

Review Article

Doped Colloidal ZnO Nanocrystals

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Colloidal ZnO nanocrystals are promising for a wide range of applications due to the combination of unique multifunctional nature and remarkable solution processability. Doping is an effective approach of enhancing the properties of colloidal ZnO nanocrystals in well-controlled manners. In this paper, we analyzed two synthetic strategies for the doped colloidal ZnO nanocrystals, emphasizing our understanding on the critical factors associated with the high temperature and nonaqueous approach. Latest advances of three topics, bandgap engineering, n-type doping, and dilute magnetic semiconductors related to doped ZnO nanocrystals were discussed to reveal the effects of dopants on the properties of the nanocrystalline materials.

1. Introduction

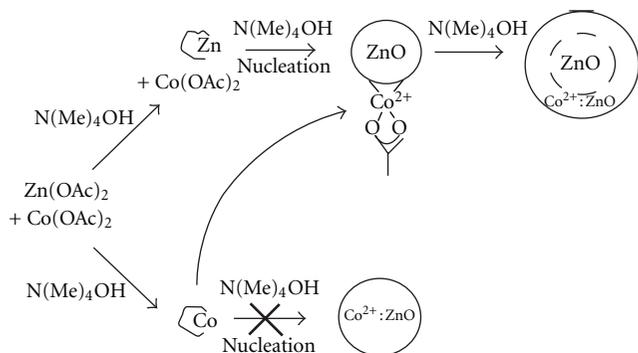
Colloidal semiconductor nanocrystals are of importance as functional materials both for basic research and technological applications due to their unique combination of solid-state properties and solution dispersibility [1–5]. Developing materials with controllable and targeted properties is a central goal for the synthetic chemistry of colloidal nanocrystals. Doping colloidal semiconductor nanocrystals refers to the modification of the compositions and properties of the nanocrystals by intentional introduction of dopants or impurities to the host lattices. In this regard, the synthetic strategies of doped nanocrystals and how the dopants shall influence the properties of the nanocrystalline materials have attracted significant attention in recent years [6–10].

We note that, the definition of doping for colloidal semiconductor nanocrystals may be different from that for traditional semiconductor industry. In the traditional semiconductor industry, doping generally means the introduction of trace amount of impurities into extremely pure semiconductors to tailor the electrical properties. From a synthetic chemistry point of view, doping for colloidal nanocrystals simply refers to the modification of compositions by the incorporation of dopant atoms into the host crystal lattices. The purpose is to enhance the properties, that is, optical, magnetic, or other properties rather than restricted to electrical properties, of the nanocrystals. In

another aspect, heavy, or high, doping level for the traditional semiconductor industry refers to the dopant concentration being on the order of 0.01%. In contrast, the doping concentrations of doped nanocrystals are much higher than 0.01% due to the limited number of atoms contained in a single nanocrystal. In some cases, the doping concentration of the doped nanocrystals can be as high as over 1–10% [11–17], which may also be considered as alloyed nanocrystals or nanoscale solid solutions.

ZnO is a technologically important and environmental friendly semiconductor with many remarkable properties, such as a direct wide bandgap of 3.37 eV, large excitonic binding energy, high electron mobility, large piezoelectric constants, high nonlinear optical coefficients, and radiation hardness. ZnO is promising for many potential applications including thin film transistors [18, 19], sensors [20, 21], light-emitting diodes [22, 23], UV photodetectors [24, 25], UV lasers [26], and piezoelectric power generators [27]. Many potential applications rely on the delicate control over the doping of ZnO materials [28–31]. This has simulated considerable efforts to explore colloidal ZnO nanocrystals and their doped counterparts. A large number of publications have appeared lately reporting the synthesis and applications of the doped colloidal ZnO nanocrystals [32–41].

In this paper we shall analyze two synthetic strategies for the doped colloidal ZnO nanocrystals, emphasizing



SCHEME 1: Synthetic strategy of Co^{2+} doped ZnO nanocrystals (Reprinted with permission from [37]. Copyright (2003) American Chemical Society).

our understanding of achieving successful doping based on the high temperature and nonaqueous approach. We select three topics, bandgap engineering, n type doping, and dilute magnetic semiconductors (DMS) and discuss the latest advances to reveal the effects of dopants on the properties of the nanocrystals, rather than attempting a comprehensive coverage of all the relevant literatures.

