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ARTICLE TYPE

Synthesis of Ag doped ZnInSe Ternary Quantum Dots with Tunable Emission

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We reported the synthesis of water soluble, non-toxic, and extremely stable Ag doped ZnInSe quantum dots (QDs) with adjustable emission colors. Proper doping ratio and solution pH were keys for preparing highly luminescent Ag:ZnInSe QDs, whereas the molar ratio of In/Zn was contributed to the adjustable emission wavelength from 504 nm to 585 nm. One amazing property of as-prepared QDs was their extremely strong stability. No obvious PL decrease was observed for Ag:ZnInSe QDs even after irradiation for several months in an ambient atmosphere under room light or ultraviolet light. Due to the extremely strong stability, good biocompatibility, lower cytotoxicity, and tunable emission, as-prepared Ag:ZnInSe QDs were expected available in optical coding, white light-emitting diode (LED), and bio-imaging.

Introduction

Due to the high cytotoxicity of Cd-contained QDs, people have paid more attention to nontoxic Zn-contained QDs [1-3]. However, the emission of pure ZnSe QDs is located in the ultraviolet range. Consequently, metal impurities dopant is required to modulate the emission of ZnSe QDs into the visible range [4, 5]. Due to the lattice mismatch between the dopant and QDs, metal impurities tend to present on the surface of QDs. As a result, photoluminescence (PL) of surface doped QDs is easily quenched with the alteration of surrounding environments. An effective way to avoid this PL quenching is doping impurities inside the lattice of QDs. In 2009, Zhang's group reported the first case of internally doped Cu:ZnSe QDs in aqueous solution [6]. As-prepared water-soluble internally doped Cu:ZnSe QDs had extremely weak chemical stability in the open air due to the inevitable oxidation of mercapto-ligand by Cu impurities. This disadvantage makes these internally doped aqueous Cu:ZnSe QDs impossible to be applied. After then, we investigated the mechanism for the weak stability of Cu:ZnSe QDs [7] and reported the first example of aqueous Cu:ZnSe/ZnS QDs with excellent stability [8]. The key for the excellent stability is the confine of exciton in the core and suppression of ligand oxidation by Cu impurities. Recently, we found that internal doped Ag:ZnSe QDs had good stability because of no oxidation between Ag ions and mercapto-ligand [9]. As far as the stability is concerned, Ag is seen better than Cu for ZnSe-based aqueous QDs.

For doped ZnSe QDs synthesized in aqueous solution, another problem is the poor tunability for QD emission wavelength. For example, aqueous Mn:ZnSe QDs show an impurity emission around 583 nm, assigning to the pseudo-tetrahedral (⁴T₁ to ⁶A₁) transitions of Mn²⁺ ions. The emission wavelength of Mn:ZnSe QDs is not influenced by the ratio of [Zn]/[Mn], the ligand, the synthesis method, and so on. For Cu or Ag doped ZnSe aqueous QDs, impurity emission can be tuned via the size of ZnSe QDs, resulting in a narrow tunable emission window from 450 nm to 510 nm [6, 9]. There are also some works attempting to tune QD emission by co-doping of two types of impurities, such as Cu and Mn. By controlling the relative PL intensity of Cu and Mn emission, co-doped QDs can be tuned to a white light emission

[10]. Though PL intensity is tunable for these co-doped QDs, it is still very difficult to tune the emission wavelength of each impurity in a broad emission window.

In this work, we reported the first example of Ag doped ZnInSe QDs, which not only have extremely strong stability but also have tunable emission in a broad emission scope. Due to the extremely strong stability, good biocompatibility, lower cytotoxicity, and tunable emission, as-prepared Ag:ZnInSe QDs are expected available in optical coding, white LED, and bio-imaging.

Experimental Section

Synthesis of Ag doped ZnInSe QDs.

All materials used in this work were analytical reagents. Zn(NO₃)₂, AgNO₃ were purchased from Beijing Chemical Factory. NaBH₄ was purchased from Guangdong Chemical Reagent Engineering Technological Research and Development Center. NaOH was purchased from Shanghai Zhongshi Chemical Company. 3-mercaptopropionic acid (MPA), In(NO₃)₃·6H₂O and Se powder were purchased from Aldrich. NaHSe solution was prepared by using Se with NaBH₄ according to the reference methods [11, 12].

