Research Article

Fast and Straightforward Synthesis of Luminescent Titanium(IV) Dioxide Quantum Dots

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The nucleus of titania was prepared by reaction of solution titanium oxosulphate with hydrazine hydrate. These titania nuclei were used for titania quantum dots synthesis by a simple and fast method. The prepared titanium(IV) dioxide quantum dots were characterized by measurement of X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), high-resolution electron microscopy (HRTEM), and selected area electron diffraction (SAED). The optical properties were determined by photoluminescence (PL) spectra. The prepared titanium(IV) dioxide quantum dots have the narrow range of UV excitation (365–400 nm) and also a close range of emission maxima (450–500 nm).

1. Introduction

Titan is one of the most abundant metals of Earth's crust. The most stable and therefore most widely used titanium compounds are the oxides, in particular titanium(IV) dioxide TiO₂. In practice, the most commonly used powder rutile is titanium white, and these fine white powders are among the best available white pigments. TiO₂ in powder form strongly scatters light and has a high opacity. It is therefore used as its pigments provide whiteness, and opacity of paints, coatings, plastics, paper, inks, food, cosmetics, and pharmaceuticals, for example, tablets or toothpaste. It is used as a food white dye E171. In cosmetics, it is added to the creams as a pigment and a thickener and as a dye it is also used in tattoos. With its high index of refraction, opacity, UV resistance, and stability it is frequently used as sunscreen ingredient. Against sunscreen based on chemical absorbers, create sunscreens containing physical absorbers, titanium dioxide, and zinc oxide, often less irritated and allergic skin reactions. In medicine, it enables growth of bones with the implants such as artificial joints and teeth. Quantum dots have remarkable advantages in bioimaging, biosensing, and other biomedical applications. Commercially prepared quantum dots based on Cd sulfides or selenides without surface treatment for

their toxicity are not suitable for biological applications. The toxicity and biosafety materials of carbon nanostructures such as carbon nanotubes, graphene, graphene oxide [1, 2], carbon, graphene quantum dots [3], iron oxide, and titanium oxide [4] are intensively under study.

The electronic structure of rutile quantum dots is investigated via the first-principles band structure method. First, propose a model to passivate the rutile titania surfaces for the local density approximation calculations. In this example, pseudo hydrogen atoms are used to passivate the surface dangling bonds, which remove the localized in-gap surface states in the titania quantum dots [5]. Self-ordered titania quantum dot array was prepared by the process of titanium anodic oxidation through a nanoporous alumina template on a silicon substrate [6]. Titania quantum dots on graphene nanosheets in water-oil suspension display high performance as an anode material for lithium-ion batteries [7].

Nonluminescent titania quantum dots were prepared for photocatalytic degradation methyl orange and methylene blue [8], carmine dye [9], and quantum dots interface in the recombination processes of quantum dot sensitized solar cells [10].

The top-down method was used for the preparation of quantum dots from natural minerals (graphite, molybdenite,

FIGURE 1: Schematic of preparation of TiO₂ quantum dots using reflux.

and tungstenite) and synthetic layered materials (h-BN, h-BCN, and g-C₃N₄). The bulk sample was exfoliated using high intensity ultrasound in the pressurized reactor and obtained nanosheets form with ethylene glycol under reflux at temperature 198°C quantum dots [11–13].

In this paper, we for the first time presented fast, simple, and scalable bottom-up method for synthesis luminescent titania quantum dots TiQDTs from titania oxosulphate and hydrazine hydrate as coupling agents and ethylene glycol, dimethyl sulfoxide, octadecene, dodecanethiol, dimethylformamide, and tetraethyl orthosilicate as solvents. The TiQDTs thus formed are highly luminescent, with the emission maxima controlled by the used excitation wavelength.

2. Experimental

2.1. Titania Quantum Dots Synthesis. All used chemicals, titanium oxosulphate TiOSO₄, hydrazine hydrate $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, ethylene glycol $\text{CH}_2\text{CH}_2(\text{OH})_2$, dimethyl sulfoxide (DMSO) $(\text{CH}_3)_2\text{SO}$, octadecene C₁₈H₃₆, dodecanethiol $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SH}$, dimethylformamide $\text{COHN}(\text{CH}_3)_2$, and tetraethyl orthosilicate (TEOS) $\text{Si}(\text{OC}_2\text{H}_5)_4$, were obtained from Sigma-Aldrich.