2. Synthetic Strategies of Doped ZnO Nanocrystals

2.1. Hydrolysis in Basic Solutions. Hydrolysis of zinc salt in aqueous or alcoholic basic solutions has been the most intensively studied route to generate ZnO nanocrystals at early stages. For example, Haase et al. prepared ZnO nanoparticles by reacting $\text{Zn}(\text{ClO}_4)_2$ with NaOH in methanol at 1988 [42]. This approach was further modified by Pacholski et al. to obtain ZnO nanorods through self-assembly of the ZnO nanoparticles [43].

A natural strategy to obtain doped ZnO nanocrystals is to introduce dopant ions into the initial solutions containing zinc salts. The Gamelin Group studied the synthesis of Co^{2+} doped ZnO nanocrystals using zinc acetate and cobalt acetate as the precursors and tetramethylammonium hydroxide as the base [37]. The results suggest that the dopant ions strongly influence the growth of the ZnO nanocrystals, that is, the dopant exclusion from the critical nuclei and subsequent incorporation of dopant ions in the growth of the nanocrystals, as depicted in Scheme 1. The same doping procedure can be applied to generate Mn^{2+} doped ZnO and Ni^{2+} doped ZnO nanocrystals [37, 41]. Nevertheless, this strategy generally leads to doped nanocrystals with a broad size distribution. The accessibility of high-quality doped ZnO nanocrystals is limited to a few examples in literature.

2.2. The High Temperature and Nonaqueous Approach. Recently the so-called high temperature and nonaqueous approach was adopted to obtain oxide nanocrystals mostly inspired by the success of the synthesis of high-quality CdSe nanocrystals [44, 45]. In 2004, Peng and coworkers

reported a general approach for the synthesis of oxide nanocrystals by reacting metal carboxylate salts in a high temperature and noncoordinating solvent [46]. The Peng group further studied the controlled synthesis of ZnO [36], In_2O_3 [47], and MnO [48] nanocrystals, demonstrating the importance of molecular mechanisms associated with the formation of the oxide nanocrystals. At the same time, the Niederberger group, the Hyeon group, and a number of other groups also contributed to the development of synthetic chemistry of oxide materials, demonstrating a variety of reaction pathways [49–58]. In general, the high temperature and nonaqueous approach may yield high-quality monodispersed oxide nanocrystals with controllable size and decent crystalline features.

These findings provide valuable foundations for the growth of doped ZnO nanocrystals. A simple and effective strategy is to use both dopant precursor and zinc precursor as reagents that undergo a same reaction pathway in the high temperature and nonaqueous approach. In our point of view, at least two factors are critical to achieve high-quality doped ZnO nanocrystals for this scenario.

The first factor is to control the reaction pathways and relative reactivity of the metal precursors. Avoiding segregation of dopant phases is one of the key issues for a successful design of doping strategy. Segregation of dopant phases may be caused by lack of the control of the reaction pathways. Segregation of dopant phases may also be due to the unbalanced crystal growth and dopant incorporation rates. In other words, careful control of the relative reactivity of the dopant precursor to the zinc precursor is obligatory. The reactivity of metal precursors can be modulated by the reaction temperature, concentration, the choice of the metal precursors, and introduction of additional ligands as activators or inhibitors. We use the synthesis of In^{3+} doped ZnO nanocrystals by the alcoholysis route as an example. In our experiments, we found that indium oxide seeds may form prior to the injection of alcohol to the initial reactions to grow the host ZnO nanocrystals because of the unintentional hydrolysis of the indium precursors at high temperature. Furthermore, indium precursor with reactivity much higher than that of zinc precursor may also lead to individual nanocrystals with cubic structures [38]. In this regard we designed a new synthetic scheme in which a solution containing metal precursors is injected into a high temperature solution containing alcohol. The temperature of the solution containing metal precursors was kept at 120°C to minimize the hydrolysis of the indium precursor. We also replaced the previous indium precursor, indium stearate by indium 2-ethylhexanoate, which exhibited much lower reactivity in the alcoholysis route, as shown in Figure 1. The new synthetic scheme led to successful doping with concentration as high as 20 mol.% [59], revealing the importance of controlling the reaction pathway and rational choice of the dopant precursors. In another study, Buonsanti et al. also suggest that balancing the relative reactivity of dopant precursors is essential for the synthesis of Al^{3+} doped ZnO nanocrystals [39]. A more reactive zinc precursor resulted in far less Al^{3+} incorporation. In an extreme case, no doping occurred if aluminum stearate was used in place

