psi_j(r_{ji}) ,
\]
(5)
\[
\frac{1}{m_i^*} \frac{d}{dr} \psi_i(r) \bigg|_{r=r_{ji}} = \frac{1}{m_j^*} \frac{d}{dr} \psi_j(r) \bigg|_{r=r_{ji}} .
\]
(6)

The Schrödinger equation was numerically integrated by means of an ordinary differential-equation (ODE) solver tool for java (RK 4/5 MultiStep) available via OpenSourcePhysics [83]. The ODE solver tool was based on a 4/5-order Runge-Kutta algorithm with variable step width. The results were verified with a second-order Runge-Kutta algorithm implemented in Fortran. Technically, the calculation resembled a shooting method which allows the calculation of wave functions in a one-dimensional or radially symmetric potential landscapes. For the calculations of \(\psi^2(r)\), the following parameters were used: energy barriers of 2 eV for the CdSe/ZnS interface [84] and 4 eV for the ZnS/matrix interface [81], and relative effective electron masses of 0.13, 0.52 and 1.00 in the CdSe core, in the confined ZnS shell, and in the surrounding matrix, respectively [4, 85]. We assumed a 1s-wavefunction confined in QD. For an even function like 1s, PSIn = 1 and PSIn+2 = 1 are given. The core of a shooting method is the value of the wave function at radial position PSIn + 2 is calculated from the values at PSIn + 1 and PSIn. Accounting for the discontinuities at the interfaces, the calculation of PSIn + 2 was altered to (6) whenever an interface was reached.

Figure 7: Scheme of QD PL quenching model. (a) Scheme of the electron delocalization in the excited CdSe/ZnS QD being attached with mesopyridyl-substituted porphyrin molecule. Upon excitation, an electron-hole pair (exciton) is created in the QD CdSe core. The electron is delocalized over the core and the ZnS shell. As a result of the finite ZnS energy barrier \(E_{ZnS}\), the electron can tunnel to the ZnS surface (and to the environment). Upon interaction with the lone-pair of a pyridyl group of a porphyrin molecule, the electron becomes partly localized in the vicinity of the attachment site. (b) Calculated radial part of the probability density function (and to the environment). Upon interaction with the lone-pair of a pyridyl group of a porphyrin molecule, the electron becomes partly localized in the vicinity of the attachment site. (b) Calculated radial part of the probability density function \(\psi(r)\) for 1 electron in a multi shell spherical potential for five QDs of different sizes: 1—CdSe = 3.5 nm, \(n = 0\); 2—CdSe = 2.1 nm, \(n = 2\); 3—CdSe = 3.0 nm, \(n = 2\); 4—CdSe = 4.1 nm, \(n = 2\); 5—CdSe = 5.2 nm, \(n = 2\) (calculation details are presented in the text).
Figure 8: Comparison of the experimentally determined quenching rate constants $k_q$ with respect to the calculated $\psi^2(r)$ values for “QD-porphyrin” nanocomposites in toluene at 295 K. (Left axis) Averaged (for molar ratios $x = 0.5 \div 8$) quenching rate constant $k_q$ for QD PL quenching induced by attached H$_2$P(m-Pyr)$_4$ molecules for one uncapped (open marker) and four ZnS-capped (solid markers) CdSe QDs. 2R = d$_{CdSe}$ corresponds to the CdSe core diameter and D to the ZnS ML thickness. (Right axis) Calculated size-dependent curves for the probability density functions $\psi^2(r = R + D)$ of a 1 s electron at the outer interface $(r = R + D)$ between the ZnS shell and the environment for various ZnS shell thicknesses $D$ for a potential barrier energy of 2 eV between the CdSe core and the ZnS shell, and a barrier energy of 4 eV between the ZnS shell and the matrix. The constant C (see (7)) has been adjusted with respect to $\psi^2(R + D)$ to fit the experimental value for QD with $d_{CdSe} = 4.1$ nm and the number of ZnS monolayers $n = 2$ ML. QD parameters: 1—$d_{CdSe} = 3.5$ nm, number of ZnS monolayers $n = 0$; 2—$d_{CdSe} = 2.1$ nm, $n = 2$; 3—$d_{CdSe} = 3.0$ nm, $n = 2$; 4—$d_{CdSe} = 4.1$ nm, $n = 2$; 5—$d_{CdSe} = 5.2$ nm, $n = 2$.

Figure 7(b) shows the calculated $\psi^2(r)$ values of an $s$-type electron wave function for four CdSe/ZnS QDs with $n = 2$ ZnS monolayers and one CdSe QD without a ZnS monolayer. It can be evidently seen that $\psi^2(r)$ becomes smaller at the outer interface (marked by a circle) upon increasing QD diameter. The corresponding value is largest for the uncapped CdSe QD ($R = 1.8$ nm). Our results are quantitatively in close agreement with other calculations [35] considering solvent effects upon optical band gap energies. We can, however, neglect direct contributions to the band gap, since we did not observe any spectral shifts of the PL upon assembly formation [25, 26, 40, 77]. Then, correspondingly, the calculated $\psi^2(r)$ values for every QD may be directly compared to the observed size dependence of the QD PL quenching for “QD-porphyrin” nanocomposites (as expressed by the quenching rate $k_q$ in Table 1). This comparison may be presented as follows:

$$k_q(r) = C \psi^2(r). \quad (7)$$

It should be noted in this respect that the constant C contains all specific properties of the binding process and cannot be determined quantitatively in our model. In case that the interaction of the chromophore at the interface may not be approximated by a point-like interaction, the constant $C$ in (7) should be modified to $C = A/4\pi r^2$, where $A$ corresponds an “effective molecular interaction area”.

Correspondingly, Figure 8 shows the comparison of the experimentally determined quenching rate constants $k_q$ with respect to the calculated $\psi^2(r)$ values both as a function of the QD core diameter $2R$ and the number of ZnS monolayers. The theoretical lines correspond to calculated $\psi^2(r)$ values shown in Figure 7(b), with one and the same proportionality constant $C$ determined in a way that the theoretical predictions for all QD capped with 2 monolayers ZnS agree with the experimental values most closely. It is clearly seen that experimental quenching rate constants $k_q$ follow closely the calculated $\psi^2(r)$ behavior for all nanocomposites based on QDs having $n = 2$ ZnS monolayers. Thus, this good coincidence between size-dependent PL quenching rate constants and calculated amplitudes of the exciton wave function supports strongly our model that a well defined chromophore-induced surface quenching mechanism other than FRET and/or photoinduced charge transfer is the main reason for QD PL quenching in “QD-porphyrin” nanocomposites. In fact, the dependence of QD PL quenching on the QD size and ZnS shell thickness (induced by only one single mesopropylid porphyrin molecule at low molar ratios) clearly resembles the tunneling of an electron (through the ZnS barrier) to the outer interface of the QD. Such tunneling is followed by the (self-) localization of the electron-hole pair (due to inductive and mesomeric effects) which opens new nonradiative channels via enhanced electron-photon coupling. The consequence is that the quantum efficiency of the subsequently photogenerated exciton will be reduced. Correspondingly, fluctuating bond formations at the QD surface (followed by changes in local charge densities or formation of surface states) result in fluctuating quantum efficiencies of the QD which are closely related to lifetime fluctuations and blinking observed for single quantum dots [86, 87].

Additionally, data presented in Figure 8 show that in spite of our model works well for capped CdSe/ZnS QDs, the quenching rate constant $k_q$ for the uncapped CdSe (point 1) is experimentally below the theoretically predicted $\psi^2(r)$ value. The reason for that might be twofold. (i) Due to differences in the binding constant of the chromophore, the Cd···N coordination is supposed to be weaker than a Zn···N one and thus the average number of porphyrins attached to the surface will be smaller which will be accompanied by a reduced quenching. This implies that we have as compared to ZnS capping to consider a smaller molar ratio $x$. In case we would be able to correct for this quantitatively, $K(x)$ would increase towards values imposed by our model calculations. (ii) Calculating $\psi^2(r)$ depends critically on the respective barrier energies at the interface, which are not known with high accuracy.

