Photoluminescent ZnO nanoparticles modified by polymers

Huan-Ming Xiong*

Photoluminescent ZnO nanoparticles, due to nontoxicity and cheapness, are promising materials applied in UV laser devices and biological labels. ZnO photoluminescence is usually composed of two parts: UV emission arising from the typical band gap transition and visible emission due to the oxygen vacancies. In order to protect ZnO nanoparticles and improve their optical properties, polymers are mixed with ZnO or modified on ZnO surfaces to produce various nanocomposites. In the meantime, some new luminescent phenomena are found when polymers and ZnO nanoparticles together participate in the luminescent process. This review will focus on the synthetic methods, structural features and photoluminescent properties of the polymer–ZnO nanocomposites.

1 Introduction

ZnO is a semiconductor material with great potential in opto-electronic devices,[1–9] such as gas sensors, piezoelectric trans-ducers, optical waveguides, UV-laser emitters and solar cells. It is also a nontoxic and cheap material that has been used in commercial sun cream, white paint, conductive glass and anti-bacterial reagent. ZnO is very stable under ambient conditions towards sunlight, water and air. These merits make ZnO a promising multifunctional material in the future. In the past decade, a great many ZnO nanostructures have been reported, [10–19] including nanoparticles, nanorods, nanotubes, nanobelts, nanoplates, nanorings and even nanoflowers. The corresponding synthetic methods vary from simple pyrolysis to strictly controlled vapor phase epitaxial growth. These synthetic methods often determine the physical properties of the final ZnO products. For example, ZnO nanoparticles derived from sol–gel methods mainly exhibit visible fluorescence while those

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nanocrystals with the same size synthesized hydrothermally are usually UV-emitters.

In most cases, the photoluminescence (PL) of ZnO nano-particles has two components. One is the typical exciton emission or near-band-edge emission, *i.e.*, photo-generated electron recombination with holes in the valence band or in traps near the valence band. This process produces UV light of about 370 nm because the ZnO band gap is 3.37 eV at room temperature. The other component is visible emission (also called deep-level emission) related with oxygen vacancies, but the corresponding mechanism is controversial and not clear so far. Two popular mechanisms for the ZnO visible emission have been suggested (Scheme 1): one is recombination of a shallowly trapped electron with a hole in a deep trap,[20,21] and the other is recombination of an electron in singly occupied oxygen vacancies (*i.e.*, deeply trapped) with a photo-generated hole in the valence band.[22,23]
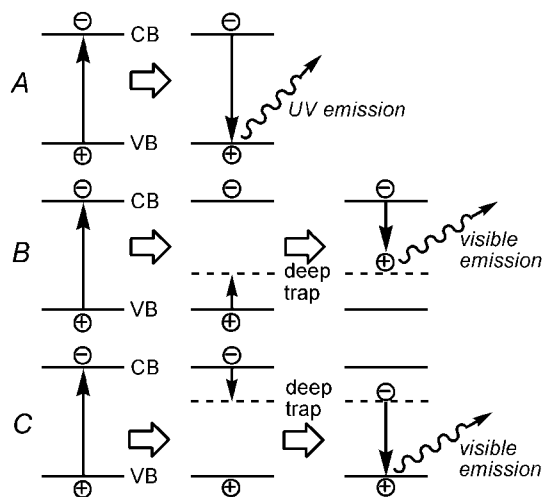

Scheme 1 Photoluminescent processes suggested for ZnO nanoparticles. (A) Typical exciton emission, (B) recombination of a shallowly trapped electron with a deeply trapped hole, and (C) recombination of a shallowly trapped hole with a deeply trapped electron. In order to simplify the maps, the shallow traps near the valence band (VB) and the conductance band (CB) are not marked here.

Since it is difficult to determine the exact location and the energy level of the deep traps, these two mechanisms have been coexisting for years.

van Dijken and co-workers assigned ZnO visible emission (green–yellow) to the first mechanism (Scheme 1B) after comparing the PL shift of ZnO nanoparticles of different diameters with a theoretical model based on the intensity ratio between two emission peaks.[24] This model has been accepted by many scientists,[25] but it encountered unexpected phenomena recently, especially the latest blue fluorescence interpreted by other models.[26–28] Nevertheless, these models agree on one point that ZnO visible emission intensity depends on its defect concentration. Therefore, pyrolysis, chemical vapor deposition and molecular beam epitaxial growth at high temperature, are popular methods to produce ZnO with fine UV emission, because the products are highly crystallized and purified ZnO nanocrystals.[29] On the contrary, the sol–gel technique and sonochemical synthesis at room temperature are the better choices to obtain ZnO with highly visible emission, because the resulting samples are small enough, nearly amorphous and contain a lot of defects.[30,31]

The sol–gel routes to prepare visible luminescent ZnO nanoparticles colloids were invented in the 1980s and were investigated intensively in the 1990s.[32–37] The most popular route is hydrolyzing zinc acetate in ethanol, which appears very simple but actually contains a series of intermediate reactions. The final product is ZnO nanoparticles with typical green–yellow emission at 500–550 nm. The as-prepared colloids are not very stable because the ZnO nanoparticles will grow upon Ostwald ripening, and finally precipitate from the mother-liquor after weeks at room temperature. This process is accompanied by a continuous red-shift of the UV-Vis absorption and the PL spectra, as well as the decay of the emission intensity. In fact, even freshly prepared ZnO colloids have a quantum yield of only about 10%. Furthermore, adding a small amount of water will cause ZnO precipitation and totally quench ZnO fluorescence because OH groups will exchange with the acetate groups on the nanoparticle surfaces so as to destroy the luminescent centers. Obviously, such prototypical ZnO nanoparticles cannot be used in biological systems.

In order to prevent ZnO nanoparticles from undergoing spontaneous growth and aggregation, scientists have tried employing various organic ligands,[27,38] coating ZnO with polymers[28] and protecting ZnO by inorganic shells such as SiO_2[39] and ZnS.[40] Among these strategies, coating ZnO with polymer through surface initiated polymerization is a good choice, because the crosslinked polymer is able to form a tight shell around the ZnO core and this shell is difficult to remove. In contrast, simple organic ligands are apt to detach from the ZnO surface while inorganic shells are usually porous. Hence, ZnO nanoparticles protected by conventional organic ligands and inorganic shells are usually not stable in water. The strategies of preparing ZnO-based polymer nanocomposites can be divided into physical methods and chemical reactions. Physical methods, i.e., mixing polymers and nanoparticles in solutions or in polymer melts, produce physical mixtures in which polymers and nanoparticles are connected via static interactions, van der Waals forces or Lewis acid–base interactions. Chemical reactions, i.e., bonding polymers and nanoparticles via chemical bonds, are able to produce multi-structured composites due to a variety of chemical syntheses and more stable products because of stronger interactions between the polymers and nanoparticles.

When the polymers are modified on ZnO nanoparticles via chemical bonds, there are at least five features of the products: (i) the products are homogeneous, usually transparent; (ii) their composition is not destroyed by solvent washing, i.e., the products can be isolated from the reaction system by non-solvent methods[36] or centrifugation–redispersion treatment;[28] (iii) there is no significant phase separation (ZnO aggregation or polymer crystallization) under TEM or AFM observation; (iv) IR spectra show the signals of chemical bonds between polymers and ZnO nanoparticles; (v) the decomposition temperature of the products are higher than the polymers themselves. These features can be used to judge the interactions between polymers and ZnO nanoparticles. In general, the stronger the interactions between the polymers and ZnO, the higher is the stability of the nanocomposites. In some cases the interactions are so strong as to influence the ZnO luminescent mechanism.

In this review, polymer–ZnO nanocomposites are classified according to the influence of polymers on ZnO luminescence. We will state how to protect ZnO nanoparticles and improve their luminescent properties by polymers (Type I), and then we will discuss some unusual composites (Type II) in which polymers are involved in the ZnO photoluminescent process. Although there are several reviews concerning ZnO luminescence in the literature,[29,30] similar reviews dealing with polymer–ZnO nanocomposites have not been published.