Aqueous Ag doped ZnInSe QDs were synthesized according to our previous work [9]. Namely, the mixture of Zn(NO₃)₂, AgNO₃, In(NO₃)₃ and MPA was adjusted to pH by using NaOH solution. Freshly prepared NaHSe solution was injected into the mixture after the solution was aerated with N₂ for 30 min. Then, the solution was refluxed at 100 °C. The total concentration of Zn in the mixture is 0.01 mol/L.

Synthesis of polystyrene microspheres coated QDs.

Typically, DVMAC (didecyl-p-vinylbenzylmethylammonium chloride, 0.03 g) was dissolved in styrene (2 mL) and then mixed with 1 mL of an as-prepared Ag:ZnInSe QDs solution under vigorous stirring. After the Ag:ZnInSe QDs were transferred into the styrene phase, the organic solution was separated by decantation and AIBN (azobisisobutyronitrile, 0.015 g) was introduced into the solution followed by 20 mL of water containing OVDAC (octadecyl-p-vinylbenzyltrimethylammonium chloride, 0.1 g) and Triton X-100 (0.1 g). Under mechanical stirring, the oil phase was emulsified. After 30 min of deaeration under N₂, the reaction mixture was heated in an oil bath at 80 °C

and maintained at this temperature for about 6 h. After polymerization, the composite beads were washed with water followed by centrifugation [13].

Cell culture

Human cervix carcinoma cell line (HeLa) was purchased from Nanjing KeyGen Biotech.Co., Ltd. and cultured in medium (DMEM) under a humidified atmosphere (5% CO₂ plus 95% air) at 37 °C. Media were supplemented with 10% heat-inactivated newborn calf serum (Hangzhou Every Green Organism Engineering Materials CO., Ltd.), and 1% Penicillin-Streptomycin (Nanjing KeyGen Biotech. Co., Ltd.). For fluorescent imaging experiment, HeLa cells were seeded into tissue culture dishes (Corning) and incubated for 24 h. Then 100 μL of Ag:ZnInSe QDs was added in to culture medium and incubated for 30 min. Before fluorescent imaging experiments the culture dishes were washed with PBS for three times.

Characterization

UV-vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV-vis near-infrared spectrophotometer. Fluorescence experiments and PL decay experiments were performed with an Edinburg FLS 920 spectrofluorimeter. The excitation wavelength was 420nm. All optical measurements were performed at room temperature under ambient conditions. The PL Quantum yield (QY) of QDs was calculated by comparison with that of rhodamine 6G which possessed known QY of 0.95. Transmission electron microscopy (TEM), high-resolution (HR) TEM, and energy dispersion X-ray spectroscopy (EDX) were recorded by Tecnai F20 electron microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was investigated by using a PHI550 spectrometer with Mg K α excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV. X-ray powder diffraction (XRD) investigation was carried out by using the D/max-2500/PC diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). For XPS and XRD measurement, Ag:ZnInSe QDs powder were used. To obtain the powder, freshly prepared QDs were precipitated from solution by addition of equal volume of isopropanol [12], and then dried at vacuum. Fluorescent images of cells were taken on an Olympus FluoView™ FV1000 fluorescence microscope.

Results and Discussion

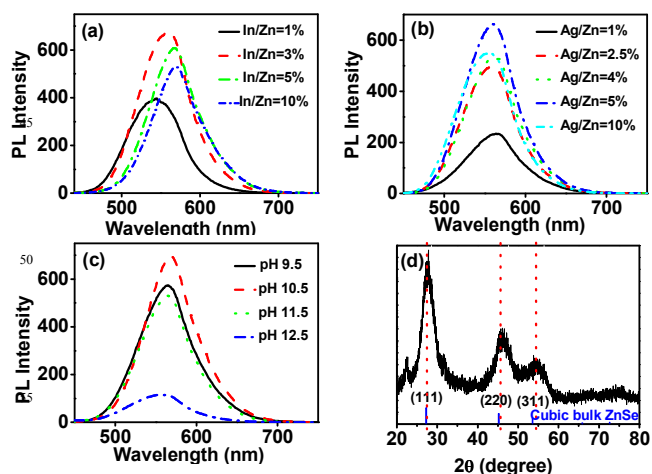


Figure 1 PL spectra of Ag:ZnInSe QDs at different feeding ratios. (a) At different In/Zn with the same Ag/Zn 5% and pH value of 10.5 (a); At different Ag/Zn with the same In/Zn of 3% and pH value of 10.5 (b); At different pH values with the same In/Zn of 3% and Ag/Zn 5% (c). XRD pattern of Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5(d).

