Facile encapsulation of SiO$_2$ on ZnO quantum dots and its application in waterborne UV-shielding polymer coatings

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This paper presents a facile method for encapsulation of a SiO$_2$ layer on the surfaces of ZnO quantum dots (ZnO QDs) to fabricate ZnO QD@SiO$_2$ nanoparticles. Coating of a SiO$_2$ layer can effectively improve the dispersion of ZnO QDs in an aqueous phase, insulate the photocatalytic activity of ZnO QDs and increase the photoluminescent quantum yield. When the as-obtained ZnO QD@SiO$_2$ nanoparticles were introduced into acrylic latex, highly transparent, excellent UV-shielding and durable waterborne polymer coatings were easily fabricated. Moreover, the polymer coatings can convert UV into blue light effectively, which is beneficial for their application as agricultural films.

Introduction

In the past decades, ZnO nanoparticles have attracted considerable attention, because of their great potential for a variety of practical applications in solar cells, catalysts, photodetectors, sensors, light-emitting devices (LEDs) and so on. As a semiconductor with a band gap of 3.37 eV, ZnO nanoparticles have also been widely used as a UV absorber in sunscreen and textile fibers due to their efficient UV light absorption and good weathering resistance. However, owing to their intense scattering of visible light, the pigmentary grades of ZnO nanoparticles usually produce opaque systems when they are embedded into polymer matrices, which seriously restrict their application in highly transparent materials.

ZnO quantum dots (ZnO QDs) are a special kind of ZnO nanoparticles that can show an obvious "quantum confinement effect". They have a very small size (usually, less than 10 nm) and retain the excellent UV absorption capability, making them excellent candidates for fabrication of highly transparent UV-shielding polymer-based nanocomposites, such as poly(methyl methacrylate)/ZnO nanocomposites, polystyrene (PS)/ZnO thin films, and poly(butyl methacrylate)/ZnO nanohybrid films. Although these reported nanocomposites were highly transparent and effectively blocked the UV light below 340 nm, the inherent photocatalytic activity of ZnO QDs was not paid attention. In fact, ZnO QDs have remarkable, even higher photocatalytic activity than the well-known TiO$_2$ nanoparticles, resulting in the decomposition of polymer matrices.

Therefore, bare ZnO QDs are actually ineligible to fabricate the long-term UV-shielding materials.

On the other hand, ZnO QDs are prominent in luminescent emission. In comparison with some classic semiconducting luminescent quantum dots like CdS, CdSe and CdTe, ZnO QDs are of particular interest for biological fluorescence label applications due to their low cost and intrinsic nontoxic nature. However, the luminescent ZnO QDs, typically prepared from a sol–gel process of a zinc salt in alcohol, are usually very unstable and seriously aggregate into aqueous systems, and water molecules are able to attack their luminescent centers on the surfaces and destroy them rapidly. These hinder the application of ZnO QDs in water-based systems, such as biological systems and waterborne polymer coatings. To work out these issues, surfactants and polymers are usually adopted to stabilize the luminescent ZnO QDs in the aqueous phase. However, as mentioned above, ZnO QDs can cause the decomposition of these surfactants and polymers, leading to the instability of the coated ZnO QDs.

Encapsulation of an inert silica layer on ZnO nanoparticles is a good strategy to insulate their photocatalytic activity as well as to increase their surface hydrophilicity. However, the sizes of these ZnO nanoparticles encapsulated with silica (ZnO@SiO$_2$) reported so far are rather too large to fabricate highly transparent films or have rather tedious synthetic procedures.