2 Polymer–ZnO nanocomposites of Type I

2.1 Physical mixtures of polymers and ZnO nanoparticles

Early attempts to protect ZnO by polymers was by simply mixing ZnO nanoparticles and polymers or adding polymers into the ZnO synthetic solutions. After vaporizing the reaction solutions, the products were solid mixtures which could not be purified. Guo and co-workers synthesized ZnO nanoparticles in poly-(vinyl pyrrolidone) (PVP) ethanol solution. The as-prepared PVP capped ZnO exhibited enhanced UV emission and their visible
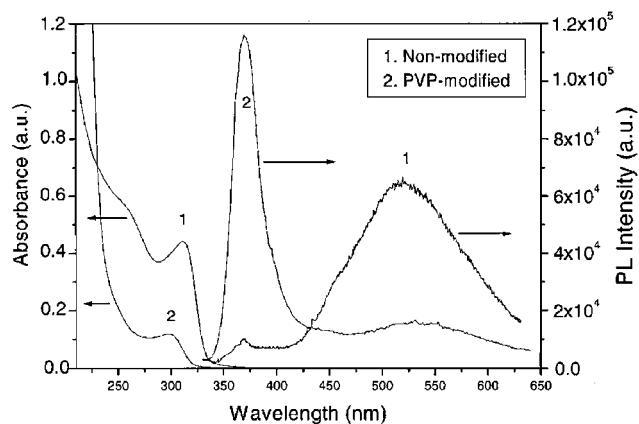

Fig. 1 Optical absorption and photoluminescence spectra of non-capped and PVP-capped ZnO nanoparticles. (Reprinted with permission from ref. 41. Copyright © 2000 American Institute of Physics).

emission was reduced in comparison with the uncapped ZnO (Fig. 1).[41,42] Obviously, PVP capping increased the ZnO crystallinity in this work, as proved by the XRD and TEM data (Fig. 2). Chang and co-workers found polyaniline modification could also enhance the UV emission of ZnO nanostructures,[43] and a similar conclusion was drawn by Pauporté upon investigation of ZnO/polyvinyl alcohol hybrid films.[44] Later researches showed that PVP could control ZnO crystallization and morphology,[45] and improved ZnO UV emission significantly because of physical adsorption.[46] On one hand, PVP capped ZnO was apt to grow into one-dimensional nanomaterials because PVP preferred to physically adsorb on a specific crystallographic plane of ZnO, which passivated this plane and facilitated the crystal growth along the c-axis. On the other hand, the PVP passivation effects reduced ZnO surface defects so as to increase the UV emission. It should be mentioned that PVP itself has a strong blue emission. When PVP was mixed with ZnO nanoparticles, the emission spectra overlapped with each other and depended on the excitation wavelength (Fig. 3).[47] If PVP content was high enough in the PVP–ZnO nanocomposite, visible emission was also enhanced.[42,46]

To study the complex interactions between polymers and ZnO, we mixed polyethylene oxide (PEO) and purified ZnO nanoparticles in solvents and then evaporated the solutions to give composite films.[48] The PL emission spectra depended on the weight ratio between ZnO and PEO in the composite films. As ZnO content increased, the ZnO emission wavelength red-shifted and its intensity decreased gradually, indicating that the nanoparticles aggregated more and more heavily. When the ZnO/PEO weight ratio was increased to 0.5, the PL intensity of the composite film was close to that of a ZnO nanoparticle pellet. Such ZnO aggregation in PEO films can be observed directly by the AFM technique.[49] Our result showed that excess polymer could protect ZnO nanoparticles, but this effect was not satisfying in a simple physical mixture. Later, Abdullah and co-workers synthesized poly(ethylene glycol) (PEG) protected
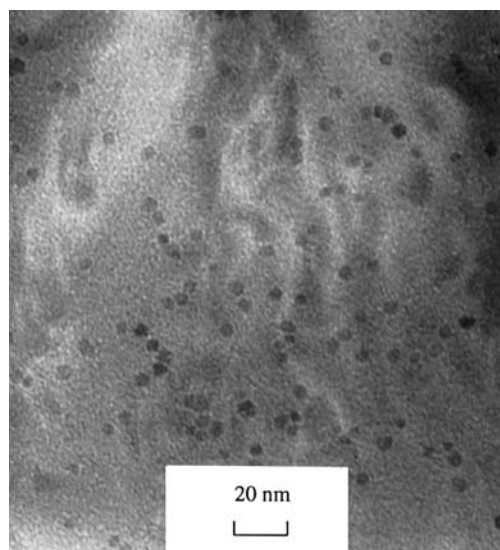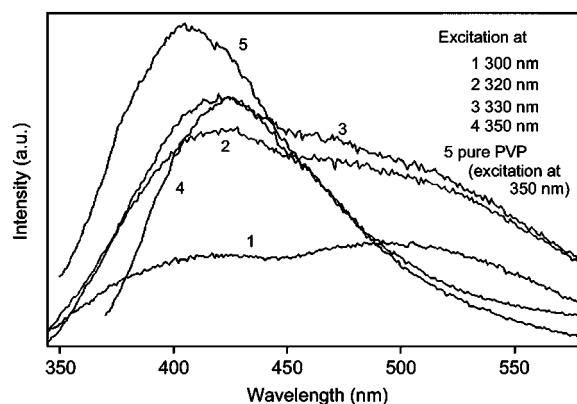
Fig. 3 Emission spectra of PVP-capped ZnO nanoparticles at different excitation wavelengths. (Reprinted with permission from ref. 47. Copyright © 2009 Elsevier B.V.)

ZnO nanoparticles through an *in situ* method.[50,51] They dissolved LiOH and PEG in hot ethanol and then mixed the solution with zinc acetate solution. The resulting mixture was dried at 40 °C for about three days to produce composite films. They found PEG incorporation could improve ZnO luminescence efficiency and more importantly, adding excess LiOH resulted in highly blue-emitting products. Since these products were actually solid mixtures containing ZnO nanoparticles, PEG, excess LiOH, acetate salts and other species, the effects of PEG and LiOH on ZnO PL could not be interpreted clearly.

Recently, Sun and co-workers[52] mixed ZnO quantum dots (QDs), α-zirconium phosphate nanoplatelets and poly(methyl methacrylate) (PMMA) in acetone, and then evaporated the solvents to cast films with a uniform thickness of 100 μm. The films dried in ambient conditions exhibited both UV emission and visible luminescence, but the films dried at 120 °C overnight showed only one strong UV emission. The authors considered that heating could remove the solvents adsorbed on ZnO, and then the surface defects were passivated by PMMA. However, they did not consider the oxidation effects by air. In fact, heating ZnO nanoparticles in air always quenches the visible luminescence because oxygen fills up the vacancies on the ZnO surface. After heating treatments, the ZnO PL emission red-shifted from 365 to 387 nm as the ZnO concentration in PMMA increased from 0.5 to 3.0 wt%. This phenomenon was explained by the coupling effect[53] between QDs, *i.e.* when the QDs are close in contact with each other, significant dipole–dipole interactions between adjacent QDs lead to quantum tunneling. Obviously, such coupling effects proved that ZnO QDs were not passivated completely by PMMA, because the PMMA molecules would obstruct electron/hole tunneling between QDs if they had exchanged completely with solvent on the ZnO surface.

If the polymer itself is luminescent, such as poly(phenylene vinylene) (PPV), ZnO incorporation often quenches the polymer fluorescence. Wang *et al.*[54] reported adding ZnO nanoparticles into a PPV/PVA composite film decreased the PPV luminescence significantly (Fig. 4). They ascribed this phenomenon to the charge separation of the excitons arising from PPV chains on the interfaces between ZnO nanoparticles and the polymers. The higher the content of the ZnO, the larger is the interface between ZnO and polymers, and thus more excitons are separated into
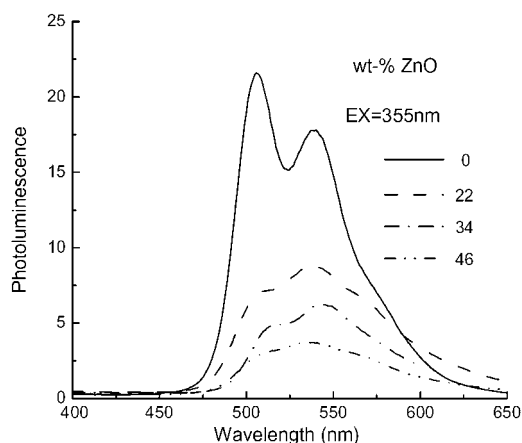
Fig. 2 TEM images of the PVP-capped ZnO nanoparticles. (Reprinted with permission from ref. 41. Copyright © 2000 American Institute of Physics).