To find the optimal synthesis conditions, we compared the PL spectra of Ag:ZnInSe QDs synthesized at different experimental conditions. As could be seen in **Figure 1a**, when the Ag/Zn molar ratio (5%) and pH value (10.5) were kept the same, the alteration of In/Zn feed ratios can not only influence the intensity of emission, but also make the red shift of the PL peak wavelength. We compared the luminescence of four samples with In/Zn molar ratio of 1%, 3%, 5%, and 10%. Clearly, the PL intensity increased with increased In/Zn molar ratio from 1% to 3%, and then decreased with increased In/Zn molar ratio from 3% to 10%. The best molar ratio of In/Zn is confirmed to be 3%. In addition, the PL peak wavelength always shifts to the red with increased In/Zn molar ratio, which makes it possible to tune the emission wavelength of QDs by QD chemical composition as we discussed in detail subsequently.

Figure 1b shows the PL spectra of QDs at different molar ratio of Ag/Zn at the preconditions of the same In/Zn molar ratio (3%) and solution pH (10.5). As can be seen, the molar ratio of Ag/Zn has little influence on the emission wavelength of Ag:ZnInSe QDs, but has great influence on the PL intensity of QDs. According to **Figure 1b**, the best doped amount of Ag in Ag:ZnInSe QDs is about 5% referring to the molar ratio of Ag/Zn.

When investigated the optimal pH values, the feed ratios of In/Zn (3%) and Ag/Zn (5%) were kept the same. As can be seen from **Figure 1c**, the full width at half maximum (FWHM) and the emission wavelength of QDs are similar at different pH values. The highest PL intensity appears at pH 10.5. In this way, we have confirmed the optimized synthesis conditions were In/Zn of 3%, and Ag/Zn(5%, and pH value of 10.5. Under the optimal conditions, Ag:ZnInSe QDs show a PL QY about 15% as compared with rhodamine 6G. The structure of QDs was measured by XRD in **Figure 1d**, which suggested a zinc blende structure of as-prepared Ag:ZnInSe QDs under the optimal conditions. Due to relative small amount of Ag and In than Zn, it is reasonable for a zinc blende structure of Ag:ZnInSe QDs with a bulk cubic ZnSe crystal.

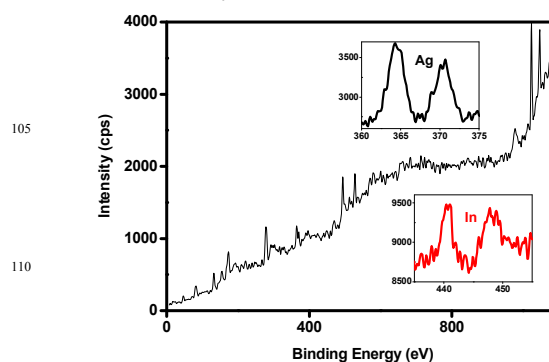


Figure 2. XPS of Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5. The measured atomic ratio of Zn/Se/In/Ag/S is 1/0.5/0.07/0.29/0.69.

The chemical composition and shape was also measured. From XPS result in **Figure 2**, the peak at binding energy of 368.5 eV was assigned to Ag⁺ (Ag₂Se), whereas the peak at 374.5 eV was assigned to 3d energy level of Ag⁺. As for In element, the peaks at 444.3 eV and 451.6 eV were assigned to In³⁺ (In₂Se₃) and 3d. Obviously, Ag and In have formed chemical bond with Se²⁻ ions in ZnSe QDs. Moreover, the atomic ratios of Zn/Se/In/Ag/S in QDs were measured as 1/0.5/0.07/0.29/0.69, suggested a QD composition of Ag_{0.29}ZnIn_{0.07}Se_{0.5}S_{0.69}. The chemical composition of the as-prepared Ag:ZnInSe QDs was also measured by EDX analysis. As can be seen from **Figure 3**, QDs were composed of Zn, Se, Ag and In ions. Moreover, the distribution of Zn, Se, Ag,

and In was similar, suggesting the homogeneous composition of QDs. In **Figure 4**, TEM image showed quasi-spherical QDs. From the inset HRTEM image in **Figure 4**, Ag:ZnInSe QDs show ordered crystalline with a diameter of 3.8 nm.