100 ml 0.3 M solution of TiOSO₄ was mixed with 20 ml 80% hydrazine hydrate, and the milk-like solution is formed; the 10 ml of this solution was added to 100 ml of ethylene glycol and the reaction mixture was heated under stirring at 180°C. For 3–5 minutes, the reaction mixture turned bright and throughout the next 15 minutes UV luminescence was originated. The reaction solution was allowed to cool to room temperature and centrifuged at 6000 rpm. The same experiment was performed with dimethyl sulfoxide, octadecene,

dodecanethiol, dimethylformamide, and tetraethyl orthosilicate instead of ethylene glycol. The schematic of synthesis TiO₂ quantum dots is presented in Figure 1.

2.2. Characterization Methods. Diffraction patterns were collected with diffractometer Bruker D2 equipped with conventional X-ray tube (Cu K α radiation, 30 kV, 10 mA). Qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database [14].

The morphology of the titania quantum dots was inspected by transmission electron microscopy (TEM) using a 300 kV TEM microscope JEOL 3010F. As a specimen support for TEM investigations, a microscopic copper grid covered by a thin transparent carbon film was used.

High-resolution transmission electron microscope (HRTEM) analysis was performed on FEI Talos F200X. The microscope is equipped with Super-X EDS system with four silicon drift detectors (SDDs) for precise and quantitative energy dispersive X-ray (EDS) analysis for advanced materials characterization. The 300-Mesh Regular Copper Grid coated by Silicon Dioxide (SiO₂)/Monoxide (SiO) was used for sample preparation.

AFM images were obtained using a Bruker Dimension ICON FastScan microscope. AFM samples were prepared by a spin-coating method that consisted of pipetting an aqueous suspension of h-BN-TiO₂ samples onto an atomically smooth support of synthetic mica. The suspension was spin coated on the mica substrate at 6000 r.p.m. For atomic force microscopy (AFM) analysis, a silicon tip on a nitride lever was used with ScanAsyst, air contact mode (resonance frequencies 50/90 kHz).

The hydrodynamic diameter and size distribution of the quantum dots were determined by dynamic light scattering using light scattering using a ZEN 1600 (Malvern Co., USA) particle size analyzer.

XPS measurements were performed with the hemispherical analyzer Phoibos 100 (Specs GmbH, Germany) at take-off angle of 90 deg and the spectra were referenced to the peak of aliphatic C-C bonds at 284.5 eV. The XR-50 (Specs GmbH, Germany) nonmonochromatic X-ray source with spectral line Al K α (photon energy 1486.6 eV) and spectral line Mg K α (photon energy 1253.6 eV) was used to induce the electron emission. The elemental composition was calculated from survey spectra taken at pass energy 40 eV. The electron flood gun was not used for charge compensation. Ti 2p high-resolution spectra taken at pass energy 10 eV were constructed from 30 measurements to obtain the information on the bonding of Ti. The program CasaXPS was utilized for the computer processing of the spectra. Relative sensitivity factor was used from built-in CasaXPS database. The Shirley background shape was used, and the components used for the peak deconvolution were mixed Gauss-Lorentzian lines (70% Gaussian and 30% Lorentzian). The ethylene glycol solution of titania quantum dots was dropped on Si wafer and dried in a vacuum chamber for 30 minutes. The residuum was visible on the wafer and immediately inserted into XPS system.

The PL and UV-vis spectra of the titania quantum dots were determined by Avantes AvaSpec 2048 equipped with high-power (5 W) LEDs at wavelengths 365, 375, 385, 395, and 405 nm as excitation sources.

3. Results and Discussion

Titanyl oxosulphate TiOSO₄ reacts with hydrazine hydrate and nanosized nucleus titania precursor from titanium oxide and hydrazine sulphate are formed:

The particle size of titania precursor measured using dynamic laser scattering is showed in Figure 2; the determined average size was <2 nm. The white titania precursor reacts with organic solvents molecules and leads to its encapsulation (micelle formation) and the reaction solution was gradually clarified. After initial encapsulation, remaining molecules of organic solvents form connections between the individual micelles to form a network within the aqueous media. The resulting hydrogel forms a diffusion and a relatively constant concentration of the encapsulated particles in the gel.

The XRD pattern of purred TiQDTs using dialysis membrane from ethylene glycol is presented in Figure 3. Only the diffraction peaks of anatase PDF 21-1272 were detected. Extending the diffraction bands and increased background is caused by the poor crystallinity of the sample.

Titanium oxides are widely reported in literature, when titanium oxides can exist in various stoichiometry and at different binding energies (BE) of Ti 2p_{3/2} for TiO₂ at

FIGURE 2: Dynamic laser scattering of nucleus titanium(IV) dioxide precursor.

FIGURE 3: XRD pattern of purified TiQDTs.