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Fig. 4 Photoluminescence of PPV/PVA and PPV/PVA/ZnO hybrid nanocomposites containing different amounts of ZnO. (Reprinted with permission from ref. 54. Copyright © 2009 Elsevier B.V.)

electrons and holes on the interfaces. Similar conclusions were also drawn by Ton-That and co-workers[55] when they mixed ZnO nanoparticles with poly[2-methoxy-5-(2′-ethyl hexyloxy)-phenylenevinylene] films to study the composite PL emission. In comparison with PPV luminescence, ZnO emission was rather weak and unimportant in these composites.

According to the above reports, mixing ZnO and polymers physically is not a good way to improve ZnO visible luminescence. Although this method is easy, it has several drawbacks: first, many polymers are able to quench ZnO visible emission through passivating the ZnO nanoparticle surface; second, polymers such as PEO, PVA and PMMA cannot suppress ZnO nanoparticle aggregation effectively; thirdly, some polymers such as PVP and PPV themselves have fluorescence so as to interfere with ZnO emission. On the other hand, incorporating polymers is not a good way to enhance ZnO UV emission either. The excitons arising from ZnO nanocrystals will be separated into electrons and holes on the interfaces between ZnO and polymers, which is not favourable to ZnO UV emission. In fact, ZnO nanomaterials with fine UV emission are usually obtained by vapor phase growth[1–3] which guarantees high crystallinity and high purity. Therefore, the following sections will discuss how to improve ZnO visible emission by chemical modifications.

## 2.2 Chemical hybrids of polymers and ZnO nanoparticles

The structures of chemically synthesized polymer–ZnO nanocomposites are divided into four types in this article (Scheme 2). (i) Polymers are grafted on the ZnO surface as independent organic ligand (like hair on the head). This type of nanocomposite can be obtained by hydrolyzation of zinc salts or
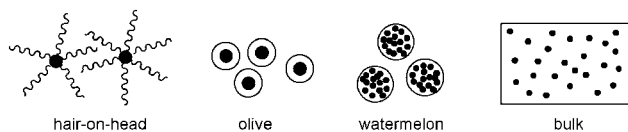
Scheme 2 Structures of polymer–ZnO nanocomposites obtained *via* chemical reactions.

ligand exchange. Hydrolyzing or decomposing organic zinc salts in the presence of polymer ligands has been widely reported to prepare ZnO nanoparticles with polymer groups, but preparation of luminescent polymer–ZnO hybrids by ligand exchange is rarely seen in the literature, because exchanging the organic groups on the ZnO surface by polymer ligands often destroys the ZnO luminescence and the degree of ligand exchange is rather low due to the large volume of the polymers. (ii) If the organic ligands on the ZnO surface are crosslinked together by polymerization, the ZnO core will be protected by the polymer tightly, and the whole structure resembles an olive, with one core and a thin orbicular shell. This type of materials are synthesized strictly by atom transfer radical polymerization (ATRP) initiated on the nanoparticle surface. (iii) Polymers can also form a microsphere (100 nm to 10 μm) containing many nanoparticles inside (like a watermelon containing many seeds). This type of structure is obtained by emulsion polymerization or solution polymerization, and occurs as a suspension in water (like milk). (iv) Bulk materials containing ZnO nanoparticles result from bulk polymerization. In comparison with the above three structures, the bulk structures are very large and can be cast into various forms.

2.2.1 Polymer–ZnO nanocomposites with 'hair-on-head' structure. Since the typical photoluminescent ZnO nanoparticles protected by acetate groups are derived from zinc acetate, one can speculate that if an organic zinc salt is hydrolyzed to produce ZnO nanoparticles, these nanoparticles will be modified with such organic groups on surface. According to this speculation,[56,57] we designed an organic zinc salt [CH$_3$O(CH$_2$CH$_2$O)$_n$CH$_2$COO]$_2$Zn in which the anions were the oxidized polyethylene glycol methyl ether (PEGME). After hydrolyzing this salt in ethanol, the resulting ZnO nanoparticles were grafted by PEGME groups as proved by IR data. The quantum yields of the polyether-grafted ZnO sols were about 30%, much higher than those of the conventional acetate-modified ZnO colloids, and their luminescent properties were stable for several weeks. Such improvements on PL and stability resulted from the covalent bonds between polymer groups and ZnO nanoparticles. Scheme 3 illustrates the difference between our method and the classical sol–gel route. After the nucleation stage, acetate-modified ZnO nanoparticles kept growing and aggregating. As
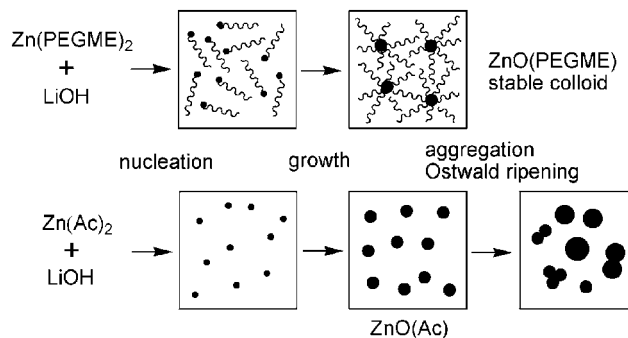
Scheme 3 Schematic representation for the formation processes of our ZnO(PEGME) nanoparticles (upper) and the conventional ZnO(Ac) nanoparticles (lower).
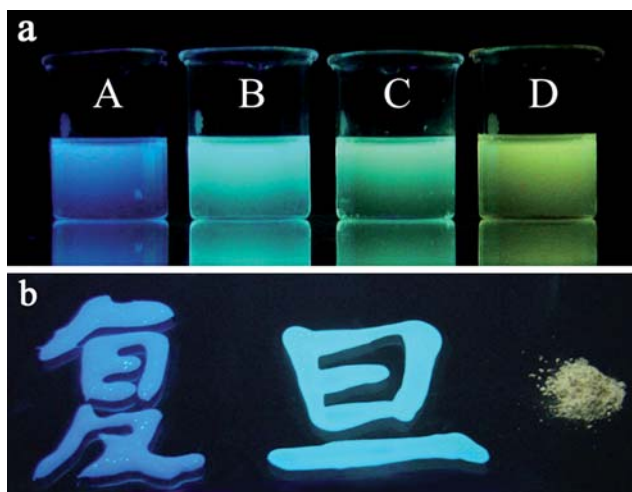
Fig. 5 Photos of ZnO samples under UV light. (a) ZnO(PEGME350) ethanol colloids prepared under different conditions. (b) Purified ZnO(PEGME350) gels of sample A and sample B (Chinese words representing Fudan University) are cast on a piece of glass by evaporating the ethanol colloids, together with the conventional ZnO nanoparticles powder protected by acetate (right). The ZnO(PEGME350) gels are transparent, with small bubbles in them. (Reprinted with permission from ref. 57. Copyright © 2005 John Wiley & Sons. Inc.)

a result, the excitation and emission wavelengths of these particles red-shifted quickly and the emission peaks broadened gradually. In contrast, the growth and aggregation of the ZnO(PEGME) were effectively hindered by the polymer groups, so the fluorescence of the ZnO(PEGME) could be adjusted from blue to yellow stably (Fig. 5). The TEM images in Fig. 6 illustrated the particle size difference between these ZnO nanoparticles. It was clear that the PL emission red-shifted from blue to yellow as the particle diameter increased from about 1 nm to about 4 nm, in accordance with the van Dijken model. Since these nanoparticles were obtained from the same reaction system, their surface states were similar, and thus, their emission wavelengths obeyed the quantum size effects.

