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Modifying emission of ZnO nanoparticles in ZnO interceded polymer based hierarchical ordered nanocapsules

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ABSTRACT

Here we report that a cationic polyamine in the presence of hydrogen phosphate spontaneously self-assemble due to ionic cross linkage to form aggregates, and when ~14 nm ZnO is added in alkaline environment ZnO mediated hierarchical ordered nanocapsules are formed. These nanocapsules are of 200–500 nm with a hydrodynamic radius of 170 nm. Such nanocapsules alter the photoluminescence of ZnO nanoparticles. The photoluminescence properties of the ZnO based nanocapsules depend on excitation wavelengths. The visible emission of ZnO nanocapsules is due to the defects or vacancies that are located mainly on the nanoparticle surfaces during the interaction between polymer and ZnO in the nanocapsules. The relative photoluminescence quenching in ZnO nanocapsules compared to ZnO in polymer solution could be referred to aggregation of ZnO nanoparticles during nanocapsule formation.
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1. Introduction

Zinc oxide (ZnO) is an important technological material. The large electromechanical coupling, combined with the lack of symmetry center in wurtzite, leads to strong pyroelectric and piezoelectric properties and the consequent application of ZnO in piezoelectric sensors and mechanical actuators. Moreover, ZnO is a semiconductor with a wide band-gap (3.37 eV); so it is suitable for optoelectronic applications of short wavelength [1]. In addition, ZnO crystal has high exciton binding energy (60 meV) that allows efficient excitonic emission at room temperature [2]. Ultraviolet (UV) luminescence at room temperature has been reported in thin films and disordered nanoparticles [1]. ZnO is transparent in the visible region of light [1] and can be doped with transition metals for spintronic applications [3]. Furthermore, ZnO exhibits sensitivity to numerous gas species, mainly carbon monoxide (CO), ethanol (C_2H_5OH), and acetylene (C_2H_2), which makes it adequate for sensing applications [2].

The optical properties of ZnO can be tuned. It has been reported that the dispersion of nickel oxide nanoparticles (NiO NPs) on ZnO surface modifies the optical properties of the latter through a solid-state electrochemical reaction at NiO–ZnO interface induced by surface OH groups. This reaction introduced some structural disorder and produced a stress relaxation to the ZnO surface [4]. Such modifications have been translated to changes in the emission spectra of ZnO; where an important in the visible bands (3 bands centred at 465, 515, 550 nm respectively) has been detected in the presence of NiO NPs. This enhancement has been attributed to the increase in the number of oxygen and zinc vacancies after the addition of NiO NPs [4].

ZnO is environmentally friendly and chemically stable material. As a result, there is a remarkable interest in studying ZnO in the form of single crystals, powders, nanostructures, or thin films [2]. A wide variety of ZnO nanostructures have been reported, including nanowires [5], nanorods and tetrapods [6]. Moreover, core/shell ZnO/SiO_2 nanoparticles have been successfully synthesized; where these structures have shown improved stability and photo-catalytic activity in acidic or alkaline solutions as compared to uncoated ZnO nanoparticles [7]. Recently a relatively new concept of capsule formation via polyamine–salt aggregate or 'PSA' has been developed [8,9]. This technique was originally termed as 'tandem self-assembly'. It involves the combination of a cationic polyamine with a multivalent anionic salt, resulting in the spontaneous generation of ionically crosslinked PSAs [8–13]. The capsule is formed through further addition of negatively charged shell material on PSAs that serves as the capsule template [9]. For further use, the polyamine–salt template can remain in the capsule's core; however, after shell formation it can spontaneously disassemble, depending on polymer and salt types, leaving a capsule with water filled core. As the polymer part participates in shell formation and is a main shell constituent, the PSA is not strictly a soft or hard templating method [9,11]. In this present letter, poly (allylamine hydrochloride) (PAH) based nanocapsules have been prepared using phosphate and ZnO to modify the optical properties of 14 nm sized ZnO nanoparticles, specifically for visible emission of ZnO.