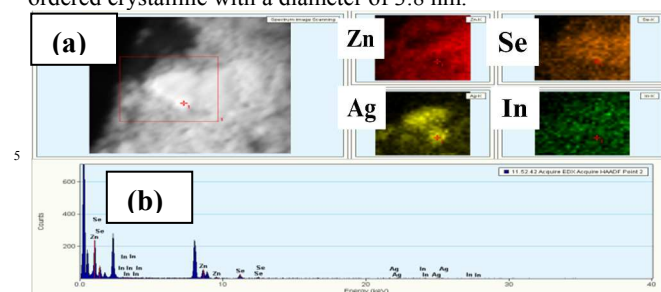


Figure 3. Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5 after refluxing for 4 hours. Distribution of Zn, Se, Ag and In elements in TEM picture (a); EDX results of all elements (b).

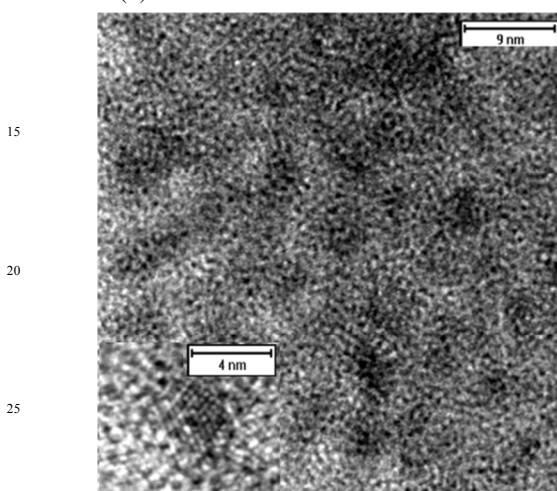


Figure 4. TEM and HRTEM (inset) of Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5. The scale bars are 9 nm (TEM) and 4 nm (HRTEM).

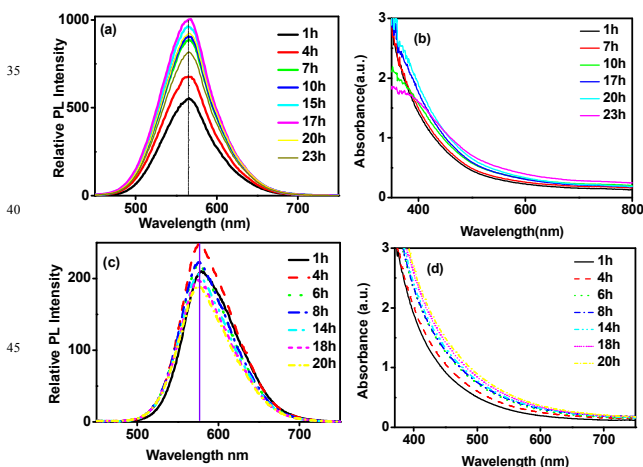


Figure 5. Time-resolved PL and absorption spectra of Ag:ZnInSe QDs at Zn/In/Ag/Se feeding ratios of 1.0/0.03/0.05/0.2, and pH 10.5 (a) and (b); Zn/In/Ag/Se feeding ratios of 1.0/1.0/0.04/0.2, and pH 10.5 (c) and (d).

Figures 5a and 5b show the PL and absorption spectra of Ag:ZnInSe QDs at different growth time under refluxing. In the case of refluxing time below 7 h, the PL intensities of QDs

rapidly increase with the refluxing time. After 7 h, the PL intensities of Ag:ZnInSe QDs show only a small increase. The maximal PL intensity appears at refluxing time of 17 h. Overall, the PL intensity and emission wavelength of Ag:ZnInSe QDs change a little after 7 h' refluxing. From another viewpoint, it also suggests as-prepared Ag:ZnInSe QDs of good thermal stability if their growth time is over than 7 h. In **Figures 5c and 5d**, we also show the time-resolved PL and absorption spectra of Ag:ZnInSe QDs at a high In/Zn molar ratio (100%). Similarly results are also observed for these QDs with high In/Zn molar ratio. There is no serious PL alteration after 6 h' refluxing, suggesting good thermal stability of as-prepared QDs.

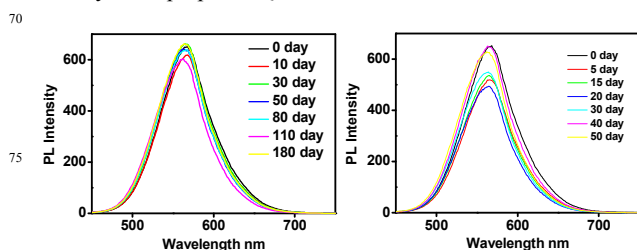


Figure 6. Time-dependent PL spectra of Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5 (a) under ambient atmosphere in the presence of air and room light illumination; (b) under ambient atmosphere in the presence of air and UV light with emission of 365 nm.