In this paper, we present a facile method for fabrication of ZnO QD@SiO$_2$ nanoparticles by in situ coating of the ZnO QDs from the sol–gel process of LiOH–H$_2$O and Zn(OAc)$_2$·2H$_2$O. Compared with bare ZnO QDs and the previously modified ZnO QDs, the as-obtained ZnO QD@SiO$_2$ nanoparticles not only absorb UV light, but also have several merits: (i) they have excellent dispersion and high photoluminescent quantum yield...
in the aqueous phase; (ii) their photocatalytic activity has been considerably decreased; (iii) when these nanoparticles are embedded into waterborne acrylic latex, highly transparent, UV-shielding and durable coatings or films can be obtained; (iv) these nanocomposite films can convert harmful UV light to nutritious blue light for plants.

Experimental procedure

Materials

Zinc acetate dehydrate (Zn(Ac)_2·2H_2O), tetraethoxysilane (TEOS), lithium hydroxide monohydrate (LiOH·H_2O), hexane, absolute ethanol, and Rhodamine B were all purchased from Sinopharm Chemical Reagent Co. Acrylic latex (PA, solid content 45.5%, PRIMAL AC-268) was supplied by Dow Chemical. All chemicals were used as received.

Fabrication of ZnO QD@SiO_2 nanoparticles

ZnO QDs were prepared through the sol–gel process of LiOH·H_2O and Zn(Ac)_2·2H_2O in absolute ethanol. Briefly, 1 mmol of LiOH·H_2O was dissolved in 50 ml of absolute ethanol, and agitated for 30 min under sonication to ensure complete dissolution of LiOH·H_2O. 0.25 mmol of Zn(Ac)_2·2H_2O was then added into this solution. The whole mixture was stirred for another 10 min to produce a clear solution. Afterwards, the mixture was heated to 70 °C and refluxed at that temperature for 3 h to get the ZnO QD dispersion. After the system was cooled down to room temperature, various amounts of TEOS (20, 40, 60, 120 or 200 μl) and 300 μl of H_2O were sequentially added to this dispersion. This mixture was immediately treated with ultrasound for 20 min and then stirred at room temperature for 6 h. The resultant solution was poured into 200 ml of hexane to precipitate the nanoparticles, and then washed with 15 ml of absolute ethanol twice. These wet ZnO QD@SiO_2 nanoparticles were dispersed in water to obtain an aqueous dispersion for further use.

Preparation of PA/ZnO QD@SiO_2 polymer coatings and films

The PA/ZnO QD@SiO_2 films were prepared via the drop-casting method. The as-obtained ZnO QD@SiO_2 aqueous dispersion and PA were mixed under sonication at room temperature for 20 min, and then dropped onto clean quartz glass slides (25 × 40 mm^2) and dried at 30 °C to obtain transparent polymer films.

Characterization

High resolution transmission electron microscopy (HRTEM) images were taken with a JEM-2100F field emission microscope (JEOL, Japan). The carbon-coated copper grid was dipped into the aqueous dispersion of the samples, and then taken out and dried in air. Scanning electron microscopy (SEM) was conducted with a Philips XL 30 microscope (Philips, Netherlands). Electrophoretic mobility (EM) measurements were performed using a Zetasizer Nano ZS90 instrument (Malvern Instrument, UK). Photobleaching experiments were carried out using a 150 W high-pressure mercury lamp as the irradiation source. UV-vis absorption and transmittance spectra were recorded using a U-4100 spectrophotometer (Hitachi, Japan). UV-shielding performance and photostability experiments of the polymer films were carried out in an accelerated weathering tester (QUV/se, USA). The emission spectra were characterized using a FLS920 fluorescence spectrophotometer (Edinburgh Instruments, UK) using a 450 W xenon lamp as the excitation source.

Photocatalytic activity of ZnO QDs and ZnO QD@SiO_2

The photocatalytic activities of ZnO QDs and ZnO QD@SiO_2 were determined by the photocatalytic degradation of Rhodamine B under UV light as follows: 10 mg ZnO QDs or ZnO QD@SiO_2 were added into 40 ml Rhodamine B aqueous solution (10 mg l⁻¹) and stirred in the dark for 2 h for complete dispersion and adsorption/desorption equilibrium. This dispersion was irradiated using a 150 W high-pressure mercury lamp under constant stirring. At regular irradiation intervals, the suspension was sampled, centrifuged, and the absorption intensity at 552 nm (A_0 and A_t correspond to the absorptions at time t and the initial time, respectively) was determined with a UV-vis spectrophotometer.