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2. Materials and methods

Materials: Zinc oxide nanoparticles were obtained from PlasmaChem with $>99\%$ purity, 14 nm particle size and 30 m^2/g. The stock solution of ZnO was prepared in de-ionized water of pH 9 and of 0.1 mg/ml concentration. PAH stock solution was prepared in de-ionized water of pH 4.4 to ensure the formation of PAH/dipotassium phosphate aggregates.

Preparation of ZnO nanocapsules: In this process 1.3 ml of PAH (3 mg/ml) was gently vortex mixed for 10 s with 7.8 ml of 2.5 mM K_2HPO_4 and aged for 30 min. After wards, 7.8 ml of ZnO nanoparticles (0.1 mg/ml) of pH 9 was added to PAH/K_2HPO_4 aggregates. The pH of ZnO solution was monitored at 9; in such basic conditions ZnO is in the form of $Zn(OH)_3^-$, consequently, this ensures its interaction with the positively charged PAH/K_2HPO_4 aggregates. The final solution was left to age for 2 h, then it was centrifuged at a speed of 4450 rpm for 20 min. The nanocapsules were washed for three times with de-ionized water and dispersed in 3 ml of de-ionized water for further characterization and investigation.

Morphological characterization: Scanning electron microscopy (SEM) analysis was done using Tescan, Vega 3 LMU with Oxford Edx detector (Inca XmaW20) SEM, where 3 mg of the NC were dissolved in 5 ml of de-ionized water, and few drops of the nanocapsule suspension were mounted on an aluminium stub, coated with carbon adhesive. After being dried the sample was ready for the SEM analyses. The particle size distribution was analyzed using DLS (Brookhaven Instruments Corps) technique with a laser source of 658 nm and a PMT detector (HAMAMATSU, HC120-30). The software used was 90Plus Particle Sizing Software Ver. 5.23 and the dust was set at 40.

Spectroscopic measurements: The absorption spectra were recorded using a JASCOV-570 UV–vis–NIR Spectrophotometer at room temperature. The steady-state fluorescence spectra (excitation and emission) were recorded at room temperature using Jobin-Yvon-Horiba Fluorolog III fluorometer and the FluorEssence program where the excitation and emission slits width were 5 nm. The source of excitation was a 100 W Xenon lamp, and the used detector was R-928 operating at a voltage of 950 V.

3. Results and discussion

Preparation and characterization of ZnO nanocapsules: ZnO based microcapsules were synthesized by the poly (allylamine hydrochloride) mediated self-assembly method described in Materials and Methods. In this method, the ionic-cross linking of the PAH chains with multivalent counter anions dipotassium hydrogen phosphate to form spherical polymer aggregates is the key step for the formation of microcapsule structure. To it 14 nm ZnO particles were added. Because of their net positive charge these aggregates afterwards facilitate the assembly of ZnO nanoparticles to form an ordered nanocapsule structure in which the shell wall acquires a composite structure consisting of positively charged PAH chains entangled with the ZnO nanoparticles (as shown in Fig. 1). The SEM images illustrating spherical morphology of the microcapsules with sizes of 200–500 nm is exhibited in Fig. 2A–C. The particle size distribution was analyzed using DLS and it was found that the capsules have an effective hydrodynamic radius of 170 nm.

Photoluminescence of naked ZnO nanoparticles: The absorption spectrum of ZnO NPs in this study is shown in Fig. 3A. It shows a maximum at around 266 nm and another band at around 330 nm. The photoluminescence spectra of ZnO NPs in ethanol at excitation wavelength 280 nm and 320 nm are shown in Fig. 3B. It is clear that the photoluminescence spectra of ZnO nanoparticles do not