Finally, the central interpretation of QD PL quenching in “QD-porphyrin” nanocomposites is that already one or a few point-like charge density modifications in the surfactant layer (composed of ligands and the attached chromophore with specific $\pi$-electron distribution) will lead to local energy minima that force one of the charge carriers of the exciton to become localized. The participation of localized charges...
is strongly supported by the observation that porphyrin-induced PL quenching significantly increases upon increase of the polarity of the solvent [88]. In addition, previous nanosecond time-resolved PL experiments show that, upon formation of nanocomplexes (in which only a few porphyrins are involved), the overall reduction of the quantum efficiency is accompanied by a shift of the nonexponential PL decay kinetics towards shorter decay times [26, 88]. We like to stress again that the presently discussed mechanism for QD PL quenching is completely distinct from the known mechanism of the photoinduced charge transfer between interacting inorganic and organic counterparts.

4. Conclusions

We could prove the complexation of tetra-mesopyridyl-substituted porphyrin molecules, H2P(Pyr)4 to CdSe/ZnS or CdSe QD surface by steady-state titration and time-resolved fluorescence measurements. At 295 K, the formation of “QD-porphyrin” nanocomposites manifests itself in the QD PL quenching (the relative intensity decrease and decay shortening). At the same molar ratios \( x = [H_2P(m-Pyr)_4]/[QD] \), the quenching is more effective for small QDs than for larger ones. It follows from experimental Stern-Volmer PL quenching plots \( I_0/I(x) \) and quantum mechanical calculations for the electron wave functions that the specificity of the excitation nonradiative decay in “QD-porphyrin” nanocomposites is due to the charge tunneling through ZnS barrier in quantum confinement conditions. We have shown quantitatively that a third mechanism clearly distinct from Förster resonant energy transfer (FRET) and the photoinduced charge transfer between the QD and the chromophore may cause the ligand-induced QD PL quenching (the so-called non-FRET). These observations are in line with the microscopic understanding of blinking phenomena of single QD. The experimental findings and conclusions done on their basis highlight that single functionalized molecules can be considered as one of the probes for the complex interface physics and dynamics of colloidal semiconductor QD. The presented results should be taken into account upon the development of nanosensors based on semiconductor CdSe QDs and organic analytes of various types.

Acknowledgments

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Research Article

Analysis on Binding Energy and Auger Parameter for Estimating Size and Stoichiometry of ZnO Nanorods

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ZnO nanorods prepared through chemical vapor deposition technique are characterized by microscopic and X-ray photoelectron spectroscopy (XPS) techniques to correlate the effect of size on the binding energy of Zn 2p3/2 photoelectrons. A positive shift in Zn 2p3/2-binding energy as compared to that in bulk ZnO is assumed to be the effect of size of ZnO tips. The shift in binding energy has been explained in terms of relaxation energy in the photoemission process. Simultaneously, Auger parameter of the nanorods is evaluated for stoichiometric composition. The extra peak in O1s spectrum of nanorods is explained as adsorbed O-bearing species or surface contaminants.

1. Introduction

One-dimensional (1-D) nanostructures of semiconducting materials have received much attention in recent years, with the expectation that they can be applied to short-wavelength optical devices and excitonic devices operating at room temperature. In particular, the exciton-binding energies in GaN and ZnO are reported so large that they can be applied to laser devices based on excitonic processes. In fact, exciton-related stimulated emission and optically pumped laser action in GaN and ZnO nanostructures have been observed at room temperature [1, 2]. Its high band gap energy of 3.37 eV at room temperature [3] and free-exciton binding energy (60 meV) [2] which is much larger than that of GaN (~25 meV) [1] along with its larger absorption coefficient compared to GaN make ZnO a potential candidate for optoelectronics applications. A detailed photoluminescence (PL) study at low temperature with assignments of excitonic peaks and associated longitudinal optical (LO) phonon replicas along with donor-pair-acceptor transitions has been reported for ZnO single crystalline sample [4]. Looking at the importance in the understanding of electronic properties for the ultimate optoelectronic applications, a study on the effect of size dispersion on electronic properties will be extremely important.

We report here the photoelectron spectroscopic studies of stoichiometric ZnO nanorods (NRs), grown by catalyst-free chemical vapor deposition (CVD) technique, with sharp facets. Role of size in these nanostructure on the binding energy of photoelectrons is studied in the light of final state effects of the photoemission process.

2. Experimental Details

ZnO NRs were grown on p+-Si (~0.001 Ohm-cm) substrate in the flow of N2/O2 (500 sccm) at 130–140°C by CVD technique using metalorganic precursor of zinc bisacetylacetonate hydrate [Zn(AA)2·xH2O; Zn(C5H7O2)2·xH2O] [5]. The morphology of the NRs was studied using field emission scanning electron microscopy (FESEM; M/S Carl Zeiss, Model Supra 55).

X-ray photoelectron spectroscopy (XPS) studies were carried out in an ultrahigh vacuum chamber fitted with dual X-ray sources (VG ESCA LAB MKII). Al Ka was used as the exciting source (1486.6 eV) of photoelectrons, and a hemispherical analyzer (150 mm diameter) was used for energy analysis. The pass energy for the high-resolution scan was kept at 20 eV. The spectrometer was calibrated by recording the binding energy of Au 4f7/2 peak at 83.9 eV. C1s peak at 284.6 eV was taken as an internal standard for correcting...
the shift in binding energy peaks due to charging of the samples which was amounting to 3.9 eV for nanorods and 0.8 eV for the bulk powder. The accuracy of measurement of the binding energy is ±0.1 eV and uncertainty ≤0.2 eV.

3. Results and Discussion

3.1. Morphological Studies. FESEM images show well-aligned NRs with diameters ~100 nm (for different orientations in Figure 1) grown using CVD technique. Structural details including small facets ~5–10 nm of the aligned NRs are reported elsewhere [5].

3.2. Photoelectron Spectroscopic Studies. Detailed XPS analyses on ZnO NRs and bulk ZnO powder were carried out by recording Zn 2p, O1s, and Zn LMM Auger lines. The photoelectron spectra from bulk ZnO powder were taken as reference peaks of Zn 2p or O1s and compared with those obtained from NRs prepared by the above method.

3.2.1. Modified Auger Parameter. Modified Auger parameter is an important energy parameter for identifying the chemical state of elements where chemical shift is very small or comparable with the energy resolution of the instrument. The chemical shift of Zn 2p3/2 peak is very small in ZnO and thus is difficult to identify the chemical state of Zn in ZnO. Finding modified Auger parameter (α′) can be an ideal method to get the chemical state and stoichiometry of ZnO NRs. In principle, the parameter is calculated by adding the binding energy of the most intense photoelectron peak with the kinetic energy of the sharpest Auger peak. For ZnO samples, the Auger parameter was calculated by taking the binding energy of Zn 2p3/2 photoelectron peak and kinetic energy of Zn L3M45M45 Auger peak (Table 1).

Table 1: Binding energy and modified Auger parameter (m-AP) obtained from different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn 2p3/2 (FWHM) (eV)</th>
<th>Zn L3M45M45 (eV)</th>
<th>m-AP (a′) (FWHM) (eV)</th>
<th>O1s (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NRs</td>
<td>1022.1 (1.9)</td>
<td>988.3</td>
<td>2010.4</td>
<td>529.9 (1.6)</td>
</tr>
<tr>
<td>ZnO Bulk</td>
<td>1021.6 (1.9)</td>
<td>988.8</td>
<td>2010.4</td>
<td>529.9 (1.6)</td>
</tr>
<tr>
<td>ZnO Bulk [6]</td>
<td>1021.7</td>
<td></td>
<td>2010.5</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2. Analysis on Zn 2p3/2 Photoelectron Peak. In Figure 2, the Zn 2p3/2 peak obtained from ZnO NRs is compared with that from bulk ZnO. The Zn 2p3/2 peak from bulk Zn was recorded at 1021.6 eV with peak width 1.9 eV which matches well with the literature value [6]. In case of aligned ZnO NRs, the peak was seen to be shifted to 1022.1 eV without changing the peak width as compared to bulk powder (Table 1).

The shift in binding energy is combination of two contributions, (i) true chemical shift of the level due to charge redistribution in process of chemical interaction and (ii) the shift due to the final state effects of the photoemission process. The shift in binding energy originating from the final state effects is explained in terms of relaxation energy involved in the process. In the photoemission process, the holes created undergo relaxation by recombining with electrons. During this process, the kinetic energy of the outgoing electron is influenced by the screening effect of the hole. It has been observed that when the cluster size ~5 nm, the relaxation is too significant to give a remarkable increase in binding energy compared to bigger clusters, as observed in case of Ag nanoparticles [7, 8]. In the presence of large number of atoms in bulk ZnO, the relaxation effect is smeared out. On the other hand, the effect is prominent with less number of electrons involved in the screening of the holes created in the photoemission process for nanosized crystal.