As an example for the method of decomposing organic zinc salts,[58] Richter and co-workers dissolved diethylzinc and stearate-modified poly(3-ethyl-3-hydroxymethyloxetane) in toluene solution and then evaporated the solvent slowly. The residue was luminescent ZnO nanoparticles modified by polymer groups. The particle diameter was controlled from about 3.1 nm to about 5.7 nm along with their emission maxima from 520 nm to 544 nm simply by changing the diethylzinc concentration in the reaction system.
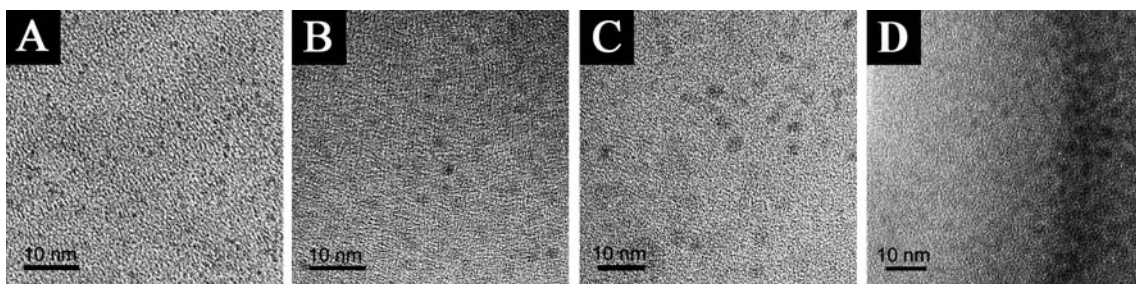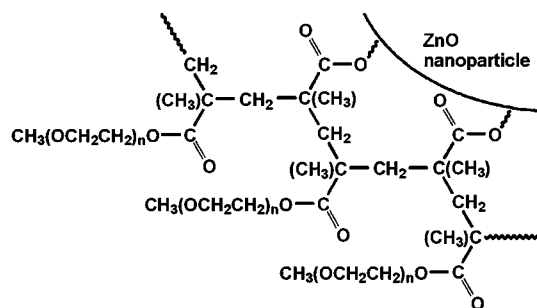
Although the polymer-grafted ZnO nanoparticles exhibited enhanced stability, equilibrium between the ligands and ZnO nanoparticles always exists so that a small change of the concentrations or temperature would shift the equilibrium and influence ZnO luminescence. Furthermore, these polymer-grafted ZnO nanoparticles, as for those protected by small organic ligands, are not stable in water. Water and hydroxyl groups can exchange the organic ligands on the ZnO surface so as to quench ZnO luminescence. Therefore, to obtain organic coatings that cannot be removed, an ideal method is to crosslink the ligands to form a hydrophobic shell by irreversible polymerization. This method produces ZnO@polymer core–shell structures which include the olive structure, watermelon structure and bulk structures referred to above. Among them, the olive structure is the most difficult to obtain because the atom transfer radical polymerization on the nanoparticle surface must be controlled carefully to avoid nanoparticle agglomeration.

2.2.2 Polymer–ZnO nanocomposites with olive structure. Recently, we synthesized aqueous ZnO@polymer core–shell nanoparticles (Scheme 4) successfully by a two-step-polymerization route.[59] After polymerization in ethanol, ZnO nanoparticles were coated tightly by a double-layer of polymer shell which had a hydrophobic PMMA layer inside and many hydrophilic PEGME groups outside. The ethanol solution was dialyzed against water for three days, and the resulting clear ZnO aqueous solution exhibited very stable luminescence with a quantum yield of over 50%. These ZnO nanoparticles were mixed with human hepatoma cells together to test their cytotoxicity and fluorescent labeling effect. We found that when the concentration of nanoparticles was below 0.2 mg mL^{-1}, more than 80% of the cells survived. This concentration was much higher than the critical safe concentration of CdSe or CdTe

Scheme 4 ZnO@poly(MAA-co-PEGMEMA) core–shell nanoparticles with olive structure.[59]

Fig. 6 TEM images of the above ZnO(PEGME350) samples.

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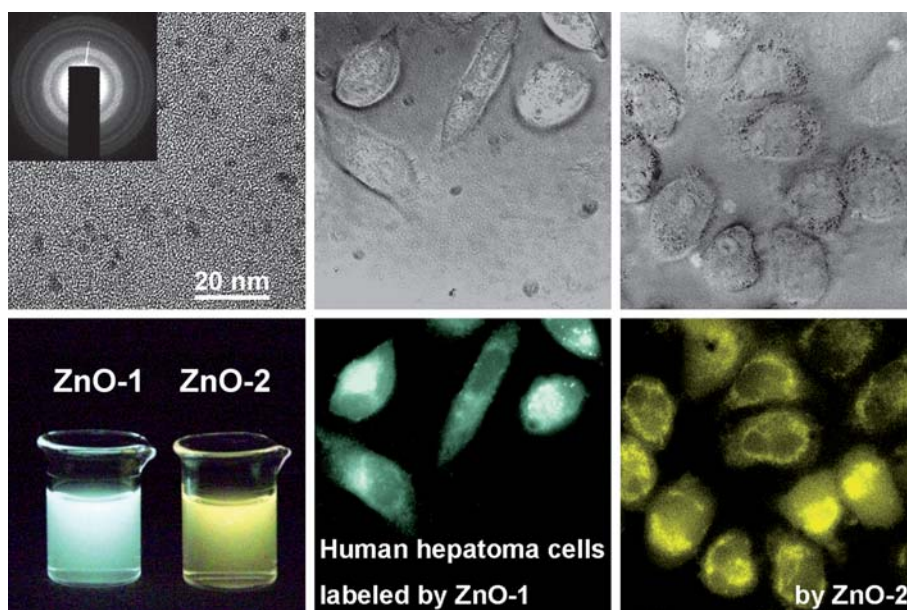*J. Mater. Chem.*, 2010, **20**, 4251–4262 | 4255

Fig. 7 Top: TEM image for ZnO@polymer nanoparticles with ED pattern (left inset) and two differential interference contrast pictures of living cancer cells labeled by ZnO-1 and ZnO-2 respectively. Bottom: photo of ZnO@polymer aqueous solutions under a UV lamp (left), and two confocal microscope images of the cells labeled by ZnO-1 and ZnO-2 nanoparticles (middle and right). (Reprinted with permission from ref. 59. Copyright © 2008 American Chemical Society).

species.[60] Below the safe concentration, ZnO@polymer fluorescent probes were mixed with human hepatoma cells. Differential interference contrast (DIC) pictures and fluorescence images of these cells were taken by a disk scanning confocal microscope. The images in Fig. 7 proved that ZnO nanoparticles penetrated into the living cells and exhibited bright fluorescence. It was interesting that for a living cell, ZnO nanoparticles were only distributed in the cytoplasm region while the nucleus appeared dark under UV light. However, after the cells died, their nuclei were even brighter than the cytoplasm, indicating that ZnO nanoparticles entered the cell nucleus. These phenomena helped us observe evolution of the cancer cells vividly.

Similar to our work, Peng and co-workers reported ZnO@P-PEGMA nanoparticles by initiating polymerization on a ZnO surface (Scheme 5).[61] However, these nanoparticles had no visible emission at all. The pristine ZnO nanoparticles were obtained by reaction between zinc acetate and KOH in methanol. The resulting ZnO nanoparticles had a diameter of >10 nm and they precipitated within 1.5 h. These ZnO particles were well crystallized, as proved by the XRD patterns, so the defect-related

Scheme 5 The preparation route of ZnO@PPEGMA nanoparticles.[61]

visible emission was not seen in the PL spectra. For all the samples, their ultraviolet band emission was ascribed to the free exciton emission and near-band-edge (NBE) emission which increased with the increasing of ATRP time (Fig. 8). The difference between our ZnO@poly(MAA-co-PEGMEMA) nanoparticles and the above ZnO@PPEGMA proved that ZnO optical features depend heavily on its surface state which is controlled by the preparation conditions.