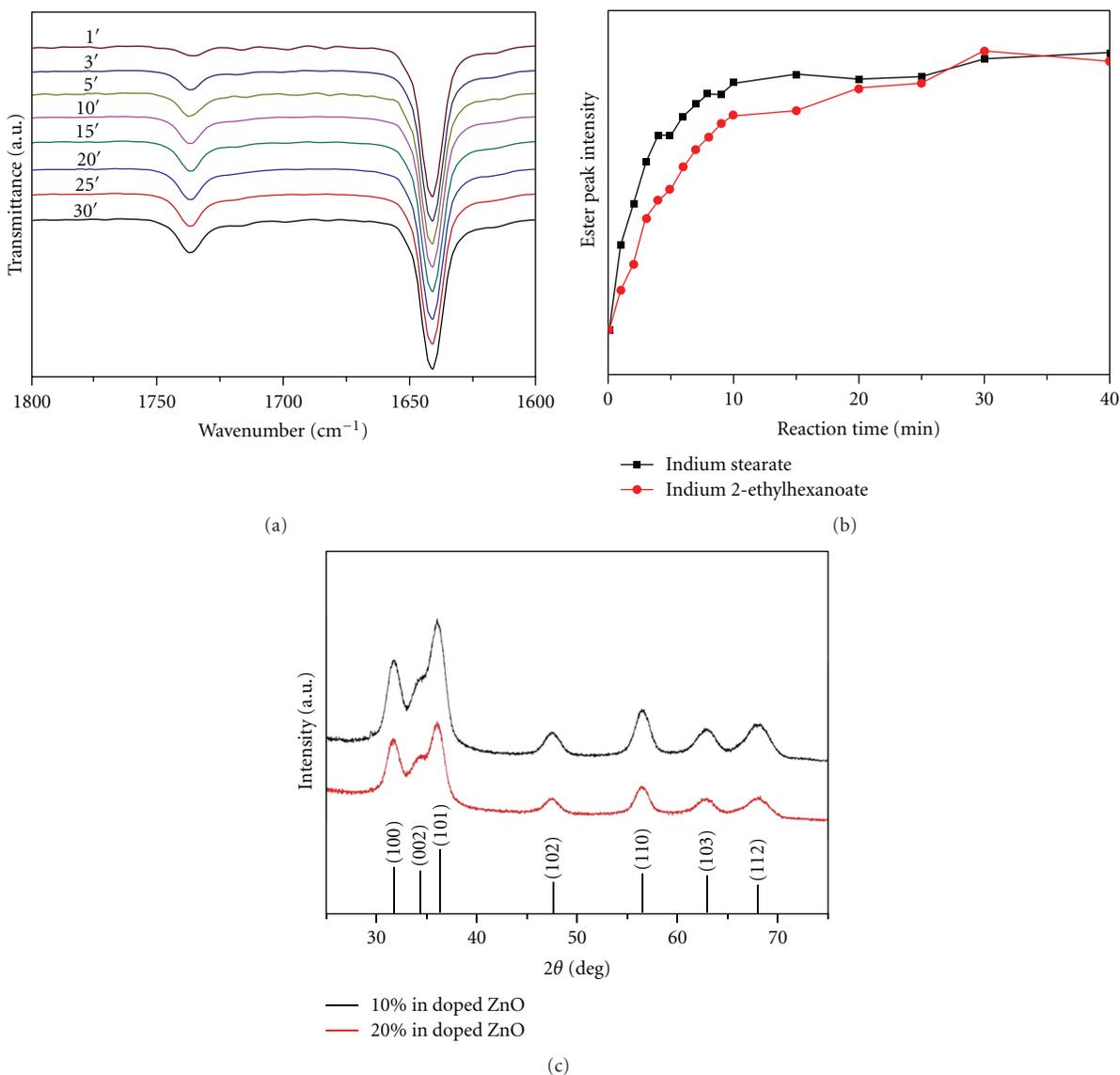


FIGURE 1: (a) Temporal evolution of the alcoholysis reaction of indium 2-ethylhexanoate. All spectra were normalized by the relatively intense C=C vibration band at 1641 cm^{-1} originating from ODE (the solvent) as the standard. (b) Temporal evolution of the normalized ester peak intensity, revealing that the reactivity of indium stearate is higher than that of indium 2-ethylhexanoate; (c) XRD patterns of the In^{3+} doped ZnO nanocrystals.

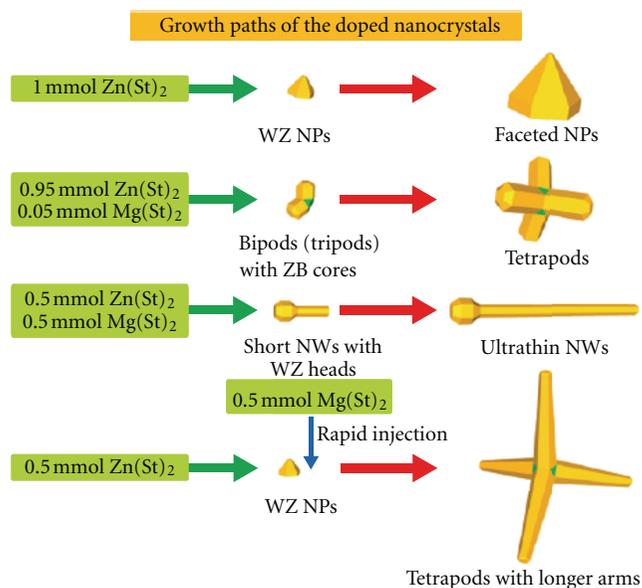
of aluminum acetylacetonate, the aluminum precursor with higher reactivity.

The second factor is to clarify the effects of dopants on the growth of the doped nanocrystals. We observed drastic dopant-induced shape evolution in the case of Mg^{2+} doped ZnO nanocrystals [40]. As shown in Scheme 2, Mg^{2+} doped ZnO nanocrystals with well-defined shapes, from nanopyramids to tetrapods and ultrathin nanowires, were generated depending on the ratio of dopant precursor in the reagents. We demonstrate that the incorporation of Mg^{2+} ions into the ZnO seeds significantly influences the growth of the host lattices at the primary growth stage, leading to initial growth seeds with different crystallographic phases and shapes by the seeded growth experiments. We found that the dopant-induced shape evolution of Mg^{2+} doped ZnO

nanocrystals may also be applied to other dopant system, such as Cd^{2+} (post-transition metal ions), Sn^{2+} (IV group metal ions), Mn^{2+} , and Ni^{2+} (transition metal ions). We suggest that doped ZnO nanocrystals with tailored shapes and desired properties can be acquired by manipulating relative reactivity of the dopant precursors and optimizing reaction parameters in the synthesis. Further theoretical work is preferred to gain more insights on the effects of dopants on the growth of the doped nanocrystals.

3. Effects of Impurities on the Properties of the Doped ZnO Nanocrystals

3.1. Bandgap Engineering. Tailoring the band structure is a central task for the research of semiconductor material. For



SCHEME 2: Growth paths of the Mg^{2+} doped ZnO nanocrystals (reprinted with permission from [40]. Copyright (2010) American Chemical Society).