The shift in binding energy in ZnO NRs assembly compared to bulk ZnO carries important information. In the work by Radnik et al. [9] on Au nanoparticles, it was indicated that nanostructures of the order of 3–5 nm undergo relaxation effects. ZnO NRs are known to grow in spirality by attachment of nanotips of dimension below 5 nm [10]. In the present case, the end of the nanorods are expected to have isolated nanotips on each nanorods. The photoelectron signal from the NRs is basically contributed from these tips ~5 nm [5]. It is right to say that majority of photoelectrons are coming from the mean free path depth of Zn 2p3/2 electrons which is of the order of 2 nm [9]. When the cluster size is of the order of 5 nanometers, the shift due to relaxation energy dominates very much compared to that in the bulk ZnO. This resulted in a reduced kinetic energy of the outgoing photoelectrons which resulted in an increase in binding energy. The narrow peak width of the Zn 2p3/2 signifies the uniform size of the nanotips of the rods.

Determination of Auger parameter was observed to be a useful tool to find stoichiometry of the surface of oxides [11, 12]. In Table 1, the modified Auger parameter of the NRs is shown and is compared with the bulk value of ZnO. The modified Auger parameter was seen at 2010.4 eV which is exactly matching with the value for bulk ZnO [6]. This indicates the formation of stoichiometric ZnO in the nanotubes even at the surface of NRs.

It is observed that though the relaxation energy of around 0.5 eV is developed in the photoemission process due to particle size, the effect has no contribution to the value of the Auger parameter. It has been observed earlier in case of Ag nanoparticles [13] that the change in binding energy due to change in the particle size also leads to the change in Auger peak energy [13]. In the present case, it is also expected that there is a corresponding negative shift in Auger kinetic energy in the relaxation process which nullifies the size effect on Auger parameter.

The importance of determination of Auger parameter is lying in the interpretation of O1s peak. In Figure 3, the O1s peak acquired from ZnO NRs is shown and is compared with bulk ZnO. The O1s peak at 529.9 eV contributed to the O2− ions in the ZnO lattice and is surrounded by Zn ions and hence indicates the bonding of ZnO. The higher energy peak at 531.9 eV has been observed earlier [14–16] and has been interpreted as defect oxygen [14] or the oxygen containing surface contaminants [16]. However,
Figure 1: FESEM image of aligned ZnO NRs with diameters ~100 nm in different orientations.

Figure 2: Zn 2p\textsubscript{3/2} photoelectron spectra obtained from bulk ZnO, and aligned NRs.

Figure 3: O 1s photoelectron spectra obtained from bulk ZnO, and aligned NRs.

the Auger parameter value strongly denies the presence of O defect sites at the surface. In general, the surface −OH may contribute to the peak at this binding energy which indicates the presence of adsorbed hydroxide or surface contamination [16]. As XPS technique includes below-surface information also, it may appear that the −OH might have originated from the bulk of ZnO NRs, but an information depth ~2-3 nm with probe energy of Al K\textsubscript{α} (1486.6 eV) can be considered as surface where the presence of −OH groups are postulated. We can also state here that XRD of the sample did not show any phase other than the ZnO [5].

4. Conclusions

In conclusion, the binding energy of Zn 2p\textsubscript{3/2} photoelectrons from ZnO NRs showed a significant shift in binding energy compared to its bulk value. The shift in binding energy is attributed to the presence of nanotips on the rods of size ~5 nm. The Auger parameter value, however, was not changed in NRs indicating the formation of stoichiometric ZnO nanorods.

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References


Research Article

Raman Spectra of Quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ Nanocrystals Embedded in Borosilicate Glass

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A series of samples with quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals with cations of three types distributed over nanocrystal lattice sites were grown in a borosilicate glass matrix by the diffusion-limited growth technique. Their Raman spectra confirm the three-mode compositional behaviour of CdS$_{1-x-y}$Se$_x$Te$_y$ phonon spectra. The compositional dependence of the LO phonon frequencies is analysed experimentally for a series of samples containing nanocrystals with $x \approx y$.

1. Introduction

Within recent decades, II–VI semiconductor nanocrystals, obtained by various techniques, have attracted continuous interest due to the size tunability of their optical properties, resulting in numerous applications [1–4]. Raman spectroscopy has proved to be a reliable tool for fast and non-destructive characterization of ternary II–VI nanocrystals, namely, the determination of their chemical composition for both one-mode and two-mode systems [5–19]. In two-mode ternary systems (CdS$_{1-x}$Se$_x$, CdSe$_{1-x}$Te$_x$), the nanocrystal composition is usually determined from the difference of frequencies of LO phonons corresponding to the two sublattices of the nanocrystal [5, 10, 12–14, 19] or from their intensity ratio [5, 6]. In one-mode systems (Cd$_{1-x}$Zn$_x$S), a good measure of composition is the LO phonon frequency which varies continuously with the component ratio. Among the ternary nanocrystal systems, the most widely studied is CdS$_{1-x}$Se$_x$ [5–8, 10, 12–14, 16, 19] where much attention has been paid to nanometer-size-related effects on the Raman spectra (phonon confinement, marked contribution of surface phonons due to the high surface-to-volume ratio, glass matrix pressure, size dispersion of NCs within the ensemble). Fewer studies have been devoted to Cd$_{1-x}$Zn$_x$S [9, 11, 17] and CdSe$_{1-x}$Te$_x$ [8, 15, 18] nanocrystals.

Even less investigated are quaternary II–VI nanocrystals, for which extremely few studies were reported, namely, our earlier work devoted to fabrication and optical identification of Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ nanocrystals in borosilicate glass [20, 21]. This system of nanocrystals was shown to exhibit a two-mode type of compositional behaviour of the phonon spectrum. Our present work is aimed at obtaining quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ semiconductor nanocrystals by diffusion-limited growth in borosilicate glass and their characterization by Raman spectroscopy. To our knowledge, no data regarding CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals have been reported so far.

2. Experimental

Quaternary II–VI semiconductor nanocrystals were obtained in borosilicate glass by the diffusion-limited growth (solid-state precipitation) technique, the basic details of which can be found in [1, 22–24]. The initial mixture for the fabrication of CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals was prepared from commercially available Schott and LZOS optical cutoff filters made of borosilicate glass doped with CdS$_{1-x}$Se$_x$ and CdSe$_{1-x}$Te$_x$ nanocrystals. After comelting of the mixture and annealing at 1000°C for 1–1.5 h, colourless transparent glass
platelets were obtained, in which Cd, S, Se, and Te atoms were more or less randomly distributed over the borosilicate glass network. The nanocrystal growth was carried out at thermal treatment for 2 to 12 h, the temperature ranging from 625 to 700°C.

The obtained samples of brownish orange to red colour with about 5 × 5 mm² lateral size were polished down to 0.2–0.3 mm thick plates for optical measurements. Raman spectra were measured using a Dilor XY 800 spectrometer with a CCD camera, the excitation was provided by an Ar⁺ (514.5 nm) or Kr⁺ (647.1 and 676.4 nm) laser. The instrumental resolution was better than 2.5 cm⁻¹. All measurements were performed at room temperature.

3. Results and Discussion

Raman spectra of the semiconductor-doped borosilicate glass samples obtained are shown in Figure 1. They clearly show the presence of three maxima which could be quite reasonably assigned to CdTe-like LO₁ (in the frequency range 150–160 cm⁻¹), CdSe-like LO₂ (190–200 cm⁻¹), and CdS-like LO₃ (260–290 cm⁻¹) phonons. Even though studies of CdS₁−x−ySeₓTeᵧ nanocrystals have never been reported before, scarce Raman spectroscopic data for individual samples of CdS₁−x−ySeₓTeᵧ single crystals report this quaternary system to show a three-mode behaviour [25–27]. For mixed nanocrystals, all the observed LO phonon frequencies are lower than those for the corresponding binary crystals (the latter are shown by vertical short-dashed lines in Figure 1). This is in agreement with the three-mode behaviour of this mixed crystal system.