Besides, Ag:ZnInSe QDs have extremely good stability under the irradiation of room light or UV light at an ambient environment. The samples were stirred to keep a homogenous irradiation of the whole solution. As can be seen from PL spectra in **Figure 6**, the emission wavelength and PL intensity of the sample do not have any change at the room light irradiation. As for the sample under the irradiation of UV light (12W, 365 nm), its emission wavelength and PL intensity show no serious alteration within 50 days' irradiation. Then, the sample appears precipitation. Our previous work has proved that the stability under UV irradiation is about 2 h for Cu:ZnSe and about 10 days for Cu:ZnSe/ZnS QDs [8]. In comparison to aforementioned reference work, the extremely strong stability against light irradiation should be an advantage of the current as-prepared Ag:ZnInSe QDs.

Table 1 XPS results for Ag:ZnInSe QDs. The measured atomic ratios of In/Se and In/Zn were calculated according to the integrated intensity and the sensitivity factor of each element.

	feeding ratios	measured ratios	feeding ratios	measured ratios
	In/Se	In/Se	In/Zn	In/Zn
	0.05	0.09	1%	4.5%
	0.2	0.16	4%	8%
	1.25	0.8	25%	62%
	2.5	1.3	50%	130%

Another advantage of Ag:ZnInSe QDs should be the broadly adjustable emission. In the above analysis of Figure 1, we have found that QD emission wavelength changed with the amount of In for Ag:ZnInSe QDs. In Figure 7, we compared PL spectra of Ag:ZnInSe QDs at a large range of In/Zn molar ratios. The molar ratio of Zn/Ag/Se is 1.0/0.04/0.2, and pH value is 10.5 in this figure. With the increased In/Zn molar ratio from 0 to 100%, the emission wavelength of Ag:ZnInSe QDs could be adjusted continuously from 504 nm to 585 nm, giving QD emitting colors from blue-green to orange-red. **Table 1** has listed the feeding molar ratios of In/Zn and In/Se as well as the measured molar

ratios of In/Zn and In/Se in Ag:ZnInSe QDs via XPS. As can be seen, with the increased In feeding ratio, the content of In for QDs also increases. It should be the reason for the adjusted emission colors of QDs in Figure 7. As far as we know, this is the first work realizing the broadly PL adjusting from 504 nm to 585 nm by using aqueous doped ZnSe QDs.

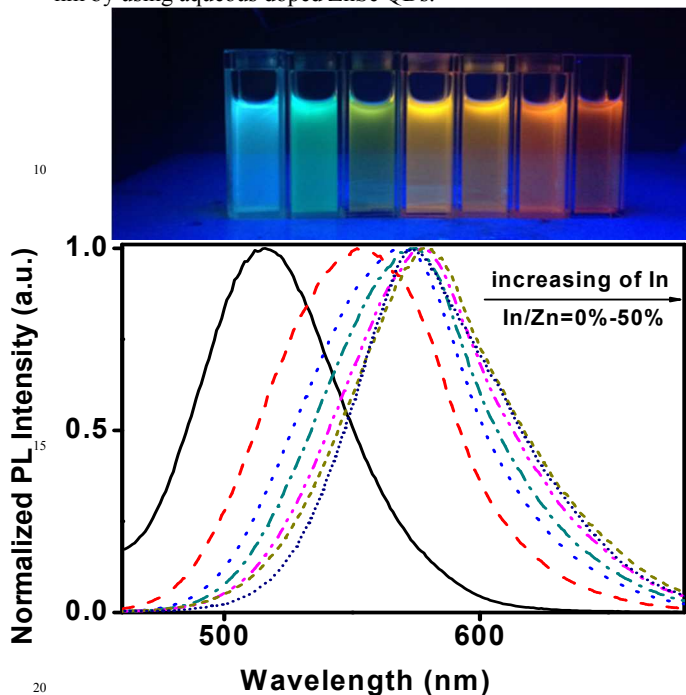


Figure 7. PL spectra and photo under irradiation of an UV lamp of Ag:ZnInSe QDs at different In/Zn feeding ratios 0%-50% from left to right. All samples are refluxed 4 hours.