In many researches, surface state is regarded as a main factor that determines ZnO visible luminescence, because ZnO visible emission arises from its defects or vacancies which are mainly located on the nanoparticle surface. In the above mentioned work,[61] ZnO nanoparticles are highly crystallized, i.e., there are almost no amorphous phases on the ZnO surface, so these ZnO particles only exhibit exciton emission. Another factor controlling the ZnO surface state is the nature of the surface groups that coordinate with Zn atoms. ZnO is an n-type semiconductor, indicating there are excess Zn atoms on the surface for coordination. The coordination groups on ZnO nanoparticles could be OH, SH, NH$_2$, acetate or ligands from the polymer matrix. OH is not a good ligand because ZnO always loses visible fluorescence in water. SH and NH$_2$ are able to quench ZnO visible emission quickly even in anhydrous solutions. In literature reports, acetate and polyethers are widely employed to protect visible-emitting ZnO. It may be interpreted that small ligands could fill up (passivate) oxygen vacancies on the ZnO surface so as to reduce defects that are visible luminescence centers, while the larger ligands supply spaces for charge separation so that the electron–hole recombination time is prolonged and the exciton emission is suppressed. In the polymer–ZnO nanocomposites, ZnO luminescence behavior is influenced in a complicated manner by many factors including coordination between ligands of polymers and Zn atoms, interactions between polymer segments and
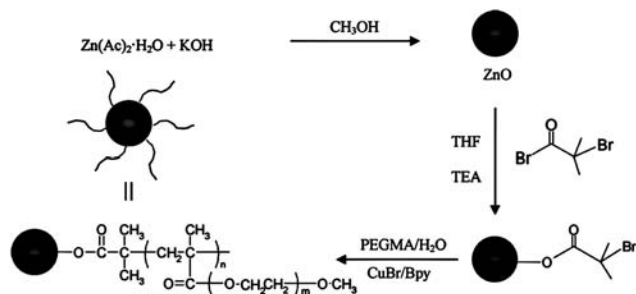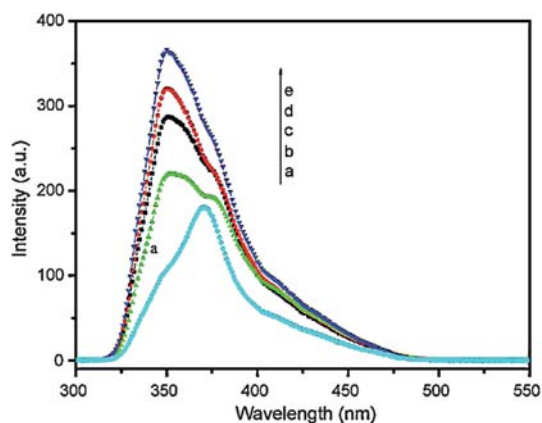
Fig. 8 Room-temperature photoluminescence spectra of (a) pristine ZnO nanoparticles and ZnO@PPEGMA nanoparticles prepared by ATRP for (b) 2 h, (c) 6 h, (d) 10 h and (e) 14 h. (Reprinted with permission from ref. 61. Copyright © 2009 Elsevier B.V.)
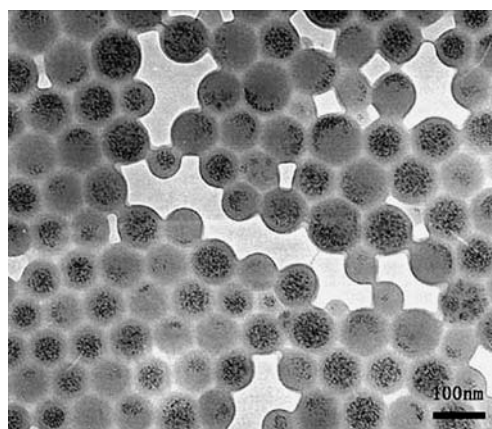

Fig. 9 TEM of the polystyrene-encapsulated ZnO core–shell hybrid microspheres. (Reprinted with permission from ref. 63. Copyright © 2006 Elsevier B.V.)

Fig. 10 Fluorescence microscope photo (left) and AFM phase image of ZnO@PMMA microspheres (right).[28] Since the hardness of the inorganic nanoparticles and that of the soft polymers are different, the dark dots in the microspheres (right) confirm the core–shell structure.

ZnO surface groups and dispersity of the nanoparticles in polymer matrix. To produce polymer–ZnO nanocomposites with highly visible emission, the ZnO surface state should be protected well by the polymer on one hand, on the other, ZnO nanoparticles of appropriate concentration should be dispersed homogeneously in the polymer matrix.

2.2.3 Polymer–ZnO nanocomposites with watermelon structure. Preparation of ZnO@polymer core–shell microspheres with watermelon structure is much easier than synthesizing the olive-like nanoparticles. Generally, ZnO nanoparticles can be modified by some surfactants such as oleic acid and then dispersed in water together with monomers for emulsion polymerization.[62] However, the resulting products are usually not luminescent because many surfactants and water will quench the ZnO surface fluorescence. Zhang *et al.*[63] used 3-trimethoxysilylpropyl methacrylate (MPS) to solve this problem. First, they synthesized ZnO nanoparticles in ethanol by zinc acetate and LiOH. MPS was then added into the colloids to protect the ZnO. Afterwards, the whole mixture was put into water for typical miniemulsion polymerization of styrene. Since the MPS could form hydrophobic shells outside ZnO nanoparticles and help ZnO enter polystyrene (PS) beads, the resulting core–shell hybrid microspheres presented yellow–green luminescence. The TEM result in Fig. 9 confirms the core–shell structure of these microspheres.

Another way to prepare the watermelon structure is dispersing ZnO nanoparticles into monomers for prepolymerization first and then putting the mixture into water for the emulsion polymerization. For example,[28] we dispersed methacrylate anion modified ZnO nanoparticles in MMA monomers for prepolymerization at 60 °C and the resulting blue-emitting mixture contained ZnO@PMMA nanoparticles and unreacted MMA monomers. This mixture was then put into boiling water for further polymerization using $K_2S_2O_4$ as initiator. After refluxing, the obtained milk-like suspension exhibited strong blue fluorescence under UV light. The fluorescence microscope images showed that the products were uniform monodispersed blue-emitting spheres with a diameter of about 200 nm and the AFM data veri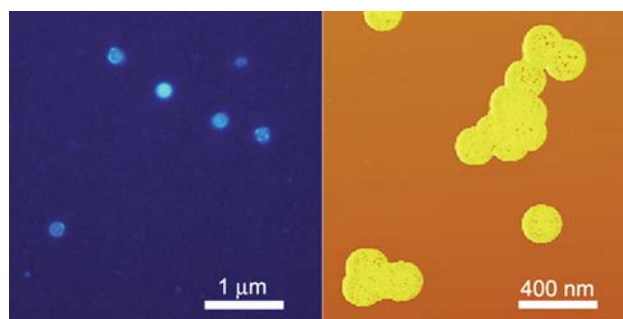fied their watermelon structure (Fig. 10). These microspheres were able to enrich proteins and peptides from extremely dilute solutions for mass analyses,[64] and the results proved the strong interactions between the PMMA shells and the ZnO cores because these microspheres did not decompose even under UV laser in vacuum.