In our case, similar to the earlier studies of other II–VI nanocrystals embedded in dielectric media [5–14, 16–21], only LO phonons are revealed in the first-order Raman spectra. This is related to the fact that the nanocrystals comprise only a tiny part (as a rule, below 1%) of the sample scattering volume. Hence, in order to obtain a detectable Raman signal, one should apply resonant Raman conditions which provide better LO phonon scattering enhancement.

It is worth mentioning that among the binary compounds formed by the elements comprising the quaternary CdS₁−x−ySeₓTeᵧ system, CdTe possesses cubic (sphalerite or zinc-blende) structure, and CdSe at normal conditions is hexagonal (wurtzite) while CdS can exist in both zinc-blende and wurtzite structures [28]. Moreover, the structure of CdS₁−x−ySeₓ nanocrystals is reported to be size dependent, and zinc-blende and wurtzite nanocrystals can coexist in the same sample [1, 24]. However, since the local environment of an atom in the two structures is very similar (tetrahedral coordination), the LO phonon frequencies for zinc-blende and wurtzite CdS are almost the same [29].

The series of spectra shown in Figure 1 illustrates the compositional behaviour of the Raman spectra of quaternary CdS₁−x−ySeₓTeᵧ nanocrystals with a strong variation of sulphur content in the nanocrystals and roughly equal content of selenium and tellurium (x ≈ y). The LO phonon frequency in CdS (305 cm⁻¹) is known to be much higher than the frequency of local vibration of the sulphur impurity in CdSe or CdTe [30]. With the decrease of the sulphur content in the nanocrystals, the CdS-like LO₃ phonon frequency decreases, tending towards the frequency of local vibration of sulphur in CdSe₁−yTeᵧ (255–260 cm⁻¹ for the given content of Se and Te). The decrease of the CdS-like LO₃ phonon frequency in the spectra in Figure 1 clearly correlates with the decrease of the corresponding band intensity revealed at lower content of S in the nanocrystals. Note that there is a spread in both the nanocrystal composition and size over the ensemble of nanocrystals in the sample; so the resonant conditions are exactly met only for those nanocrystals, for which the energy of the incident or scattered light matches the energy gap. Since the gap varies with both composition and size, the variation of these two parameters clearly affects the signal-to-noise ratio in the spectra, clearly seen from Figure 1.

The rich second-order Raman spectrum obtained under resonant conditions confirms the composition of CdS₁−x−ySeₓTeᵧ nanocrystals obtained by diffusion-limited growth in borosilicate glass (see Figure 2). One can clearly see all the maxima corresponding to the processes with simultaneous generation of two LO phonons. The frequencies of the observed two-phonon bands enable their clear identification. Such a rich and distinct two-phonon spectrum is evidence for both the good quality of the samples obtained (relatively low dispersion of the nanocrystal composition and size) and...
the efficiency and sensitivity of the Raman spectroscopic technique at the correct choice of the resonance conditions. Similarly to ternary II–VI nanocrystals [5, 6, 10, 18–21], the intensity of the second-order Raman features in the spectrum is considerably lower than the first-order Raman peaks due to the lower probability of two-phonon processes at room temperature.

It should be noted that for many of the experimental Raman spectra of the CdS\textsubscript{1−x−y}Se\textsubscript{x}Te\textsubscript{y} nanocrystals in borosilicate glass, besides the above discussed peaks due to first- and second-order LO phonon scattering, one more less intense band was observed at 117–120 cm\textsuperscript{−1}. This feature can most likely be related to Raman scattering from acoustic phonons with nonzero wavevectors revealed in the Raman spectra due to the breakdown of selection rules. The latter can be caused by the phonon confinement in nanocrystals. The frequencies of acoustic phonons observed in the Raman spectra of II–VI semiconductor nanocrystals due to phonon confinement depend on the nanocrystal size [31–34]. Additionally, a noticeable disorder in the anion sublattice due to the random occupation of its sites by three types of anions (S, Se, and Te) results in the frequency of acoustic phonon density of states revealed in the Raman spectra. A similar effect of disorder-activated longitudinal and transverse (DALA and DATA) acoustic phonons in first-order Raman scattering is known for semiconductor solid solutions [35]. From the frequency of the band observed at 117–120 cm\textsuperscript{−1}, it can be assigned to DALA phonons.

Raman spectra of CdS\textsubscript{1−x−y}Se\textsubscript{x}Te\textsubscript{y} nanocrystals in borosilicate glass at different thermal treatment conditions are shown in Figure 3. This series of samples was obtained from the same initial mixture at different thermal treatment durations and temperatures. It can be seen from the figure that in most of the spectra (with the exception of those subjected to the least intense and the most intense thermal treatments) the frequencies of CdTe-like (LO\textsubscript{1}), CdSe-like (LO\textsubscript{2}), and CdS-like (LO\textsubscript{3}) phonons in the spectra do not differ much, and the intensity ratio for these bands is about the same for all the samples. Hence, the composition of the CdS\textsubscript{1−x−y}Se\textsubscript{x}Te\textsubscript{y} nanocrystals formed of the same initial mixture is relatively stable with the variation of thermal treatment duration \(\tau\) and temperature \(T_a\) within a certain interval which is optimal for the II–VI nanocrystal formation. The observed slight spread of the LO phonon frequencies is, in our opinion, an evidence for fluctuations of the nanocrystal composition rather than for a systematic trend with the thermal treatment characteristics. Meanwhile, for CdS\textsubscript{1−x−y}Se\textsubscript{x} nanocrystals grown in the borosilicate glass we observed earlier a clear trend of increase of the predominant chalcogen content with \(\tau\) and \(T_a\) and pushing the minor chalcogen atoms out of the nanocrystals across the nanocrystal/glass interface [19]. However, one should keep in mind that, as follows from the frequencies and intensities of the LO phonon bands in the Raman spectra, for the batch of samples studied, the initial mixture contains three chalcogens (S, Se, and Te) in roughly equal quantities. This very probably ensures better stability of the nanocrystal composition under variation of the thermal treatment conditions.

It is also known that in case the thermal treatment parameters (\(\tau\) and \(T_a\)) are beyond the optimal interval for the Se- and Te-containing II–VI nanocrystal formation, one can expect precipitation of elemental selenium or tellurium in the form of molecular Se\textsubscript{2} or Te\textsubscript{2} clusters or even larger
aggregations which can be clearly evidenced by Raman spectroscopy [36]. Here, as seen from Figure 3, we clearly observe Raman bands corresponding to crystalline tellurium phonons (90, 120, and 139 cm$^{-1}$) as well as $\mathrm{Te}_2$ molecular dimer vibrations (215.5 cm$^{-1}$) for the least intensely ($T_a = 625 \, \degree \mathrm{C}, \tau = 2 \, \mathrm{h}$) and the most intensely ($T_a = 700 \, \degree \mathrm{C}, \tau = 12 \, \mathrm{h}$) heat-treated samples. This agrees well with our earlier data showing Raman evidence for tellurium precipitation as an alternative to the formation of II–VI nanocrystals with high Te content [36]. Still, within the range of $\tau$ and $T_a$ optimal for the II–VI nanocrystal formation their composition appears to be quite stable with respect to the thermal treatment characteristics.

4. Conclusions

A series of samples with quaternary $\mathrm{CdS}_{1-x-y} \mathrm{Se}_x \mathrm{Te}_y$ nanocrystals were grown in a borosilicate glass matrix by diffusion-limited growth technique. Their Raman spectra confirm the presence of cations of three types distributed over nanocrystal lattice sites. The $\mathrm{CdS}_{1-x-y} \mathrm{Se}_x \mathrm{Te}_y$ system is shown to possess three-mode compositional behaviour of the phonon spectrum. The compositional dependence of the LO phonon frequencies is shown experimentally for a series of samples containing nanocrystals with $x \approx y$. In the second-order Raman spectrum, the presence of distinct bands, corresponding to different two-phonon processes, confirms both the quality of the nanocrystals obtained and the Raman technique sensitivity for the identification of matrix-embedded $\mathrm{CdS}_{1-x-y} \mathrm{Se}_x \mathrm{Te}_y$ nanocrystal composition.