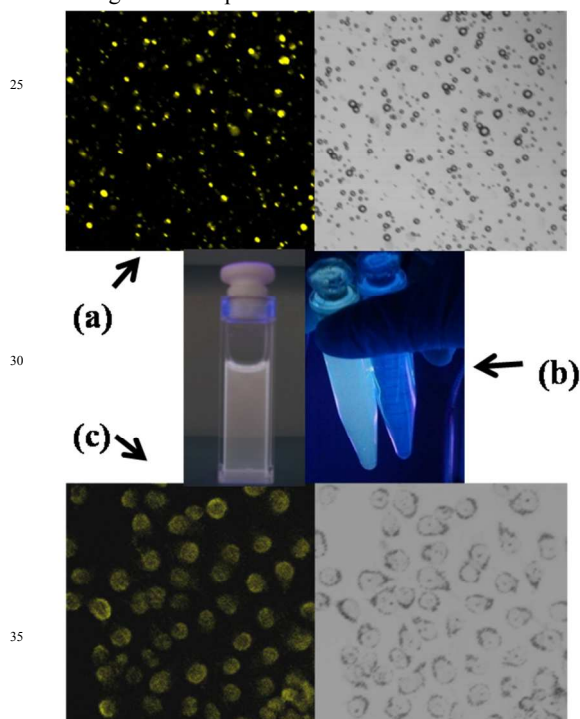


Figure 8. The images of Ag:ZnInSe QDs with In/Zn of 3%, and Ag/Zn 5%, and pH value of 10.5 in polystyrene microspheres and the corresponding PL images with an excitation wavelength of 458 nm (a); photo of white light Ag:ZnInSe mixing QDs with different color under irradiation of an UV lamp (12 W, 365 nm)

(b); The images of HeLa cells stained by Ag:ZnInSe QDs in the light field and the corresponding PL image with an excitation wavelength of 514 nm.

Due to the extremely strong stability and broadly emission wavelength, as-prepared QDs are available in many fields. In the following text, we would like to show the application of QDs. First, as-prepared QDs are available in optical coding. Ag:ZnInSe QDs have good stability, which can ensure their PL during the process of radical polymerization in solution. As can be seen in **Figure 8a**, as-prepared QDs-polystyrene microspheres show bright PL. In addition, Ag:ZnInSe QDs have broadly adjustable emission wavelength. Therefore, different colored Ag:ZnInSe QDs can be coated in polystyrene microspheres together, which is available for optical encoding. Second, as-prepared QDs can also be used in white LED. **Figure 8b** shows the PL photograph of a mixture using blue-green and orange-red Ag:ZnInSe QDs under the irradiation of an UV lamp (12W, 365 nm). Clearly, the mixed QDs have a white emission. Thus, Ag:ZnInSe QDs can be used as a luminescent material of white LED. As far as we know, significant recent advances have been reported in UV and visible LEDs by using high Al-content AlGaIn [14-16] and InGaIn [17-21] QW technologies. The advances in both UV and visible LEDs based on III-Nitride technology [14-21] result in the potential integration of these excitation sources with the QDs technology developed here in practical white LEDs. Third, as-prepared QDs can be applied in bio-imaging. Due to the high cytotoxicity of Cd-contained QDs, more investigators have paid more attention to Zn-contained QDs, especially doped ZnSe QDs. However, doped ZnSe QDs can only be excited by ultraviolet with high energy, which tends to bring hurting to organism. Due to the ability for absorbing long wavelength excitation light, as-prepared Ag:ZnInSe QDs in this work can avoid aforementioned problem. **Figure 8c** shows the images of HeLa cells stained by Ag:ZnInSe QDs in the light field and the corresponding PL image (excited by 514 nm). In fact, the excitation wavelength can be change from 350 nm to 550 nm by using Ag:ZnInSe QDs, providing more choices of excitation than that using doped ZnSe QDs.

80 Conclusions

In conclusion, we reported the synthesis of Ag:ZnInSe QDs in aqueous solution. Proper doping ratio and solution pH are the key for prepared lightly luminescent QDs. The emission wavelength of Ag:ZnInSe QDs can be controlled by the molar ratio of In/Zn, resulting in tunable emission from green to red. As-prepared QDs have extremely strong stability. The emission of QDs can keep for several months under the irradiation of ultraviolet light. Due to the extremely strong stability, good biocompatibility, lower cytotoxicity, and broadly tunable emission scope, as-prepared Ag:ZnInSe QDs can be used in many fields, for instance optical coding, white LED, and bio-imaging.

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Notes and references

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Ag:ZnInSe QDs with extremely good stability, good biocompatibility, lower cytotoxicity and continuously tunable spectra from 504 nm to 585 nm.