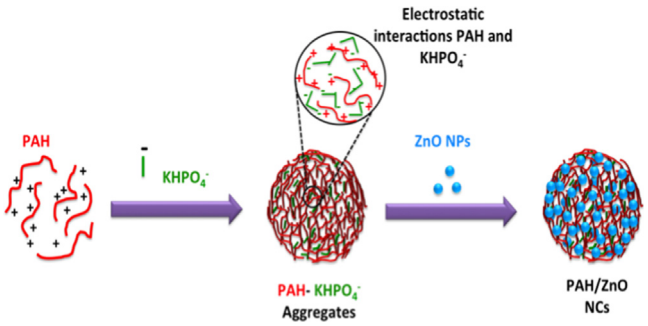

Fig. 1. Illustration of PAH/dipotassium phosphate aggregated interacting with ZnO NPs to form NCs.

change with excitation wavelength, and the emission maximum was observed at around 377 nm and two small bands at around 360 nm and 310 nm. These emission bands could be related to different emission centres of ZnO. At the same time the excitation spectrum of ZnO at emission wavelength 370 nm in solution was found to be similar to absorption spectrum, these observations establish the fact that no other species are involved in the excited state except the same species present in the ground state of ZnO nanoparticles. ZnO band gap is 3.37 eV at room temperature, therefore, the emission in 300–380 nm could be due to exciton emission of ZnO similar to reported in literature [14]. It should be noted that visible emission has earlier been reported for ZnO [15–19], which was not detected in the ZnO nanoparticles in ethanol we used in our study. This visible emission reported in the literature arises from its defects or vacancies that are located mainly on the ZnO surface, which is termed as deep-level emission and its mechanism is controversial and not yet clear [19]. However, surface state is the main factor that determines visible luminescence of ZnO [15–19]. In our case, ZnO used from the commercial source was highly crystallized and devoid of any surface modification; thus, absence of visible emission is expected in ethanol. Nevertheless, when the photoluminescence of ZnO nanoparticles was measured in double distilled water as depicted in Fig. 4A, the photoluminescence intensity of ZnO nanoparticles remarkably was quenched compared to that in ethanol. At the same time compared to emission band at around 377 nm a sharp high intense exciton emission peak of ZnO NPs was observed at 310 nm that was significantly small (minor humps) in ethanol. Such increase in exciton emission for ZnO nanostructures has been linked with surface defects [15]. The photoluminescence quenching at 377 nm is also not surprising due to the fact that it is well established hydroxyl groups of water coordinate on the surface of ZnO nanoparticles and a little amount of water would kill the photoluminescence of ZnO [19] by destroying luminescence centers [16].

Photoluminescence of ZnO nanocapsules at 280 nm excitation: The normalized photoluminescence spectra of ZnO capsules (see Fig. 4A) prepared from ZnO nanoparticles was compared with naked ZnO at excitation wavelength 280 nm. A sharp exciton emission was observed in ZnO nanocapsules, which was similar to the results obtained for ZnO nanoparticles in water. But this peak intensity was much more pronounced in naked ZnO NPs compared ZnO nanocapsules. It is known in the literature that surface defects increase the exciton emission [15]; therefore, ZnO nanocapsules have higher surface defect compared to ZnO NPs in ethanol but less than that of ZnO NPs in water. The enhancement in exciton emission has also been linked with increase in crystallinity. Chang et al. have found that polyaniline modification could enhance the UV emission of ZnO nanostructures [17]. At excitation 280 nm, although the emission maximum at around 377 nm of ZnO NPs appeared in water and ethanol, an emission maximum