References


Research Article

Vibrational Spectroscopy of Chemical Species in Silicon and Silicon-Rich Nitride Thin Films

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Abstract

Vibrational properties of hydrogenated silicon-rich nitride (SiN_x:H) of various stoichiometry (0.6 ≤ x ≤ 1.3) and hydrogenated amorphous silicon (a-Si:H) films were studied using Raman spectroscopy and Fourier transform infrared spectroscopy. Furnace annealing during 5 hours in Ar ambient at 1130°C and pulse laser annealing were applied to modify the structure of films. Surprisingly, after annealing with such high-thermal budget, according to the FTIR data, the nearly stoichiometric silicon nitride film contains hydrogen in the form of Si–H bonds. From analysis of the FTIR data of the Si–N bond vibrations, one can conclude that silicon nitride is partly crystallized. According to the Raman data a-Si:H films with hydrogen concentration 15% and lower contain mainly Si–H chemical species, and films with hydrogen concentration 30–35% contain mainly Si–H_2 chemical species. Nanosecond pulse laser treatments lead to crystallization of the films and its dehydrogenization.

1. Introduction

The interest in amorphous, nano- and microcrystalline silicon films on nonrefractory inexpensive substrates and their crystallization is stimulated by demands of giant microelectronics. For example, the enlargement of sizes of flat-panel displays with active thin film transistor matrix can be described as “reverse Moor’s law.” Scientific interest in the silicon-rich nitride (SRN) films is growing due to their perspectives for application. The most important applications of SRN films are silicon-based optoelectronic devices [1], nonvolatile memory (flash-memory) devices [2], and new tandem solar cells based on silicon and silicon oxide (silicon nitride) heterostructures [3]. Silicon nanoclusters and SRN films can be applied in novel quantum-dots-based solar cells with enhanced efficiency [4].

Modern plasma-enhanced chemical vapor deposition (PECVD) technique allows the production of amorphous silicon films and SRN films with temperature of substrate lower than 100°C [5]. As reagents containing hydrogen are mainly used in PECVD, as-deposited films are hydrogenated. Hydrogen plays important role in electrical and optical properties of the films and also has influence on stability of the films. So, it is important to develop express, nondestructive spectroscopic approaches for studies of hydrogen in amorphous hydrogenated silicon (a-Si:H) films and hydrogenated SRN films. The present paper is devoted to studies of as-deposited films as well as furnace- and pulse-laser-treated films with the use of Raman spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

2. Experiment Details

Hydrogenated SRN films (SiN_x:H) of different stoichiometry were deposited on the Si (100) substrates with the use of low-frequency PECVD method. The frequency of discharge was 55 kHz, and the films were deposited from the gas mixture of ammonia (NH_3) and monosilane (SiH_4). The stoichiometry parameter x depends on the ratio of ammonia/monosilane flows. The growth technology is described elsewhere in more details [6]. All SRN films were deposited at substrate temperature 100°C, the reactor pressure during deposition was 150 Pa, the deposition time was 16 minutes, and the plasma power was 400 W. Parameters of the films are shown in Table 1.

Amorphous silicon films were deposited on glass substrates using two methods. The first method is evaporation...
of monocrystalline silicon target by electron beam in high vacuum and deposition onto unheated substrate. The films deposited by this method do not contain hydrogen. The second method is PECVD at various temperatures using different PECVD reactors. The parameters of the films are shown in Table 2. It is known that optical gap of a-Si:H depends on hydrogen concentration [7]. According to optical gap measurements from light transmission and reflection data, the films grown at temperature 280 °C contain \( \approx 10 \) atomic % of hydrogen (optical gap \( \approx 1.4 \) eV); the films grown at temperature 225 °C contain \( \approx 15 \)% of hydrogen (optical gap \( \approx 1.6 \) eV); the films grown at temperature 200 °C contain 30–35% of hydrogen (optical gap \( \approx 2 \) eV).

Laser ellipsometry (\( \lambda = 632.8 \) nm) was applied to measure the thickness of the films. To study the states of hydrogen and vibration of the Si–N bonds, the FTIR spectroscopy was applied. The FTIR spectrometer FT-801, produced by scientific enterprise “SIMEX” (Novosibirsk, Russia), was used. The spectral range of the spectrometer is from 550 to 5500 cm\(^{-1}\), and the spectral resolution can be optionally changed from 4 to 0.5 cm\(^{-1}\). The structural properties of as-deposited and annealed films were studied using Raman spectroscopy technique. All Raman spectra were recorded in the back-scattering geometry. The 514.5 nm Ar\(^+\) laser line was used as a light source. Triple spectrometer T64000 (Horiba Jobin Yvon) with micro-Raman setup and liquid-nitrogen-cooled CCD matrix detector was used. The spectral resolution was not worse than 1 cm\(^{-1}\). All spectra were measured at room temperature. To avoid heating of the films, the laser beam was slightly defocused; the spot diameter was equal to about 4–6 \( \mu \)m; the laser power reaching the sample was within 2–3 mW. The spectra were registered in the Z(XX)Z polarization geometry. Furnace annealing of the samples in Ar ambient for 5 hours at temperature 1130 °C was performed at the Institute of Electron Technology (Warsaw, Poland). The triple harmonic of YAG:Nd laser (\( \lambda = 335 \) nm, pulse duration of 10 ns) was used for laser treatments of the as-deposited films.

### 3. Results and Discussion

In Figure 1 one can see Raman spectroscopy and FTIR data concerning N–H valence (stretching) vibrations in sample 611 (stoichiometry is estimated as SiN\(_{1.3}\):H). For convenience, the FTIR data was multiplied by 20 times. According to both Raman data and FTIR data, the position of N–H valence vibration peak is 3350 cm\(^{-1}\). An advantage of Raman spectroscopy method is the possibility to use substrates that are not transparent in IR region. When the substrate is not transparent, only reflection setup can be used. Using multiple internal transmission, the sensitivity of IR spectroscopy can be notably improved [8]. Figure 2 shows shift of the position of N–H valence vibration peak versus NH\(_3\) to SiH\(_4\) ratio during deposition of SiN\(_x\):H films. With changing of stoichiometry parameter \( x \) (1.3, 0.95, and 0.6) the frequency also changes (3350, 3342, and 3335 cm\(^{-1}\)) accordingly. The frequency of Si–H valence vibrations changes from 2170 to 2100 cm\(^{-1}\) with decrease of stoichiometry parameter \( x \) from 1.3 to 0.6 [6]. This is because of influence of neighboring atoms on frequencies of valence modes of Si–H and N–H bonds. It should be noted that Ali with coworkers [9] have also observed the shift of the position of N–H valence vibration peak versus stoichiometry of SiN\(_x\):H films.

In Figure 3 one can see Raman spectroscopy and FTIR data concerning Si–H valence vibrations for SiN\(_{1.3}\):H film. According to the FTIR data the position of Si–H valence vibration peak is 2170 cm\(^{-1}\), but according to the Raman spectroscopy data the position of peak is 2187 cm\(^{-1}\). A mercury lamp was used for back lighting of LCD monitor of experimental setup, and parasitic light can reach input slit of spectrometer. So, one can see in the Raman spectra a doublet (leakage from mercury lamp). One can see also a peak

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Thickness, nm</th>
<th>Growth temperature, °C</th>
<th>Hydrogen concentration, atomic per cents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>280</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>225</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>200</td>
<td>30–35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Thickness, nm</th>
<th>Growth temperature, °C</th>
<th>Raman</th>
<th>FTIR (*20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>611</td>
<td>5</td>
<td>240</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>613</td>
<td>1.5</td>
<td>400</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>615</td>
<td>0.5</td>
<td>450</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1:** Growth parameters, thickness, and composition of hydrogenated SRN films.

**Table 2:** Growth parameters, thickness, and hydrogen concentration of amorphous silicon films.
due to Raman scattering on N₂ molecules in atmosphere. Both Raman and FTIR peaks are asymmetric, so one can assume presence of Si–H and SiH₂ bonds in this film. From fitting of FTIR spectrum by two Gaussians one can assume that frequency of Si–H valence vibration is 2170 cm⁻¹ and frequency of Si–H₂ valence vibration is 2260 cm⁻¹. The difference in positions of the Raman scattering and the FTIR peaks may be due to different contribution of Si–H and SiH₂ bond valence vibration in dipole moment and polarisability.