2.2.4 Polymer–ZnO nanocomposites with bulk structure. If ZnO nanoparticles are dispersed into pure monomers with initiator, the polymerization will produce a bulk material. Hung and Whang modified ZnO surfaces with 3-(trimethoxysilyl)propyl methacrylate (TPM) and then polymerized hydroxyethyl methacrylate (HEMA) monomers with these modified ZnO particles.[65] The resulting TPM-ZnO/PHEMA nanocomposites had better dispersibility and controllable luminescence in comparison with their counterparts which were derived from unmodified ZnO nanoparticles and HEMA. In Fig. 11, using the same size of ZnO as the starting materials, the PHEMA containing those unmodified ZnO nanoparticles showed weaker and red-shifted luminescence, while the TPM-ZnO/PHEMA composites exhibited stronger luminescence because the TPM groups helped ZnO nanoparticles to disperse homogeneously in the bulk materials. The TEM images of the unmodified ZnO nanoparticles and the TPM-modified ZnO in
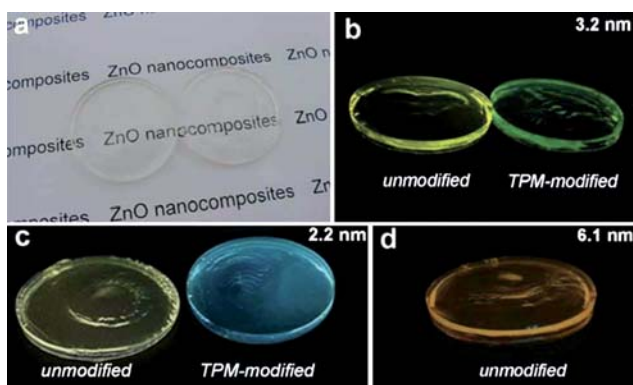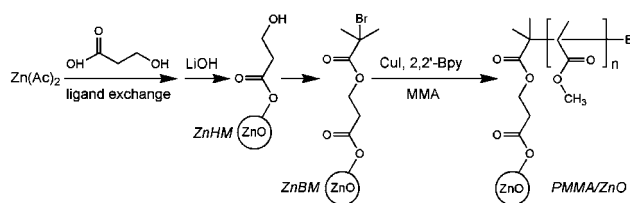
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Fig. 11 Photographs of transparent ZnO/PHEMA nanocomposites with various particles sizes (a) under daylight and (b)–(d) under a UV lamp. These luminescent nanocomposites were fabricated by ZnO particles with an average diameter of (b) 3.2 nm, (c) 2.2 nm and (d) 6.1 nm, respectively. (Reprinted with permission from ref. 65. Copyright © 2005 the Royal Society of Chemistry).

Scheme 6 Reaction route to prepare PMMA/ZnO nanocomposites.[66]

3-hydroxypropionic acid group modified ZnO nanoparticles (designated as ZnHM) were synthesized by ligand-exchange and hydrolyzation, followed by organic synthesis to obtain ZnO nanoparticles with 2-bromo-2-methylpropionyl groups (designated as ZnBM). Then the ZnBM nanoparticles were copolymerized with MMA monomers. Finally, solid PMMA/ZnO nanocomposites were produced and subsequently dissolved in organic solvents for PL measurements. The PL emission of the ZnHM nanoparticles was typical, including a UV emission peak at 353 nm and a visible emission band centered at 515 nm whereas ZnBM showed no fluorescence at all because the synthetic reactions had destroyed the ZnO luminescence centers. Strangely, after polymerization the final PMMA/ZnO nanocomposites showed a broad blue emission at 407 nm. This emission cannot be ascribed to ZnO or PMMA solely, which will be discussed below.

the PHEMA matrix were compared in Fig. 12. Obviously, to prepare bulk polymer–ZnO nanocomposites with good optical properties, the key is to avoid ZnO aggregation during polymerization.

Sato et al. reported PMMA/ZnO nanocomposites with bulk structure[66] and Scheme 6 illustrates the synthetic route. First,

3 Polymer–ZnO nanocomposites of Type II

As mentioned above, when polymers participate in the photoluminescent process, the situation becomes complicated but also suggests a new way to change the nature of ZnO luminescence. Recently, we utilized the inherent free radicals on the ZnO surface to initiate polymerization in MMA monomers, and the reaction was stopped when the ZnO nanoparticles were coated by a thin layer of polymer.[67] The as-prepared ZnO colloids exhibited strong blue fluorescence, even in sunlight, with quantum yield of above 85% (Fig. 13). Detailed analyses confirmed the ZnO@polymer core–shell structure, and the ethanol colloids were stable even under refluxing conditions. It was interesting that the PL spectra of the ZnO@polymer nanoparticles were much different from the typical ZnO quantum dots (Fig. 14). The excitation band became very broad while the emission band narrowed significantly. In comparison with the starting material ZnO–MAA, the ZnO@polymer excitation band red-shifted but the emission band blue-shifted which could
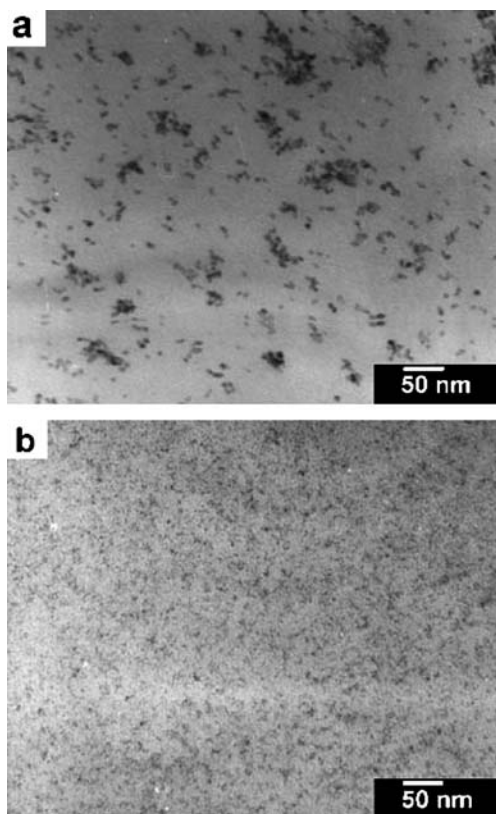

Fig. 12 Cross-section TEM images: (a) 6.1 nm unmodified ZnO particles in PHEMA matrix and (b) 3.2 nm TPM-modified ZnO particles in PHEMA matrix. (Reprinted with permission from ref. 65. Copyright © 2005 the Royal Society of Chemistry).
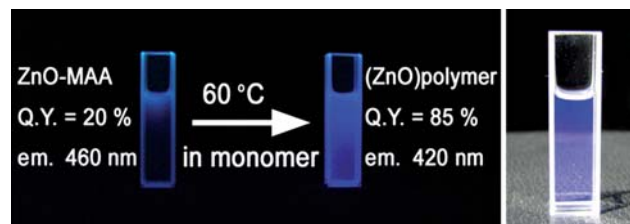

Fig. 13 The freshly prepared ZnO nanoparticles with MAA groups are used to synthesize ZnO@polymer core–shell nanoparticles (left in UV light). The ethanol solution of the product exhibited strong blue fluorescence in the sunlight (right).[67]
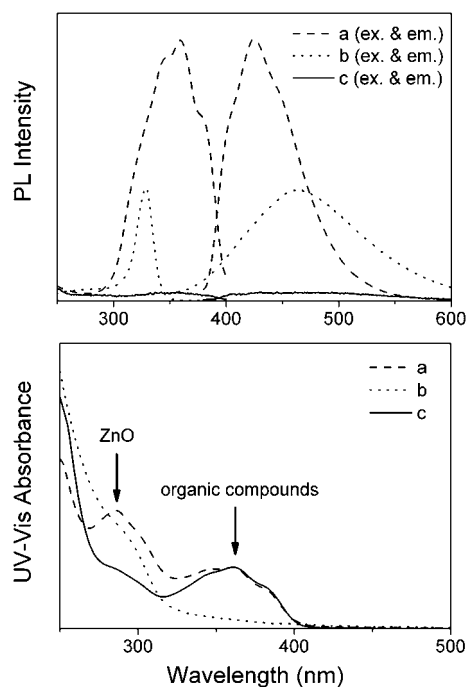
Fig. 14 PL spectra (upper) and UV-vis absorption (lower) of samples: (a) ZnO@polymer core–shell nanoparticles, (b) ZnO–MAA starting material, and (c) the polymer shell resulting from decomposition of ZnO@polymer by HCl. (Reprinted with permission from ref. 67. Copyright © 2006 John Wiley & sons. Inc).

Fig. 15 UV-Vis absorption (solid lines), excitation spectra (dashed lines) and emission curves (dotted lines) for ethanol colloids of ZnO@PMMA and ZnO@PS core–shell nanoparticles. (Reprinted with permission from ref. 28. Copyright © 2007 the Royal Society of Chemistry).