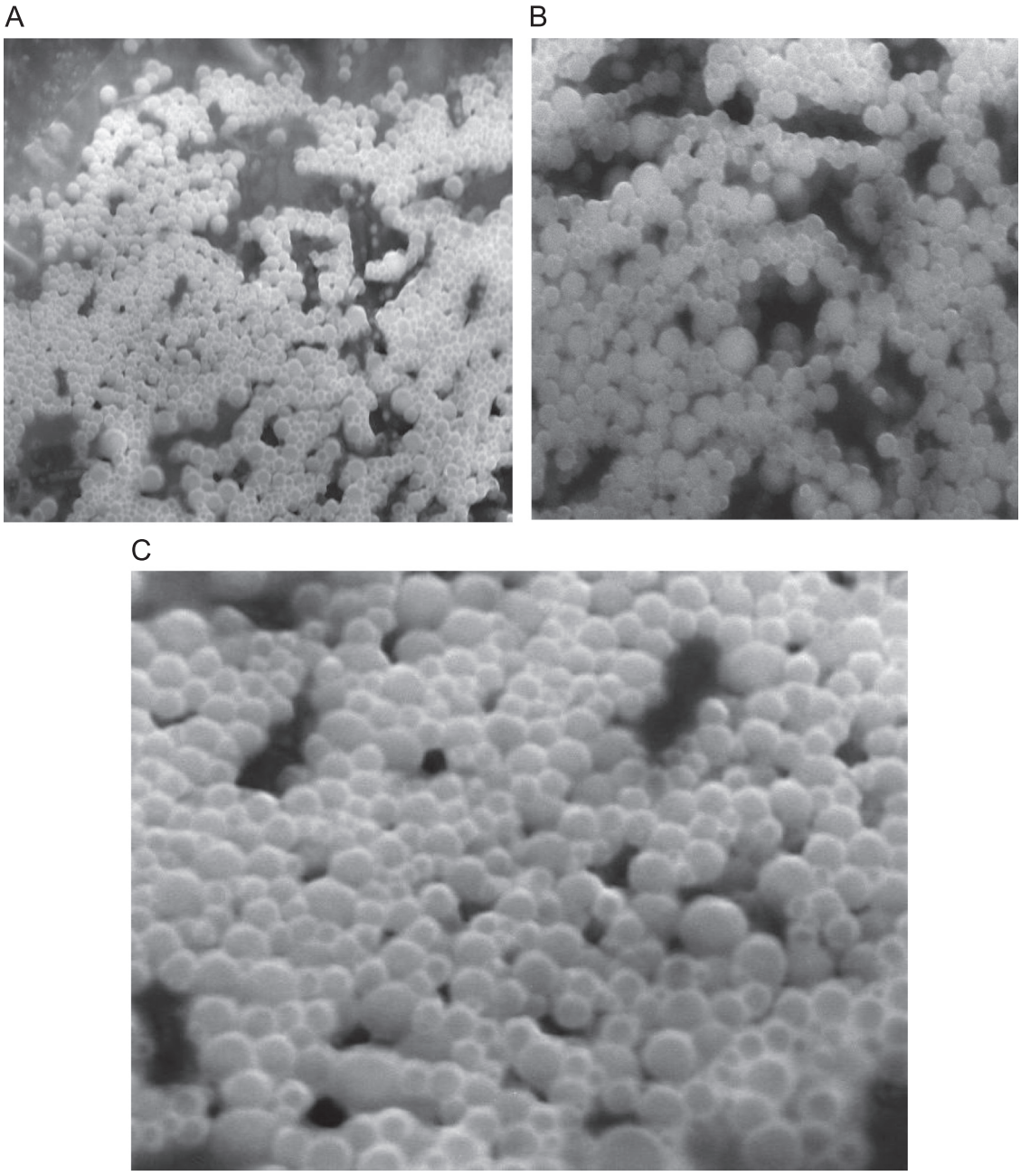

Fig. 2. (A–C) SEM images of ZnO congregated capsules. (A) 5 μm resolution; (B) 2 μm resolution; (C) 1 μm resolution.

was observed at around 350 nm (instead of 377 nm) for ZnO nanocapsules. This change in emission centre is explained subsequently because the photoluminescence of ZnO in polymer matrix is complex and can be better understood at excitation wavelength 310 nm (at the tail of the band [16]).