Knowing the thickness of a film and effective absorption cross-sections for Si–N, Si–H, and N–H bonds, one can calculate the concentration of chemical bonds. The effective absorption cross-section $S_{	ext{eff}}$ for valence vibration of Si–N bonds is $1.6 \cdot 10^{-19}$ cm² [10], and $S_{	ext{eff}}$ for valence vibration of Si–H bonds is $0.57 \cdot 10^{-19}$ cm² [11]. According to different data, $S_{	ext{eff}}$ for valence vibration of N–H bonds is $0.48 \cdot 10^{-19}$ cm² [11] or $0.8 \cdot 10^{-19}$ cm² [12]. Concentration of chemical species can be calculated as $N(\text{cm}^{-3}) = A/(d(\text{cm}) \cdot S_{	ext{eff}} (\text{cm}^2))$, where $A$ is the height of absorbance peak (dimensionless parameter) and $d$ is thickness. The results are shown in Table 3. The concentration of N–H species is calculated using $S_{	ext{eff}}$ according to Lanford [11] and Stein [12]. It should be noted that Stein and Wegener [12] have used multiple internal transmissions but Lanford and Rand [11] used normal transmission geometry. We also have used normal transmission geometry. So, the $S_{	ext{eff}}$ obtained by Lanford is more preferable for analysis of our data. From Table 3 one can see that total concentration of Si–N, Si–H, and N–H bonds decreases with decreasing of stoichiometry parameter $x$. This is because vibrations of Si–Si bonds do not change dipole momentum and are not active in FTIR. But they are active in Raman scattering. And Raman signal from amorphous silicon clusters was detected for sample number 615 [6]. The total concentration of Si–N bonds in stoichiometric Si₃N₄ is about $15.5 \cdot 10^{22}$ cm⁻³ [13]. So, one can assume that annealed near stoichiometric sample number 611 (Table 3) contains not only Si–N and Si–H bonds but also some concentration of Si–Si bonds. But concentration of such bonds is not high enough to be detected by Raman spectroscopy.

The FTIR spectra of as-deposited and annealed SiN₁₋₃:H films are shown in Figure 4 in range from 500 to 3900 cm⁻¹. Surprisingly, this nearly stoichiometric silicon nitride film still contains hydrogen after annealing with high-thermal budget, mainly in the form of the Si–H bonds. In this film, the peak, corresponding to absorption on stretching vibrations of the Si–H bonds, becomes even higher. The peak at 1175 cm⁻¹ in spectrum of as-deposited film can be related to absorbance by bending vibrations of the N–H bonds [14]. Peculiarities at 850–900 cm⁻¹ in spectrum of annealed film can be related to absorbance by stretching vibrations of the Si–N bonds in the α-modification of crystalline silicon.
Table 3: Concentration of chemical species in SRN films according to FTIR data.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Si–N (10^{22} \text{ cm}^{-3})</th>
<th>Si–H (10^{22} \text{ cm}^{-3})</th>
<th>N–H (for (s_{eff}) according to Lanford) (10^{22} \text{ cm}^{-3})</th>
<th>N–H (for (s_{eff}) according to Stein) (10^{22} \text{ cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>611</td>
<td>8</td>
<td>3.2</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>611 annealed</td>
<td>10.5</td>
<td>6</td>
<td>bellow 0.1</td>
<td>bellow 0.06</td>
</tr>
<tr>
<td>613</td>
<td>5.58</td>
<td>3.64</td>
<td>0.9</td>
<td>0.54</td>
</tr>
<tr>
<td>615</td>
<td>3.75</td>
<td>2.92</td>
<td>0.32</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 5: Raman spectra of a-Si:H films in frequency range of valence vibration of Si–H bonds.

Figure 6: Raman spectra of as-deposited a-Si:H film and crystallized by laser pulse annealing film in frequency range of valence vibration of Si–H bonds.

nitride [15, 16]. Maybe partial crystallization of silicon nitride retards the dehydrogenization of the film. It has been detected earlier [17] that the closer is the stoichiometry parameter of the SRN films to that of stoichiometric Si₃N₄, the higher temperature is needed for effusion of hydrogen (dehydrogenization) from these films. However, short-time annealing at temperature 850°C [17] and annealing at 800°C for 2 hours [18] lead to total dehydrogenization of the SRN films, with the stoichiometry parameter \(x\) below 1. So, as it was abovementioned, one can assume that, for the case of nearly stoichiometric silicon nitride film, furnace annealing leads to so-called hardening of silicon nitride inhibiting hydrogen outdiffusion.

Figure 5 shows Raman spectra of amorphous silicon films with different hydrogen concentrations. All films were deposited on glass substrates that are not transparent in IR region, so it was impossible to analyze them using FTIR in normal geometry. One can see peaks due to scattering on valence vibrations of Si–H bonds. In Raman spectrum of the only film deposited in vacuum (without hydrogen) this peak is absent. As one can see from Raman spectra, film deposited at temperature 200°C contains mostly Si–H₂ bonds, because the position of Si–H₂ peak is about 2100 cm⁻¹. The frequency of Si–H peak is about 2000 cm⁻¹ [19]. The films deposited at temperatures higher than 200°C contain mostly Si–H bonds. It should be noted that frequencies of stretch vibrations of Si–H bonds in silicon nitride and in a-Si:H are notably different: about 2200 cm⁻¹ for the first case and 2000–2100 cm⁻¹ for the second case. As it was shown by Hien et al. [20], the frequency of stretch vibrations of Si–H bonds in the case of neighbouring N and H atoms can reach 2122 cm⁻¹. In the case of only Si neighbouring atoms this frequency is 2012 cm⁻¹ [20]. FTIR method can be used for quantitative hydrogen measurements [21], but for transmission experiments the substrate should be transparent in IR range.

Figure 6 shows the Raman spectra of as-deposited a-Si:H film and nanosecond-pulse-annealed film. The Raman spectrum of amorphous silicon contains broad peaks at approximately 480 cm⁻¹ appearing as a result of effective density of transverse optical (TO) vibration modes [19]. Due to scattering on optical phonon modes localized in the nanocrystals, the Raman spectrum of nanocrystals is characterized by narrow peak at position between 500 and 520 cm⁻¹. The position and the width of the peak strongly depend on size and structure of the nanocrystals according to dispersion of the localized modes [22]. The peak width is mainly determined by size dispersion of the nanocrystals. The intensity of the “nanocrystal” peak depends on the volume of nanocrystal phase. So, one can determine the
volume part of nanocrystal phase: \( V_{\text{nano-Si}}/V_{\text{full}} = I_{\text{NC}}/(I_{\text{NC}} + \sigma I_{A}) \), where \( I_{\text{NC}} \) and \( I_{A} \) are integral intensities of crystalline and amorphous peaks and \( \sigma \) is relation between the integral Raman cross-sections of nanocrystal Si and a-Si. According to the literature data, \( \sigma \) can change from 0.1 for large grain polycrystalline silicon up to 1.1 for nanocrystalline Si [23]. As one can see, the used nanosecond treatment leads to almost total crystallization of as-deposited film. According to peak position, the size of nanocrystals in our case should be about 10 nm [22]. It should be noted that no Si–H peaks were detected in nanosecond-pulse-annealed film. So, the pulse annealing can be used not only for crystallization but also for dehydrogenization.

4. Conclusion

In conclusion, the FTIR method was applied for determination of concentrations of chemical species in silicon-rich nitride films containing amorphous silicon nanoclusters. It was observed that nearly stoichiometric hydrogenated silicon nitride film contains hydrogen mainly in the form of the Si–H bonds even after 5 hours of annealing at temperature 1130°C. According to Raman spectroscopy data, nanosecond pulse laser treatment leads to crystallization and dehydrogenization of a-Si:H films with initial concentration of hydrogen up to 35%.

Acknowledgments

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References

Research Article
Room Temperature Synthesis and Catalytic Properties of Surfactant-Modified Ag Nanoparticles

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Well-dispersed Ag nanoparticles with size of 20–30 nm were synthesized in water at room temperature with a self-made novel imidazoline Gemini surfactant quaternary ammonium salt of di (2-heptadecyl-1-formyl aminoethyl imidazoline) hexanediamine. Transmission electron microscopy, X-ray powder diffraction, ultraviolet-visible absorption spectra, and Fourier transform infrared ray were used to characterize the Ag nanoparticles. Results showed that the micellized aggregation of imidazoline Gemini surfactant in water, the growth of Ag initial particles, and the interaction (adsorption and coordination) between surfactant and Ag+/Ag nanoparticles took place simultaneously to form the well-dispersed Ag nanoparticles. Catalytic results show that the surface-modified Ag product was an active metal catalyst for methyl orange reduction reaction due to the effective adsorption between Ag nanoparticles and methyl orange molecules, which was of promising application in environmental protection.