Scheme 7 Conceptual diagram illustrating the luminescent mechanism for ZnO@polymer nanoparticles.[28]

not be ascribed to the quantum size effects of semiconductors. On the one hand, the blue emission at 420 nm was not from the polymer shells as confirmed by controlled experiments. On the other hand, if this emission was just from the ZnO band edge transition as Sun[52] reported, its peak should be located in the 360–390 nm range, and the corresponding excitation curve should located below 360 nm. Hence, the blue emission in Fig. 14 cannot be solely ascribed to either the ZnO cores or the polymer shells.

In order to study such unexpected luminescent phenomena, we synthesized ZnO@PMMA and ZnO@PS core–shell nanoparticles by similar routes.[28] Although these nanoparticles had different energy band structures as shown in both their absorption spectra and excitation spectra, their emission spectra were alike (Fig. 15), but much different from that of the original ZnO-MAA nanoparticles (Fig. 14(b)). We speculated that the photo-generated electrons transferred from the excited state of polymer shells to the conduction band of ZnO nanoparticles, and then combined with those shallowly trapped holes in ZnO surface vacancies (Scheme 7). These holes were captured from the polymer shell by the vacancies on ZnO surface. If such a mechanism is correct, it will be possible to change ZnO excitation light to the visible spectrum, so that UV damage to ZnO-labelled cells can be avoided.

However, this luminescent model for ZnO@polymer nanoparticles is controversial at present. Wang *et al.* coated anatase, γ-Al₂O₃, SiO₂ and ZnO nanoparticles with a PMMA layer by γ or electron radiation.[68] All samples possessed blue fluorescence which could be destroyed by annealing in air. Hence, the authors ascribed the luminesc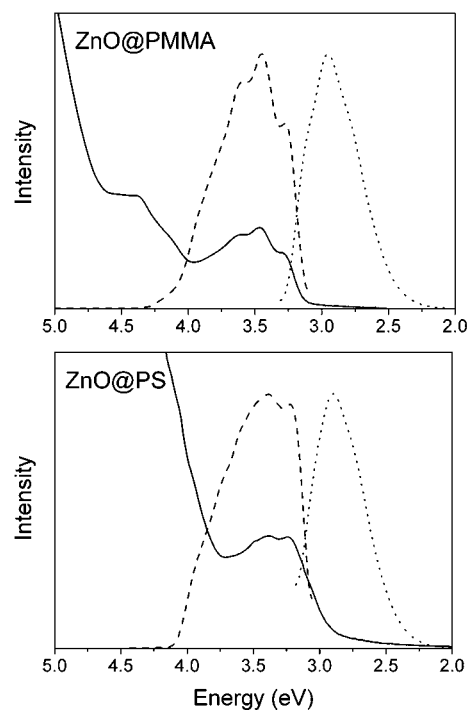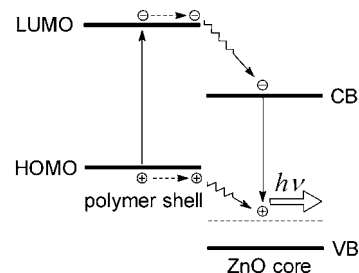ence to the carbonyl adjacent to the nanoparticle surface. Actually, this point had been suggested by Vollath and co-workers who observed blue fluorescence from PMMA coated HfO₂, ZrO₂ and Al₂O₃ nanoparticles.[69] However, the above two papers did not provide any absorption data so that luminescent efficiencies of these PMMA coated nanoparticles were probably rather weak. If the emission only arises from the carbonyl groups, ZnO@polymer with similar structure will always possess blue fluorescence. On the contrary, we have prepared green and yellow emitting ZnO@poly(MAA-co-PEG-MEMA) (see Fig. 7), and ZnO@PPEGMA core–shell nano-particles reported by other researchers are UV emitters (see Fig. 8). Furthermore, Kahn and co-workers prepared amine-modified ZnO nanoparticles which also possessed strong blue emission,[26] while Fu *et al.* obtained oleic acid related blue-emitting ZnO with a quantum yield of 76%.[27] Hence, we believe when carbonyl groups coordinate with nanoparticles these particles might appear blue under UV light, but such blue emission is

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rather weak and it will be overlapped by the ZnO emission. In fact, Vollath *et al.* found PMMA coated ZnO nanoparticles had two emission maxima. One was weak at 496 nm and the other was strong at 529 nm.[69] They ascribed the former to polymer–ZnO interactions on surface and the latter to ZnO emission.

Li and co-workers hydrolyzed zinc acetate with mono-ethanolamine in ethanol and then added MMA monomer for polymerization. The products were bulk transparent PMMA-ZnO hybrid materials with good UV shielding capability (PZHM).[70] Even a very small amount of ZnO could make the bulk materials exhibit strong blue fluorescence, while the pure PMMA had no fluorescence (Fig. 16). The theoretical calculation results based on the UV-Vis absorption of the ZnO nanoparticles in PMMA indicated that the ZnO particles had a diameter of about 4.6 nm, which should be yellow-emitting for conventional ZnO quantum dots. Another phenomenon in Fig. 16 is that the change of the ZnO concentration in the PZHM did not render a significant change of the emission intensity. If such blue emission was from the carbonyl groups conjugated on nanoparticles, the emission intensity should increase significantly as the ZnO concentration is increased from 0.017 to 0.110 wt%. Hence, the possible luminescent mechanism for these PZHM may be similar with our model in Scheme 7, and the small change of emission intensity could be ascribed to the typical luminescent features of quantum dots, such as self-absorption and concentration quenching.

Another proof is the latest polymer–ZnO nanocomposite[71] using P3EEET ligands (2-(2-ethoxyethoxy)ethoxy modified poly-thiophene). This nanocomposite has a blue emission at 400 nm

Fig. 17 PL Emission spectra of ZnO-P3EEET nanocomposite in CH_2Cl_2 layer (dashed line) and ZnO (solid line) in aqueous layer. (Reprinted with permission from ref. 71. Copyright © 2009 the Royal Society of Chemistry).

with quantum yield over 50%. Fig. 17 shows the PL intensity of the polymer nanocomposites in organic solvents is more than 100 times higher than that of the ligand-free ZnO particles in water. Controlled experiments proved that the blue fluorescence was from neither P3EEET nor Zn^{2+}-P3EEET in solution. The authors concluded that the highly intense 400 nm band originates from ZnO (encapsulated by P3EEET) direct band-gap emission, according to the lifetime measurements on the P3EEET-ZnO nanocomposite. P3EEET has a much different structure from PMMA and PS (see Scheme 8). Its polyether groups can coordinate with Zn^{2+} ions so that the ZnO nanoparticles were capped and dispersed homogeneously in the polymer matrix (see Fig. 18). In contrast, ligand-free ZnO nanoparticles agglomerated heavily in water. It should be mentioned that both the P3EEET-ZnO and ligand-free ZnO nanoparticles had the same diameters about 3.5 nm, but their PL emission were totally different. This result proved that the relationship between ZnO emission wavelength and ZnO particle size as predicted by van Dijken's model can only be applied under the conditions that ZnO nanoparticles have similar surface states.
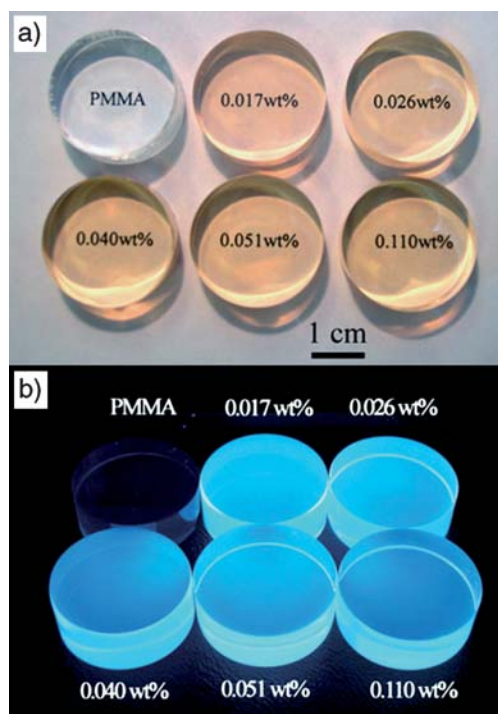