UV-shielding performance of polymer films

The degradation behavior of Rhodamine B in an acrylic resin film was employed to evaluate the UV-shielding performance of the nanocomposite polymer films under UV radiation. The Rhodamine B-doped acrylic resin film (i.e. Rhodamine B film) was prepared as follows: 2.5 g of Rhodamine B aqueous solution (4.5 g l⁻¹) and 5 g of PA were mixed under sonication for 20 min to achieve a homogeneous system, and then coated on a quartz glass slide with a 120 μm rod and dried at room temperature. The quartz glass slide coated with a Rhodamine B film was placed in an accelerated weathering tester. Then a quartz glass slide coated with the UV-shielding polymer film was put on the top of this Rhodamine B film to protect Rhodamine B molecules from degradation by UV light, as shown Scheme 1. The wavelength of the employed UV light was 310 nm, and the measured light power reaching the surface of the sample was 0.71 W m⁻². The photodegradation reaction was conducted at 60 °C. At given intervals, the Rhodamine B film was taken out and the absorption intensities at 552 nm were determined with a UV-vis spectrophotometer.

Scheme 1 Schematic illustration of the UV-shielding performance test of polymer films.
Results and discussion

Fabrication of ZnO QD@SiO2 nanoparticles

The ZnO QD@SiO2 nanoparticles were obtained through two steps. Pure ZnO QDs were firstly prepared via the sol–gel process of LiOH·H2O and Zn(Ac)2·2H2O. Then, a silica layer was in situ coated on the surfaces of ZnO QDs through hydrolysis–condensation reaction of TEOS in a mixture of ethanol and water. It should be noted that direct charge of TEOS and water into the as-obtained ZnO QD dispersion was very important to obtain the well dispersed nanoparticles. This was because the freshly obtained ZnO QDs were actually protected by excess LiOH, and tended to aggregate or underwent Ostwald ripening to form large nanoparticles if they were separated from the dispersion.

Fig. 1 demonstrates the HRTEM images of ZnO QDs and ZnO QD@SiO2. The average size of ZnO QDs is estimated to be about 3 nm (Fig. 1a). The inset reveals the visible lattice fringes of ZnO QDs with the lattice distance of 0.26 nm, corresponding well with that of the d-spacing of (002) planes of wurtzite ZnO. However, it is hard to observe the lattice fringes of ZnO QD@SiO2 from Fig. 1b–f, suggesting the formation of a silica layer on ZnO QDs. The silica layer on the surface of ZnO QDs is not easy to be distinguished because of the low contrast between the silica layer and the carbon film on the copper grid, especially for those ZnO QD@SiO2 nanoparticles prepared with the amounts of TEOS of 20, 40 and 60 µl. Nevertheless, the silica layer on the ZnO QD@SiO2 nanoparticles prepared at 120 µl of TEOS is observed, as shown in the inset of Fig. 1e. The energy-dispersive X-ray (EDX) spectrum (Fig. 1g) shows that this sample was mainly composed of Zn, O and Si, confirming the existence of the silica layer. When 200 µl of TEOS was used, the ZnO QD@SiO2 nanoparticles tended to form a particle network due to the excessive amount of TEOS (Fig. 1f).