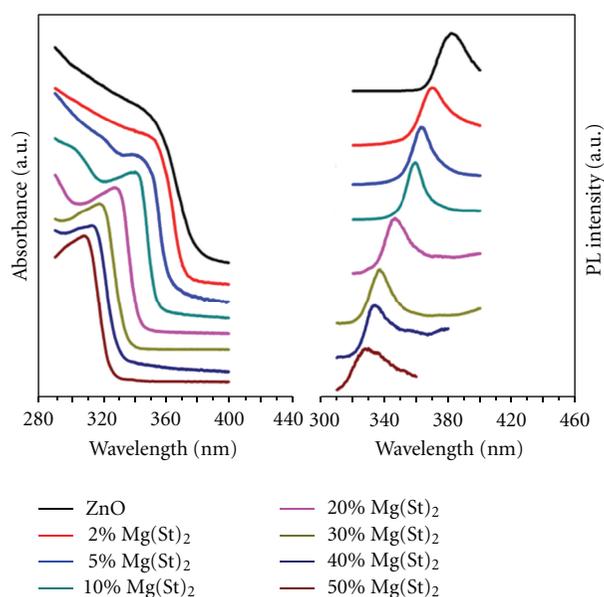


FIGURE 2: Tunable optical bandgaps of the Mg^{2+} doped ZnO nanocrystals (reprinted with permission from [40]. Copyright (2010) American Chemical Society).

many colloidal semiconductor nanocrystals, such as CdSe, CdS, PbSe, and PbS [60–63], the bandgap or band structure of the material is found to be size dependent owing to the well-known quantum confinement effects. Nevertheless, quantum confinement effects may be significant only for ZnO nanocrystals with very small dimensions, for example, ultrathin nanowires and ultrasmall dots, due to the small dielectric constant and small Bohr radius of the photogenerated excitons. For ZnO nanocrystals with dimensions larger

than 5 nm, the bandgap or band structure of the crystals is more or less size independent.

Doping, or alloying with Mg^{2+} or Cd^{2+} , provides an effective approach to achieve bandgap engineering of colloidal ZnO nanocrystals. The Bandgap of bulk ZnO, MgO, and CdO is 3.37 eV, 7.7 eV, and 2.3 eV, respectively. The bandgap of the crystals can be increased (decreased) by incorporating Mg^{2+} (Cd^{2+}) into the ZnO lattices. MgO and CdO assume that the rock-salt structure is not the same as the ZnO wurtzite structure. This may cause a problem for doped ZnO nanocrystals with high content of Mg^{2+} or Cd^{2+} , in which case phase separation is expected to occur.

Wang et al. fabricated Mg^{2+} and Cd^{2+} doped ZnO nanocrystals by thermolysis of a family of metal cupferrates in oleylamine [64]. In spite of the formation of agglomerates in the products, the authors observed that the bandgap of the doped nanocrystals could be tuned in the range of 2.92–3.77 eV. In our lab, we demonstrated that the doping concentration of Mg^{2+} could reach 22.6%, and the optical bandgap of the Mg^{2+} doped ZnO nanocrystals was continuously tuned from 3.3 to 3.9 eV [40], as revealed by the UV-vis absorption and photoluminescence spectra (Figure 2). Primary results on Cd^{2+} -doped ZnO showed that the optical bandgap could be tuned from 3.3 to 3.0 eV by incorporating Cd^{2+} ions.

3.2. *n*-Type Doping. An important aspect of tailoring the electronic properties of the nanocrystals is to control the free carrier type and concentration. We concentrate on the *n*-type doping of ZnO nanocrystals in this paper because the long-term stability of *p*-type doping of ZnO materials is controversy. Pursuing *n*-type doping of ZnO nanocrystals is largely motivated by the appealing goal of achieving low-cost printable transparent electrodes and integrating into emerging flexible electronics by taking advantage of the excellent solution processability of colloidal nanocrystals. ZnO-based transparent conducting oxide (TCO) is considered as a lower cost, environment friendly, and earth-abundant alternative to the widely used indium tin oxide.