Fig. 16 (a) Photographs of the PZHMs under visible light with a thickness of 1 cm. (b) PZHMs containing various concentrations of ZnO QDs under a low intensity UV light ($\lambda = 362$ nm) show significant blue emission from the ZnO QDs in the PMMA matrix (Reprinted with permission from ref. 70. Copyright © 2007 John Wiley & Sons. Inc).
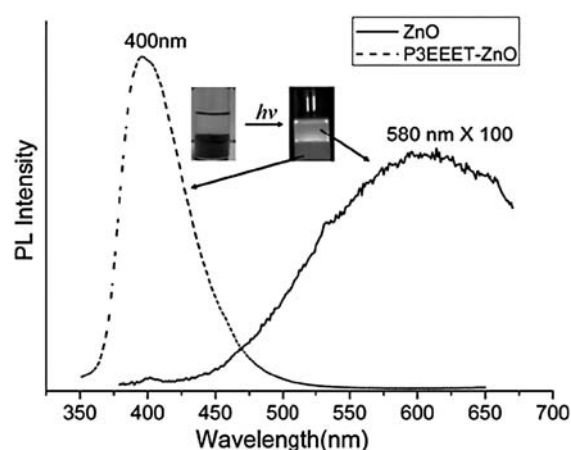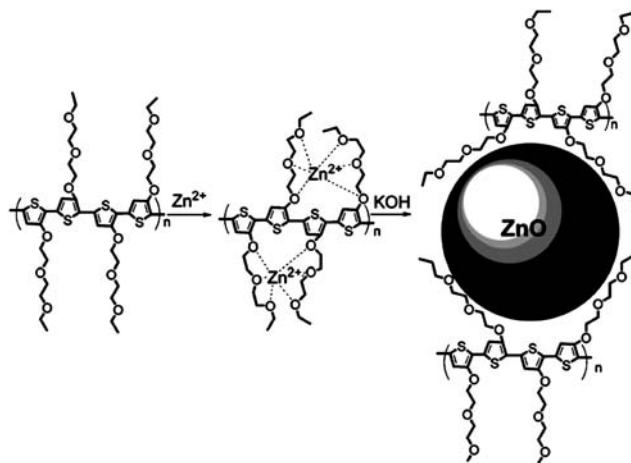

Scheme 8 Complexation of polymer backbone with Zn^{2+} ion and the resulting ZnO nanoparticles capped by P3EEET.
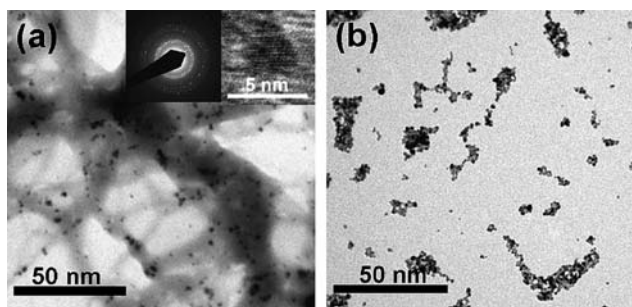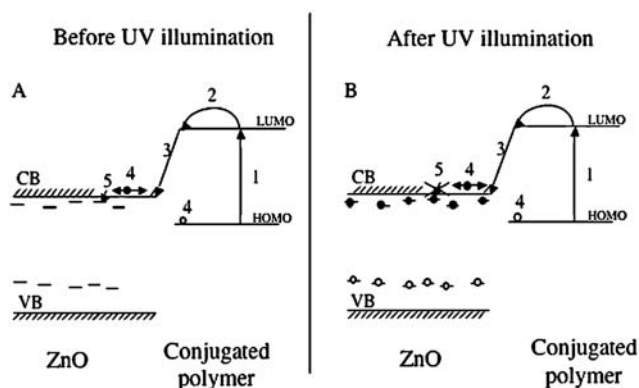
Fig. 18 TEM images of (a) P3EEET-ZnO nanocomposite and (b) ZnO nanoparticles. (Reprinted with permission from ref. 71. Copyright © 2009 the Royal Society of Chemistry.)

Scheme 9 Before UV illumination (A), excitation of the polymer with visible light (1), exciton diffusion (2), and electron injection (3) result in mobile electrons in ZnO, which contribute to the photoconductance (4) until the electron is trapped (5). After UV illumination (B), electron traps are occupied and electrons injected from the polymer are trapped to a lesser extent, and thus, the photoconductance is increased.[72]

Quist and co-workers modified two conjugate polymers onto ZnO nanoparticles to study their photoconductance (Scheme 9).[72] They found when the samples were excited by visible light, the photo-generated electrons transferred from the LUMO of the polymer to the conductance band of ZnO, and were then trapped by the ZnO surface vacancies. Under this condition, the photo-conductance of the polymer–ZnO nanocomposites was rather low. When the samples were illuminated by UV light, the photo-generated electrons from the ZnO valence band would occupy vacancies on the ZnO surface. As a result, the photo-generated electrons from the LUMO of the polymer would move freely on ZnO surface, showing enhanced photoconductance. This experiment confirmed that visible light is able to excite some conjugated polymers to inject photoelectrons onto the ZnO conductance band just like the situation of dye-sensitized ZnO in solar cells.[8] Whether the photo-generated holes in the HOMO of polymers can be captured by ZnO surface traps (as shown in Scheme 7), however, remains to be verified by future investigations.

4 Summary

In general, ZnO visible emission depends on the oxygen vacancies which mainly locate on the nanoparticle surface. If the polymers only have weak interactions on ZnO QDs, the ZnO QDs are apt to aggregate together and thus ZnO PL emission will red-shift and its intensity will decrease significantly. If the polymers have strong interactions on ZnO QDs, the situations will be rather complicated: (i) the coordination of polymers with ZnO always makes the QDs disperse homogeneously in the polymer matrix or in a solvent, so that the ZnO luminescence will be protected well and even enhanced because of concentration effects and exciton charge separation; (ii) some polymer ligands are able to fill up (passivate) the defects on ZnO surface and thus ZnO visible emission will be quenched while UV emission will be improved; (iii) some polymers are electron donors for ZnO QDs while some polymers trap photoelectrons from ZnO QDs, so the ZnO PL spectra will be influenced correspondingly; (iv) if the polymers themselves are photo-luminescent, there will be resonance energy transfer between polymers and ZnO, and thus the complex PL spectra of the composite depends on the relative energy levels of polymers and ZnO QDs. It should be emphasized that these interactions between polymers and ZnO are not only based on the nature of the two components, but also dependent on the preparation process of the materials. The surface state, dispersity, crystallinity and purity of ZnO QDs could be changed during preparation, so the resulting polymer–ZnO nanocomposites with the same compositions would exhibit quite different optical properties.

This review has covered the last decade's researches on photo-luminescent polymer–ZnO nanocomposites. Progress in this field can be divided into two aspects. One is improvement on preparation method, from physically mixing polymers and ZnO nanoparticles to controlled polymerization on the ZnO nanoparticle surface. Different synthetic routes produce various structures which always influence the product luminescence. Progress has also been made in terms of enhancement of luminescent properties, from enhanced quantum yield and multicolor emission to novel polymer involved luminescent mechanism. As a highlight in this review, we reported ZnO@polymer core–shell nanoparticles for cell imaging which is an important application of ZnO quantum dots with visible emission. Although ZnO probes are safe and cheap, they have some drawbacks in photo-luminescence, such as requirement of UV excitation, broad emission and sensitivity to water. To overcome these drawbacks, modifying polymers on the ZnO surface is promising because there are so many choices for polymer species and chemical modification methods. The latest reports concerning polymer–ZnO cooperating luminescence have confirmed the possibility to further reshape the ZnO photoluminescent process. Therefore, photoluminescent ZnO nanoparticles modified by polymers will have a bright future.

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