1. Introduction

In recent years, metal nanoparticles have been studied extensively due to their noticeable electrical, optical, and catalytic properties [1–4]. As one of the traditional noble metals, Ag nanoparticles have been synthesized for various applications, such as biomedical antibacterial materials [5, 6], catalysis [1, 7, 8], tribology [9], and surface-enhanced Raman scattering (SERS) [10–12].

Different methods have been employed to prepare Ag nanoparticles with various morphologies, such as single-source precursor heat treatment at 550°C for synthesizing Ag nanoparticles [13], microwave-assisted route for Ag nanorods [14] and nanowires [15], microwave-solvothermal synthesis for monodispersed Ag nanoparticles [16], and solvothermal synthesis of chainlike and dendritic Ag nanostructures [17]. Other methods such as photochemical γ-ray reduction [18], ultraviolet [19], sonochemical [20], and ultrasonic synthesis [21], and so forth have also been exploited recently. However, most of these methods are concerning high-temperature treatment, complicated processing procedures, and exposure to sound or light danger. Thus, exploitation of a facile, energy-efficient, and safe route still remains a challenge.

Room temperature synthesis routes for the fabrication of Ag nanoparticles have been investigated recently, showing promising application feasibility and reliability for large-scale manufacture with energy saving and safety. Zhang et al. [5] and Huang et al. [6] prepared Ag nanoparticles at room temperature, showing excellent antibacterial properties; Li et al. [22] prepared Ag nanoparticles at room temperature, which was confirmed to be effective for detecting mercury ion with high sensitivity and selectivity; snowflake-like dendritic Ag nanostructures [23] and Ag nanowires [24] were also prepared at room temperature. As the concept of “green methods” has become more and more important since the last decade [6], nanomaterials scientists start to pay more attention to facile, safe, and environmentally friendly routes for synthesizing Ag nanoparticles, and room temperature is one of the most promising routes to realize this goal.

Herein, we report a room temperature route to prepare well-dispersed Ag nanoparticles in the presence of a novel imidazoline Gemini surfactant quaternary ammonium salt of di (2-heptadecyl-1-formyl aminoethyl imidazoline) hexanediamine (SHAEIHDI) prepared in our lab [25], which plays multifunctional roles in the whole synthesis procedure of Ag nanoparticles. Catalytic results for reducing methyl
orange (MO) by NaBH₄ show that the obtained imidazoline Gemini surfactant-modified Ag nanoparticles product is an active, efficient, and promising catalyst for environmental protection.

2. Experimental

2.1. Chemicals. All the chemicals, including silver nitrate (AgNO₃), 80% hydrazine hydrate (N₂H₄ · H₂O), sodium borohydride (NaBH₄), ethanol, and methyl orange (MO), were of analytical purity and used as received without further purification. The used imidazoline Gemini surfactant quaternary ammonium salt of di (2-heptadecyl-1-formyl aminoethyl imidazoline) hexanediame (SHAEIHDI) was synthesized according to our previous work [25], and its molecular structure was shown in Figure 1. Water was distilled.

2.2. Preparation and Characterization of Ag Nanoparticles. 0.34 g (0.0020 mol) AgNO₃ was dissolved completely into 20 mL distilled water, and an appropriate amount of SHAEIHDl was dissolved into another 20 mL distilled water. The two systems were mixed slowly and completely under vigorous stirring to form an orange suspension. Then 1 mL 80% N₂H₄ · H₂O was dropped slowly into the above suspension, which was maintained in dark at room temperature for 24 hours to form black precipitates. The obtained precipitates were washed by distilled water and ethanol for several times, dried in vacuum at 70 °C for 8 h, and collected carefully for further characterization. The concentration of SHAEIHDl was varied systematically from 0, 2, 4, 6 to 8 g · L⁻¹ to investigate its effect on the formation of Ag nanoparticles.

The morphologies and size of the Ag nanoparticles were observed by transmission electron microscopy (TEM) (JEM-2000EX Electro-Microscope, Jeol Co., Japan). The Ag products were characterized by X-ray powder diffraction (XRD), using Rigaku (Japan) D/max r-B X-ray diffractometer with Cu/K radiation (λ = 0.15418 nm) operating at 40 kV and 30 mA with 2θ ranging from 10° to 80°. The samples were also measured by ultraviolet-visible absorption spectra (UV-vis) (756CRT UV-vis spectrophotometer, Shanghai Precision and Scientific Instrument Co. Ltd., China) and infrared ray (IR) (510P Fourier transform infrared spectrophotometer, Nicolet, USA).

2.3. Catalytic Properties of Ag Nanoparticles. 0.005 g Ag nanoparticles and 0.02 g NaBH₄ were added into 20 mL 1 × 10⁻⁵ mol L⁻¹ MO solution, and the system was mixed under stirring. The change in color of the system could be indicated by detecting the absorbance variation at the wavelength of the absorbance maximum (λ_max = 463 nm) of MO using the Varian Cary 50 UV-vis spectrophotometer (Varian Co., Australia).

3. Results and Discussion

3.1. Characterization of Ag Samples. Figure 2 shows the typical TEM images and SAED pattern of Ag samples prepared with varied SHAEIHDl concentration. It can be seen from Figure 2(a) that only irregular Ag agglomerates with serious aggregation can be obtained without SHAEIHDl. When 2 g·L⁻¹ SHAEIHDl is used as shown in Figure 2(b), Ag nanoparticles with diameter of 50–100 nm have been obtained with improved dispersion. Further increasing the surfactant concentration to 4 g·L⁻¹ shown in Figure 2(c) can give rise to the formation of better-dispersed Ag nanoparticles with diameter of 30–50 nm. Figures 2(d) and 2(e) show the TEM image and SAED pattern of Ag nanoparticles prepared with 6 g·L⁻¹ SHAEIHDl, indicating that well-dispersed Ag nanoparticles product with uniform size of 20–30 nm has been obtained, which is of single-crystal structure. When the SHAEIHDl concentration is increased up to 8 g·L⁻¹ as shown in Figure 2(f), the size of Ag nanoparticles becomes larger (30–80 nm) and not uniform. Thus, 6 g·L⁻¹ is the optimum concentration for the best dispersion of Ag nanoparticles with uniform size.

The XRD pattern of Ag nanoparticles with 6 g·L⁻¹ SHAEIHDl is shown in Figure 3. The intensive diffraction peaks can be indexed to the cubic Ag nanocrystals (JCPDS file no. 04-0783), corresponding to its plane of (111), (200), and (220). The sharp diffraction peaks indicate the relatively high crystallinity of the obtained Ag nanoparticles product. In addition, the two small peaks at around 19° and 28° could come from orthorhombic AgNO₃ crystalline (JCPDS file no. 06-0363), and the peak at about 32° could be attributed to hexagonal Ag₂O crystals (JCPDS File No. 42-0874) [4]. These results might be resulted from the washing procedures in this room temperature synthesis route, as well as the confinement effect [4].

Figure 4 showed the FT-IR spectra of SHAEIHDl (a) and 6 g·L⁻¹ SHAEIHDl-modified Ag nanoparticles (b). In Figure 4(a), the absorption peak at 3319 cm⁻¹ was attributed to the stretching vibration of N–H, and the peaks at 2919 ~ 2851 cm⁻¹ were attributed to the aliphatic C–H vibrations in the long-chain alkyl (–C₁₇H₃₅). The absorbance peak at 1660 cm⁻¹ was attributed to –NH–C=O. The absorbance of imidazoline ring and C=O in carboxyl were revealed at 1604 cm⁻¹ and 1746 cm⁻¹, respectively. The typical peaks of SHAEIHDl also existed in Figure 4(b), indicating that a little amount of SHAEIHDl was adsorbed.
onto the surface of Ag nanoparticles to form a modification layer and could not be washed off totally by ethanol and distilled water. Moreover, the absorbance of –NH–C=O at 1660 cm⁻¹ in Figure 4(a) weakened obviously in Figure 4(b), showing that there was a strong coordination effect between C=O bond in SHAEIHDI and Ag nanoparticles, which is in good agreement with the color change in the preparation Section 2.2 of Ag nanoparticles, indicating that SHAEIHDI is not only a surface-modification agent to Ag nanoparticles, but a coordination agent as well.