Photoluminescence of ZnO nanocapsules at 310 nm excitation: Interestingly, when we excited at 310 nm, we observed a different emission pattern for ZnO nanocapsules. It should be noted that the emission maximum of ZnO NPs in ethanol remained the same irrespective of excitation wavelengths (280 nm or 310 nm). On the other hand, the emission maximum was observed at around 420 nm for ZnO nanocapsules as shown in Fig. 4B. This emission line (wavelength) has also been reported for ZnO as a defect emission [20,21]. The excitation wavelength dependence of the photoluminescence change of ZnO nanocapsules was about 80 nm in wavelength scale. This kind of excitation wavelength dependence photoluminescence properties violates Kasha's rule of excitation wavelength independence of the emission spectrum. Nevertheless, such excitation dependency of emission behaviour of ZnO colloid for different capping agent has been reported. Irimpan et al. have shown and explained this phenomenon in terms of existence of a distribution of energetically different molecules in the ground state coupled with a low rate of excited state relaxation process [18]. Such relaxation process includes solvation and energy transfer for excitation dependent photoluminescence behaviour of ZnO nanocapsules. This visible emission is expected for ZnO nanocapsules due to the defects or vacancies that are located mainly on the nanoparticle surfaces during the interaction between PAH and ZnO in the nanocapsules. The red shift in photoluminescence spectra has also been reported for ZnO nanoparticle aggregates [19,20]. In ZnO nanocapsules, obviously, congregation of ZnO NPs is expected (as explained in the synthesis procedure). But it is also known that ZnO nanoparticle aggregation decreased the photoluminescence intensity along with a red shift in the spectra [19]. To prove that there is a

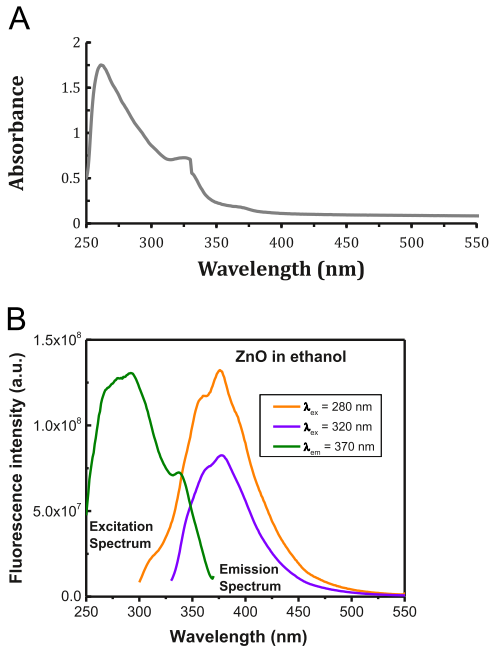

Fig. 3. (A) Absorption spectrum of 14 nm ZnO nanoparticles; (B) photoluminescence excitation and emission spectra of 14 nm ZnO nanoparticles in ethanol.

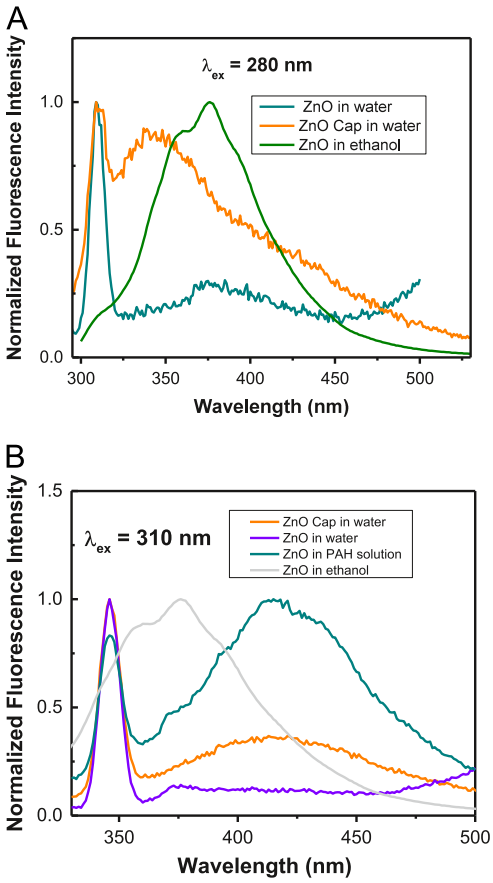

Fig. 4. (A) Photoluminescence spectra of ZnO capsules at excitation wavelength 280 nm; (B) photoluminescence spectra of ZnO capsules at excitation wavelength 310 nm.