It is well known that the electrical conductivity of ZnO-based TCOs can be significantly improved via the incorporation of aluminium [39, 66], gallium [67, 68], or indium [38, 69]. Hammarberg, et al. prepared suspensions of In^{3+} doped ZnO and Al^{3+} doped ZnO nanocrystals in diethylene glycol by means of microwave heating [69]. Both *n*-doping zinc oxide nanocrystals are synthesized with high yields. The as-prepared nanoparticles turn out to be single crystalline with an average diameter of 10–15 nm. Lu and coworkers prepared near-spherical Al^{3+} doped ZnO nanocrystals with an average particle size of 40 nm via a solvothermal method [66]. The spin coated films using the as-prepared Al^{3+} doped ZnO nanocrystals were calcined under a H_2 atmosphere to improve the electrical conductivity. Buonsanti et al. report a rational synthetic strategy for high-quality colloidal Al^{3+} doped ZnO nanocrystals [39]. Tunable surface plasmon absorption in the near-infrared region were observed in their samples, as shown in Figure 3, owing to the high density of free electrons in the nanocrystals which

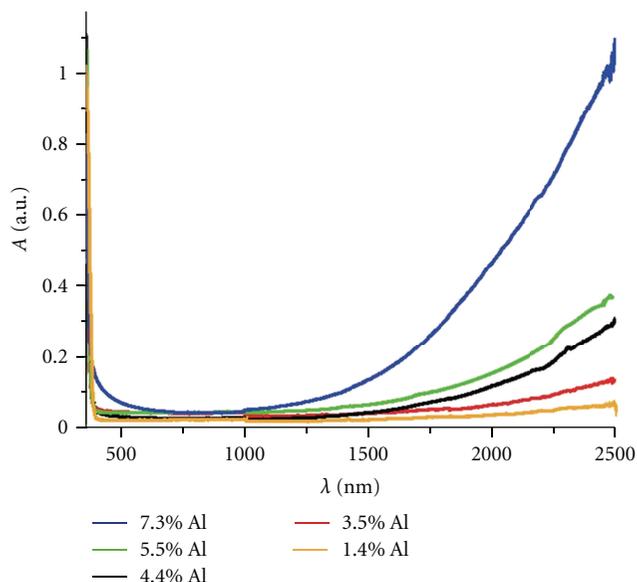
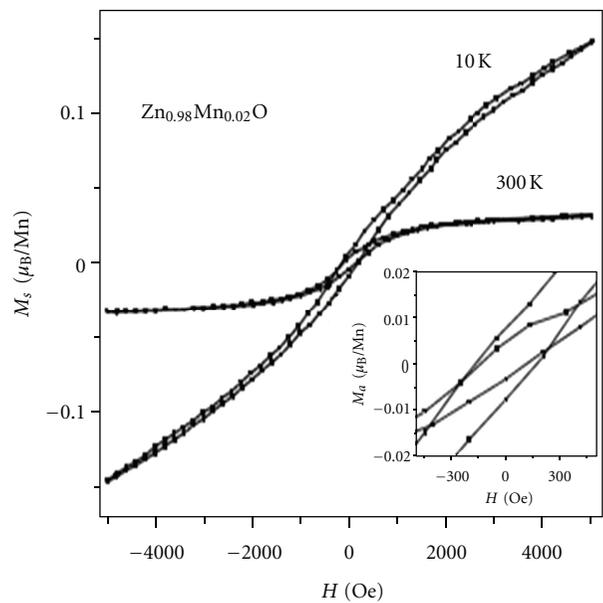


FIGURE 3: Optical properties of Al^{3+} doped ZnO nanocrystals (reprinted with permission from [39]. Copyright (2011) American Chemical Society).