The different morphologies of ZnO QD@SiO2 nanoparticles caused by the different amounts of TEOS can also be seen from the appearance of the freshly prepared nanoparticle dispersions, as shown in Fig. 2. The freshly prepared ZnO QDs in alcoholic dispersion was almost transparent. When inadequate amounts of TEOS (20, 40 or 60 µl) were used, the as-obtained ZnO QD@SiO2 dispersions were opaque. When sufficient amounts of TEOS (120 or 200 µl) were used, the as-obtained dispersions were clear. The more the TEOS amount, the more transparent the resultant dispersion was. This should be attributed to the destabilization of bare ZnO QDs in an ethanol–water system, causing the aggregation of ZnO QDs. When enough TEOS was used, none of bare ZnO QDs was left and all the ZnO QD@SiO2 nanoparticles were well dispersed in the ethanol–water system, producing a clear dispersion.

Photocatalytic activity of ZnO QD@SiO2 nanoparticles

Fig. 3 shows the decay curves of the absorption peak of Rhodamine B aqueous solutions as a function of UV radiation time in the presences of ZnO QDs and ZnO QD@SiO2 nanoparticles. With bare ZnO QDs, Rhodamine B was almost completely degraded after 80 min of UV irradiation. The ZnO QD@SiO2 nanoparticles also caused the degradation of Rhodamine B. Nevertheless, as the amount of TEOS increased, the degradation rate gradually reduced. For these ZnO QD@SiO2 nanoparticles prepared with 120 µl of TEOS, only about 20% of Rhodamine B was degraded after 80 min UV radiation. This indicates that the photocatalytic activity of ZnO QDs has been efficiently insulated by the SiO2 shell. Further increasing the TEOS amount (200 µl) did not change the degradation rate of Rhodamine B, suggesting that 120 µl has already been sufficient to completely encapsulate ZnO QDs, which is consistent with the HRTEM observation.
Dispersion and stability of ZnO QD@SiO$_2$ in water

Fig. 4 shows that the ZnO QD@SiO$_2$ aqueous dispersion (concentration: 1 wt%) was transparent, with as high as 99% of transmittance within the visible region, and the dispersion emitted bright blue light under UV light, which did not decay even after 4 month storage (Fig. 5a). This suggests the excellent storage stability of ZnO QD@SiO$_2$ nanoparticle dispersion. The high stability resulted from their high zeta ($\zeta$) potential, i.e., $-42.0$ mV for the freshly prepared ZnO QD@SiO$_2$ aqueous dispersion and $-31.2$ mV after 4 month storage. In contrast, although the freshly prepared bare ZnO QD alcoholic dispersion was transparent, as shown in Fig. 5b, it became turbid and seriously flocculated within 10 min after water was added because both the aggregation and the growth of ZnO QDs upon Ostwald ripening produced precipitates from the dispersion. This process was always accompanied by a red-shift of the emitting spectrum. The fluorescence of the ZnO QD aqueous dispersion gradually changed from blue to green and yellow within few minutes, and finally disappeared, since the visible emission of ZnO QDs is related to oxygen vacancies that are easily destroyed by the hydroxyl groups of water. These results indicate that encapsulation of silica can greatly improve the stability and dispersibility of ZnO QDs in water.

UV-vis absorbance of nanocomposite polymer films

Fig. 6a presents the UV-vis transmittance spectra of a neat PA film and PA/ZnO QD@SiO$_2$ nanocomposite polymer films containing different concentrations of ZnO QD@SiO$_2$ nanoparticles. All the film thicknesses were measured to be $28 \pm 1$ $\mu$m. The neat PA was nearly transparent for 250–700 nm wavelength of light. In contrast, the nanocomposite films could block the UV light below 340 nm. When the ZnO QD@SiO$_2$ concentration increased from 2.2 to 11%, the UV-shielding performance of the films increased,
and their transparency were still very high in the visible region, being close to that of the neat PA film. Further increasing the ZnO QD@SiO₂ content to 15% would cause a little loss of transparency. However, these films could not block the UV light within the entire 200–340 nm range at the thickness of 28 ± 1 μm. According to Bouguer–Lambert–Beer law, the absorbance of a film is directly proportional to the film thickness. ¹⁴ That is to say, increasing the film thickness will be an efficient way to attain good UV-shielding performance. Fig. 6b shows the UV-vis transmittance curves of neat PA and PA/ZnO QD@SiO₂ polymer films with 3.7% of ZnO QD@SiO₂ nanoparticles but different thicknesses. The transmittance of the film below 340 nm gradually reduced as the film thickness increased. Almost all the UV light below 340 nm (whole 200–340 nm) was blocked at the film thickness of 440 ± 5 μm. Even for such a thick film, no obvious transparency loss within 400–700 nm was observed, which was further confirmed by the comparison in the photograph between the neat PA and nanocomposite films in Fig. 6c. This is ascribed to the extremely small size of the ZnO QD@SiO₂ nanoparticles and their good dispersion in waterborne acrylic latex.