Figure 5 showed the UV-vis spectra of SHAEIHDI (a) and 6 g·L⁻¹ SHAEIHDI-modified Ag nanoparticles (b). The two peaks appeared at 200 and 240 nm in Figure 5(a) corresponded to the absorption of imidazoline ring and conjugated C=O, respectively. In Figure 5(b), the absorbance of imidazoline ring still existed, but the absorption of C=O at 240 nm in Figure 5(a) weakened in Figure 5(b), showing that there was a strong coordination effect between C=O and Ag nanoparticles, which could give rise to the good stability and dispersion capacity of the prepared Ag nanoparticles in both organic and inorganic medium. The wide peak appeared at around 275 nm corresponded to the absorbance of Ag nanoparticles [26]. Interestingly, the surface plasmon resonance (SPR) band at round 400 nm [26, 27] is weak and not very obvious in Figure 5(b), which might be caused by this novel imidazoline Gemini surfactant-assisted room temperature synthesis route, and the exact reason deserves further investigation. The UV-vis analysis can further confirm the good surface-modifying effect of SHAEIHDI on Ag nanoparticles, which is in good accordance with the FT-IR results.

3.2. Formation of Ag Nanoparticles. In the preparation process of Ag nanoparticles, imidazoline Gemini surfactant
SHAEIHDI is served as not only surface-modification agent, but also a coordinating agent, which can be confirmed by the color change (orange) after mixing SHAEHIDI and AgNO₃ solutions. Furthermore, the FT-IR and UV-vis measurements can also proof that SHAEHIDI can coordinate with Ag⁺ to form a SHAEHIDI-Ag⁺ complex. During the growth of Ag nanoparticles, the long-chain alkyls (–C₁₇H₃₅) in SHAEHIDI (its formula structure is shown in Figure 1) have excellent steric effects, which can stop the new-formed Ag nanostructures from aggregating and make them stabilize in aqueous medium. The formation speed of Ag nanoparticles can also be controlled by the SHAEHIDI adsorbed on the surface of Ag nanoparticles and thus prevent them from aggregating as well. The special micellization behavior of SHAEHIDI molecules in water and the interaction between SHAEHIDI molecules and Ag nanoparticles take an active part in the whole procedure.

In our previous studies, an imidazoline surfactant quaternary ammonium salt of 2-undecyl-1-dithiooureido-ethyl-imidazoline (SUDEI) has been synthesized [28] and used as the surface-modifying agent for preparing nanomaterials, and its sphere-like micelles in water have been confirmed [29, 30]. Imidazoline Gemini surfactant SHAEHIDI has the similar molecular structure to SUDEI but with more active elements N and O, which can also form sphere-like micelles in water, and Ag nanoparticles will grow along the hydrophilic groups in the micelles. The micellized aggregation of SHAEHIDI in water, the growth of Ag initial particles, and the adsorption and coordination of SHAEHIDI on Ag⁺ and Ag nanoparticles will take place at the same time to form the final well-dispersed Ag nanoparticles with narrow size distribution [31, 32].

In addition, an appropriate concentration of SHAEHIDI will also play a vital role in the formation of well-dispersed Ag nanoparticles. When 2 g·L⁻¹ SHAEHIDI is used (see Figure 2(b)), the aggregation of SHAEHIDI is not enough, and sphere-like micelles cannot form effectively, thus only Ag nanoparticles with size of 50–100 nm can be formed, and the aggregation is obvious. Further increasing the SHAEHIDI concentration to 4 g·L⁻¹ can improve the dispersion of Ag nanoparticles, and the size can be further tailored to 30–50 nm (see Figure 2(c)), indicating that the micelles of SHAEHIDI are taking more effective role in the formation of Ag nanoparticles. When 6 g·L⁻¹ SHAEHIDI is employed, SHAEHIDI will aggregate effectively to form perfect sphere-like micelles, giving rise to the successful formation of well-dispersed Ag nanoparticles with narrow size of 20–30 nm (see Figure 2(d)). However, if more SHAEHIDI (8 g·L⁻¹) is used as shown in Figure 2(f), SHAEHIDI molecules will aggregate excessively to form larger micelles, which can lead to the formation of larger-sized Ag nanoparticles (30–80 nm) with aggregation to a certain degree. Moreover, the formed Ag nanoparticles are stable in aqueous medium and can be dispersed easily in water without obvious precipitation, which is important for the later catalytic experiments. However, the Ag particles are not monodispersed as shown in all of the above samples prepared with varied surfactant concentrations, and more work should be done to further tailor the particle size to a desirable and monodispersed range for potential applications.

In a word, an appropriate amount of SHAEHIDI is necessary and vital for the successful formation of well-dispersed
Ag nanoparticles. The surfactant SHAEIHDI prepared in our lab is served as surface-modifying agent, coordinating agent, morphology-controlling agent, and stabilizing agent for the formation of well-dispersed Ag nanoparticles. This imidazoline Gemini surfactant and the facile room temperature process could be extended to the synthesis of other metal nanoparticles with potential applications.

3.3. Catalytic Activity of Ag Nanoparticles. Ag nanoparticles sample with diameter of 20–30 nm (Figure 2(d)) was used to test its catalytic properties for the reaction of MO reduced by NaBH₄. The Ag nanoparticles can be dispersed very well in the MO solution system with good stability due to the excellent surface-modifying and stabilizing effects of surfactant SHAEIHDI.

The catalytic results of Ag nanoparticles were shown in Figure 6. It can be seen from Figure 6(a) that the blank experiments performed without any Ag catalysts show nearly no absorbance change of MO solution at its λ_max, indicating that MO is not reduced effectively by NaBH₄, or the reduction rate is very slow. However, when Ag nanoparticles were added as shown in Figure 6(b), the absorbance of MO solution decreased quickly with reaction time to almost none within the last 3 minutes (17–20 min), indicating that MO was reduced effectively by NaBH₄ under the catalytic effect of Ag nanoparticles.

Today environmental protection has become more and more important for human beings, and some toxic and stable dye molecules like MO are dangerous to the environment [33]. MO is an organic sulfosalt dye, which can be reduced by reductants like NaBH₄ to form small organic molecules firstly and nontoxic species finally, but the reduction rate is very slow. Metal nanomaterials with high reactive activity and specific surface area can accelerate the reduction rate of dyes, thus increasing the reducing efficiency. Chen et al. [34] prepared PS/Ni nanocomposite spheres, showing noticeable catalytic performance for reducing methylene blue trihydrate (MBt) by NaBH₄; Saha et al. [1] prepared Ag nanoparticles, which is proved to be a very effective catalyst for reducing 4-nitrophenol to 4-aminophenol by NaBH₄, and adsorption of the reactants on the surface of the catalyst can mainly account for the catalytic mechanism.

In this paper, after adding Ag nanoparticles into the MO and NaBH₄ solution as the catalyst, adsorption can take place between the well-dispersed Ag nanoparticles and MO molecules. The large specific surface area of Ag nanoparticles can help increase the specific surface area of MO, thus increasing its reactive activity. The modification layer of SHAEIHDI on the surface of Ag nanoparticles can make them stable with good dispersion in the MO aqueous system, which can also promote the effective adsorption between Ag nanoparticles and MO molecules. As a consequence, the oxidation-reduction reaction between the active MO and NaBH₄ can happen more easily, effectively, and faster, indicating that the Ag nanoparticles product is an active and promising catalyst for environmental protection.

4. Conclusion

A facile room temperature synthesis route has been presented for preparing well-dispersed Ag nanoparticles with uniform size of 20–30 nm in the presence of imidazoline Gemini surfactant SHAEIHDI prepared in our lab. Characterization results show that SHAEIHDI plays multifunctional roles in the whole formation procedure of Ag nanoparticles, such as surface-modifying agent, coordinating agent, morphology-controlling agent, and stabilizing agent. The SHAEIHDI-modified Ag nanoparticles sample shows excellent catalytic performance for reducing MO by NaBH₄, indicating that the obtained surface-modified Ag nanoparticles product is a potential and promising catalyst for environmental protection. The imidazoline Gemini surfactant SHAEIHDI
and the facile room temperature synthesis route could be extended to the preparation of other metal nanoparticles for various applications.

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