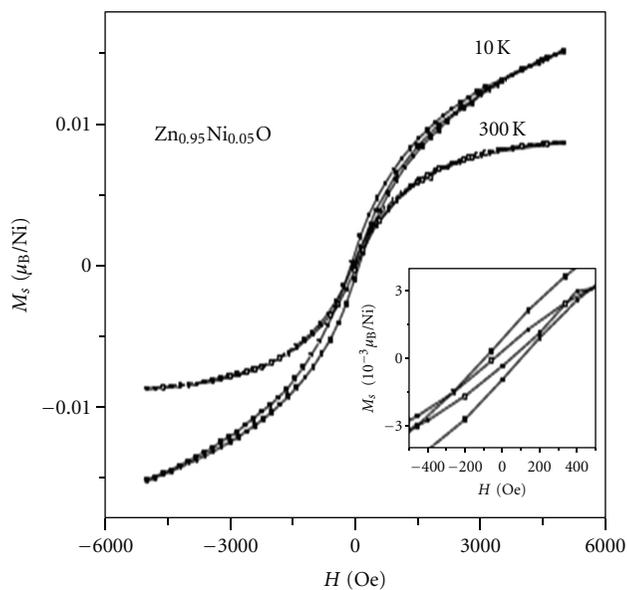
demonstrated the presence of substitutional aluminum in the ZnO lattices.

3.3. Dilute Magnetic Semiconductors. DMS are magnetic materials produced by substitutional doping of semiconductors with paramagnetic transition metal ions, such as Mn^{2+} , Co^{2+} , and Ni^{2+} . The use of transition metal dopants to alter the electronic structures of colloidal semiconductor nanocrystals are attracting intense interests in the field of solar energy conversion, nanospintronics and spin-photonics, optical labels [70–74]. ZnO-based DMS are of particular interest due to a high Curie temperature (T_c) of above 300 K, implying the possibility of achieving room-temperature ferromagnetism. The optical transparency in the visible region of ZnO-based DMSs makes them attractive for magneto-optoelectronic applications.

The Gamelin Group reported Co^{2+} and Ni^{2+} doped ZnO nanocrystals involving hydrolysis and condensation in dimethyl sulfoxide [37]. The as-synthesized nanocrystals were verified to be homogeneous substitutional doping by high-resolution low-temperature electronic absorption and magnetic circular dichroism spectra. Zeeman splitting effects and ferromagnetism with $T_c > 350$ K of the doped ZnO nanocrystals were observed. The Gamelin Group further synthesized colloidal Mn^{2+} -doped ZnO nanocrystals with extremely homogeneous dopant speciation [41]. The authors observed robust ferromagnetism in the spin-coated thin films of the Mn^{2+} doped ZnO nanocrystals, with 300 K saturation moments up to $1.35 \mu_B/\text{Mn}^{2+}$ and $T_c > 350$ K. In a recent study, Cheng and coworkers prepared Mn^{2+} and Ni^{2+} doped ZnO nanocrystals with average diameters of ca. 20 nm, which exhibit ferromagnetism behavior at room temperature by a low temperature solution processing method



(a)



(b)

FIGURE 4: Magnetization hysteresis loops of $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ nanoparticle samples measured at 10 and 300 K. Inset figures contain magnifications of the hysteresis loops [65].

[65], as shown in Figure 4. The Niederberger synthesized Co^{2+} doped ZnO nanorods which are ferromagnetic with T_c exceeding room temperature by the benzyl alcohol reaction pathway [75].

4. Conclusions and Future Prospective

Doping is an effective approach to modify the properties of nanocrystals by means of tailoring the crystal's compositions, which is able to create doped nanocrystals with unprecedented properties. For colloidal ZnO nanocrystals, doping is important in terms of tailoring the bandgap,

carrier concentration, and optical and magnetic properties. The high temperature and nonaqueous approach has achieved impressive progress in recent years, demonstrating the potential of designing and fabricating doped ZnO nanocrystals with desirable size, shape, and compositions.

The advances of the synthetic chemistry of doped colloidal ZnO nanocrystals shall enable the creation of materials with targeted properties, which is critical for use in practical applications. For example, ZnO nanocrystals have been processed as electron transport and hole-blocking interlayers in organic solar cells [76, 77]. For such an application, the band alignment between the ZnO interlayer and the organic active layer is important in terms of achieving selective charge carrier extraction. In addition, the ZnO interlayer should be reasonably conductive to minimize the series resistance of the solar cells. The synthetic strategies discussed in this paper would be able to generate ZnO nanocrystals with tunable band structures and electrical conductivity, allowing the fabrication of ZnO interlayers with enhanced properties.

Acknowledgments

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