459.1 eV, Ti₃O₅ at 457.9 eV, Ti₂O₃ at 456.7 eV, TiO at 455.1 eV, and last metal Ti at 453.9 [15, 16]. Each Ti oxide is also a component in O 1s but the reliable literature data are rather poor for some of the oxides. The elsewhere reported shift in Ti 2p between Ti⁴⁺ and Ti³⁺ is from 1.2 eV [16] up to 1.6 eV [17, 18] and between Ti⁴⁺ and Ti²⁺ from 2.4 eV [12] up to 3.1 eV [15]. The reported BE of components varies in the literature due to the calibration process and the charging effect. There are also reported binding energies of Ti 2p_{3/2} and also O 1s for TiO₂ at 458.5 eV–530 eV, Ti₂O₃ at about 455.6 eV–531.5 eV, and TiO at 454.3 eV–531.4 eV [16]. The BE of Ti 2p_{3/2} for TiO₂ is commonly referred to values about 459 eV [17–19] and corresponding to O 1s to values about 530 eV [20] or 531 eV [18]. Photoelectrons from Ti 2p are spin splinted to Ti 2p_{3/2} and Ti 2p_{1/2} separated about 5.73 eV [17].

The basic composition of the sample was calculated from survey spectra taken by Mg source (see Figure 4(a)) because Al source induced Auger's electrons not related to Ti atoms from the sample with kinetic energy about 1025 eV which is also kinetic energy of photoelectrons from Ti 2p; see

FIGURE 4: (a) XPS survey spectra of titanium oxide quantum dots with Mg anode. (b) XPS high-resolution spectra of Ti 2p region with indicated spin-orbit split and FWHM values for each orbital taken with Mg anode (full square) and spectra taken with Al anode on the same sample (full circle) and taken with Al anode on diluted sample (Ti at not detectable level) for Auger peak confirmation (open circle).

in Figure 4(b), full circles. It was confirmed on the sample with Ti 2p under detection limit (diluted sample); see in Figure 4(b), open circles. The basic sample composition in [at.%] is C = 55.1 (RSF 1), Ca = 0.5 (RSF 5.13), N = 2.0 (RSF 1.77), Na = 0.5 (RSF 7.99), O = 26.8 (RSF 2.85), S = 1.4 (RSF 1.74), Si = 13.6 (RSF 0.865), and Ti = 0.3 (RSF 7.9). The silicon is probably the wafer used in sample preparation and oxygen content is influenced by native SiO₂ on the wafer surface. The titanium content is rather small, but after data accumulation for 30 times it is well defined and shown in Figure 4(b). The relative sensitivity of XPS to Ti (Ti 2p orbitals) is given by RSF, listed above, and the value for Ti 2p is one of the highest from the detected elements; moreover the presence of Ti in the sample was confirmed by XRD measurements. A possible misinterpretation of Ti 2p with an Auger line was avoided by comparison between spectra obtained at two different excitation energies.

Moreover the Ti 2p spectra were successfully deconvoluted to the single peaks representing Ti2p_{3/2} and Ti2p_{1/2} with the spin-orbital split about 5.6 eV, about 3% less than expected, and the fit keeps the theoretical 3:2 ratio of peak areas. It confirms that these two peaks are p orbitals and in this part of spectrum it can be only Ti 2p. The other element in close distance is Ru 3p_{3/2} at 461 eV and Ru 3p_{1/2} at 483 eV but it cannot explain peak at 466 eV belonging to Ti 2p_{1/2}. The FWHM values indicated in Figure 4(b) are rather bigger, but it can be the influence of data accumulation process. Therefore we conclude that the titanium is present in XPS detectable level and the binding energy of Ti2p_{3/2} about 459 eV indicates dominant presence of TiO₂ state.

Figure 5 shows the typical particle size distribution of synthesized titania quantum dots in dimethyl sulfoxide, octadecene, dodecanethiol, dimethylformamide, tetraethyl orthosilicate, and ethylene glycol measured by dynamic laser scattering. The size of the particles as determined by laser scattering is considerably larger than that measured by TEM. The laser scattering gives a mean hydrodynamic diameter of

FIGURE 5: Hydrodynamic diameter of prepared TiQDTs for different solvating agents.

TiO₂ core surrounded by the organic solvating layers, which is influenced by viscosity and concentration of the solution. In other words, TEM analysis determines the size of the core quantum dots. Hydrodynamic diameter increases depending on the length of the carbon chain with several molecular sizes of a solvating agent.