UV-shielding performance of the nanocomposite polymer film

In order to investigate the UV-shielding performance of the polymer coatings, a Rhodamine B-doped acrylic resin film (i.e. Rhodamine B film) protected with neat PA or the nanocomposite polymer films (ZnO QDs@SiO₂ concentration: 3.7 wt %, thickness: 440 ± 5 μm) was exposed to intense UV light. The absorption intensity of the Rhodamine B films at 552 nm was determined. As shown in Fig. 7, an obvious degradation of the Rhodamine B was observed for the sample protected with neat PA due to the poor dispersion of ZnO QDs in water, and gradually decreased as the accelerated weathering time increased. About 16% of the transparency loss was observed after 200 h of weathering tests. In contrast, no obvious change was observed for the UV-vis transmittance spectra of the neat PA film and PA/ZnO QD@SiO₂ nanocomposite polymer films after they were weathered for different times (Fig. 8b), indicating a long-term durability. The surface morphologies of neat PA, PA/ZnO QDs, and PA/ZnO@SiO₂ QD films were also checked by SEM before and after accelerated weathering tests, as shown in Fig. 9. All the films were quite flat and crack-free before the test. After accelerated weathering tests for 200 h, the neat PA (Fig. 9b) and PA/ZnO QD@SiO₂ films (Fig. 9d) did not display obvious morphological changes, while the PA/ZnO QD film (Fig. 9f) cracked into many small pieces. These morphological evolution phenomena have also been reported in the weathering tests of polymer/TiO₂ nanocomposite films. ³⁵,⁴⁶

Durability of polymer coating

Though inorganic sunscreen nanoparticles, i.e. nano-TiO₂ and nano-ZnO, are inherently stable, their strong photocatalytic activity will shorten the service time of polymers when they are introduced into polymeric coatings. To further evaluate the weatherability, the PA/ZnO QD@SiO₂ nanocomposite polymer film with 3.7% of ZnO QD@SiO₂ and 74 ± 2 μm of thickness was placed in an accelerated weathering tester. For the sake of comparison, the PA/ZnO QD polymer film with the same ZnO QD content and thickness was used as the control sample. As shown in Fig. 8a, the transparency of PA/ZnO QD polymer film displayed a slight loss in the visible region compared to the neat PA film due to the poor dispersion of ZnO QDs in water, and gradually decreased as the accelerated weathering time increased. The thickness of PA/ZnO QD polymer film increased. About 16% of the transparency loss was observed after 200 h of weathering tests. In contrast, no obvious change was observed for the UV-vis transmittance spectra of the neat PA film and PA/ZnO QD@SiO₂ nanocomposite polymer film after they were weathered for different times (Fig. 8b), indicating a long-term durability. The surface morphologies of neat PA, PA/ZnO QDs, and PA/ZnO@SiO₂ QD films were also checked by SEM before and after accelerated weathering tests, as shown in Fig. 9. All the films were quite flat and crack-free before the test. After accelerated weathering tests for 200 h, the neat PA (Fig. 9b) and PA/ZnO QD@SiO₂ films (Fig. 9d) did not display obvious morphological changes, while the PA/ZnO QD film (Fig. 9f) cracked into many small pieces. These morphological evolution phenomena have also been reported in the weathering tests of polymer/TiO₂ nanocomposite films. ³⁵,⁴⁶

![Fig. 7](Image) Photodegradation curves of Rhodamine B films protected by neat PA and PA/ZnO QD@SiO₂ polymer films (the inserted photographs: the corresponding films; the white circle: UV irradiation area).