decrease in photoluminescence, the photoluminescence of ZnO nanocapsules was compared with that of ZnO in PAH solution (without making any nanocapsules) and we found that no major

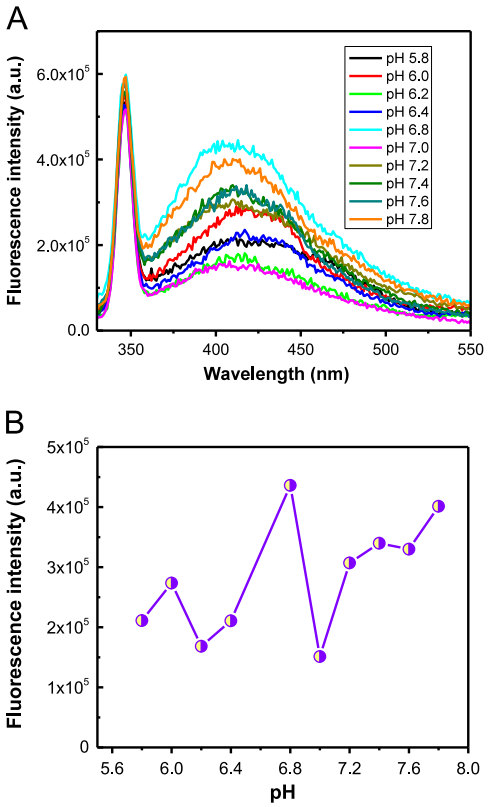

Fig. 5. (A) Photoluminescence spectra of ZnO capsules in different pH (phosphate buffer) solution at excitation wavelength 310 nm. (B) Relative change in fluorescence intensity with pH.

change in spectral position was observed. However, the relative photoluminescence intensity of ZnO NPs in the visible region (at 420 nm), as compared to UV exciton emission, has increased in PAH solution. It is expected that PAH will cause defects or vacancies on the nanoparticle surface, so it is normal that ZnO NPs in PAH solution and ZnO nanocapsules could have similar emission maximum as depicted in Fig. 4B. However, congregation of ZnO NPs are not expected in PAH solution, thus, the relative photoluminescence quenching in ZnO nanocapsules could be referred to aggregation of ZnO NPs during nanocapsule formation.

Effect of pH on photoluminescence of ZnO nanocapsules: pH plays a crucial role in photoluminescence applications and alters the fluorescence properties. The influence of pH on emission properties of ZnO nanocapsules as synthesized was studied in the pH range 5.8–8 using phosphate buffer. In this study, we selected the physiological pH range because we were interested in utilizing such capsules for biological applications later on. The photoluminescence spectra of ZnO nanocapsules in different pH conditions are shown in Fig. 5. There is no appreciable change in spectral position, however, the photoluminescence intensity varied with the pH of the solution. The variation was not systematic indicating such nanocapsules can't be used for monitoring pH.

4. Conclusion

In summary, PAH/dipotassium phosphate aggregates assemble ZnO nanoparticles to form spherical nanocapsules. The hydrodynamic radius of the nanocapsules is equal to 170 nm. The photoluminescence emission of ZnO in the nanocapsule is modified where it emits in the visible region (peak at 420 nm). The visible emission of ZnO is explained by the modification of its surface; thus, photoluminescence in the visible region can potentially be

useful for sensing and optoelectronic applications in such nanocapsules.

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