Image processing analysis (ImageJ software) of HRTEM micrograph was used to achieve a refinement of microstructure in the sense that we can more accurately analyze crystalline and amorphous domains and the boundaries between them. Also, from Fourier transform (FFT) it is possible to determine and to index crystallographic planes and find their orientations. Figure 6 shows HRTEM micrograph of anatase quantum dots prepared in ethylene glycol. The area used for

FIGURE 6: (a) HRTEM image of anatase quantum dots. The area used for image processing is marked with a black square. A: amorphous region. C: crystalline area. (b) Selected area and (c) Fourier transform of selected area.

image processing is marked with a black square indicating amorphous region (domains) and C denoted crystalline area. Figure 6(b) shows the region of the original image taken with mask of 512×512 pixels; Fourier transform of this area is in Figure 6(c) giving the interlayer spacing to 0.35 nm corresponding to (101) crystal plane of anatase (PDF 21-1272). Considering precise HRTEM investigation, we found a small fraction of amorphous materials. Crystalline anatase quantum dots are with some amorphous domains with the average diameter of 5-6 nm and are interlayered. Figure 7 presented Selected Area Diffraction Patterns (SAED) of prepared quantum dots analyzed by program ProcessDiffraction [21], the diffraction patterns well corresponding with anatase TiO₂ (PDF 21-1272).

For HRTEM investigation is important to sample preparation, and remains of DMSO were well washed from TEM grid. In the TEM Figure 8(a) see solitary quantum dots of large size of about 4 nm. The HRTEM investigation in Figure 8(b) shows the darker cover and crystalline core; the FFT analysis determines the interlayer spacing 0.19 nm. Corresponding $d_{hkl} = 0.189$ nm (200) for anatase has intensity

FIGURE 7: SAED pattern of TiQDTs analyzed by ProcessDiffraction software.

~ 35 a.u. and for carbon about $d_{hkl} \sim 0.19$ nm has intensity < 10 a.u. Based on hkl intensities it is possible to assign this interlayer spacing to anatase and then carbon; origin

(a)

(b)

(c)

FIGURE 8: Titania quantum dots prepared in DMSO. (a) TEM images, magnification 600,000x, (b) HRTEM images, magnification 2,000,000x, and (c) STEM images of mapping of elements, Ti green dot.

of carbon with DMSO carbonization is not probable [22]. Mapping of elements of the same sample solution, where atoms Ti are displayed green, is in Figure 8(c).

(a)

(b)

(c)

FIGURE 9: Titania quantum dots prepared in DMF. (a) TEM images, magnification 600,000x, (b) HRTEM images, magnification 2,000,000x, and (c) STEM images of mapping of elements, Ti green dot.

In the next images, Figure 9 is TEM images of titania quantum dots prepared in dimethylformamide solution. The HRTEM analysis in Figure 9(b) consists again of amorphous

FIGURE 10: AFM topography of TiQDTs prepared in (a) ethylene glycol and (b) dodecanethiol.

and crystalline areas, and the interlayer spacing was calculated into 0.19 nm and 0.29 nm [121], which correspond to brookite (PDF 29-1360), metastable modification of TiO₂, and Figure 9(c) presented mapping of elements again. Titania QDTs prepared in ethylene glycol and dodecanethiol, respectively, were used for AFM investigation, and results are showed in Figure 10. In the insets of figures particle size analysis is shown (height profiles, lateral diameters), where it is shown that dots consist preferably of core crystallite height <2.3 nm for ethylene glycol and <16.4 nm for dodecanethiol. Size distribution of dots is not too wide, but a certain degree of polydispersity is due to partial agglomeration of quantum dot at samples for measurement preparation.

Obtained photoluminescence spectra are shown in Figure 11. The prepared titania quantum dots were excited at different wavelengths ranging from 365 to 405 nm, wavelengths over 405 nm (ethylene glycol, octadecene, and DMSO) and over 395 nm (dodecanethiol, DMF, TEOS) already nonexcited luminescence. The increasing wavelength of the excitation light changes the emission maxima of the dispersion, emission maxima observed to vary only between 450 and 500 nm. Emission peaks of quantum dots prepared with top-down method from graphene oxide [14] and ultrasound and exfoliated MoS₂ [15] and h-BN and h-BCN [23],

respectively, have the much wider range (400–600 nm), indicating their larger polydispersity. Monodispersed character of TiQDTs is the result of bottom-up method, which leads to an increase in cover dots due to temperature or reaction time.

4. Conclusions

Titanium oxides QDTs were prepared with very simple, fast, and cheap bottom-up method. The quantum dots core nuclei precursors were prepared by reaction of titanium oxosulphate and hydrazine hydrate. Formation of quantum dots will never be over 15 min of a reaction of these nuclei with a suitable solvating agent (ethylene glycol, dimethyl sulfoxide, octadecene, dodecanethiol, dimethylformamide, and tetraethyl orthosilicate). The prepared Ti QDTs are the characteristic narrow range of UV excitation (365–400 nm) and also a narrow range of emission maxima (450–500 nm). Given the characteristics of TiO₂, which is nontoxic and biocompatible, one can assume the use of TiO₂ quantum dots in biological applications.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

FIGURE 11: PL spectra of TiQDTs prepared in different solvating agents.

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