![Fig. 8](Image) UV-vis transmittance spectra of (a) PA/ZnO QDs, (b) PA/ZnO QD@SiO₂ and neat PA polymer films before and after accelerated weathering for different times.
Photoluminescent behavior of ZnO QD@SiO₂

Fig. 10a shows the emission spectra of the freshly as-prepared ZnO QDs and ZnO QD@SiO₂ nanoparticles with the same concentration. Both the ZnO QDs and ZnO QD@SiO₂ emitted strong and comparable blue light centered at about 480 nm, indicating the excellent luminescent properties of ZnO QD@SiO₂. This is different from other luminescent QDs, i.e., CdTe QDs whose emission intensity partly decreased after coating with a silica layer. To check whether the silica shell emits or not, the ZnO QDs were removed from the ZnO QD@SiO₂ nanoparticles by treating with the concentrated hydrochloric acid. As expected, the remaining silica displayed no fluorescence (Fig. 10a). This means that the blue light emission of ZnO QD@SiO₂ indeed came from ZnO QDs. The quantum yield (QY) of bare ZnO QDs and ZnO QD@SiO₂ were determined and calculated using the standard Rhodamine 6G (QY = 95%) as in the ref. 48. The QY of neat ZnO QDs was about 13.4%, while the QY of the freshly prepared ZnO QD@SiO₂ increased to 27%. This is in agreement with the previously reported modification of ZnO QDs with a silane coupling agent. This QY increment is caused by their surface defects that were well remained after encapsulation. As discussed above, bare ZnO QDs tend to aggregate, decreasing the surface defects, and thus lowering the QY. However, the silica layer can efficiently prevent the aggregation of ZnO QDs, producing a high QY. More interestingly, the QY of the ZnO QD@SiO₂ aqueous dispersion still remains 25.7% even after storage for 4 months, which is comparable to that of the freshly prepared ZnO QD@SiO₂, further demonstrating the excellent stability of ZnO QD@SiO₂ in water. After incorporation of ZnO QD@SiO₂ nanoparticles into the acrylic latex, the strong blue emission centered at 473 nm was observed under the excitation light of 307 nm, as indicated in Fig. 10b, which originates from the recombination of a shallowly trapped electron with a hole in a deep trap or an electron in singly occupied oxygen vacancies with a photo-generated hole in the valence band. The strong blue emission means that the PA/ZnO QD@SiO₂ nanocomposite polymer film can absorb UV light and further convert the absorbed UV light into blue light effectively. Thus, the nanocomposite polymer film can convert the UV light (harmful to growth of chlorophytes) in the sun into the blue light, which is beneficial and necessary for photosynthesis of chlorophytes, and may also find some potential applications in the agricultural field for promoting the photosynthesis of plants.

Conclusion

ZnO QD@SiO₂ nanoparticles were fabricated through the facile sol–gel procedure. The ZnO QD@SiO₂ nanoparticles have excellent dispersion in the aqueous phase and storage stability. The photocatalytic activity of ZnO QDs was efficiently insulated by the silica layer formed with the adequate amount of TEOS. In addition, the ZnO QD@SiO₂ aqueous dispersion can still emit bright blue light under UV radiation, with a high photoluminescent quantum yield.

The ZnO QD@SiO₂ nanoparticles can be easily introduced into waterborne acrylic latex to fabricate highly transparent and excellent UV-shielding polymer films. Moreover, the as-obtained nanocomposite film has long-term durability and can convert UV into blue light effectively, and may find some
important application such as transparent, UV-shielding and durable polymer coatings, and agricultural films for promoting photosynthesis of plants.

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