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Effects of Zinc Oxide on Polyacrylic Acid: A Core-Shell Nanoparticles

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Abstract

Polymeric core-shell nanocomposites, which are hybrid of polymer and modified inorganic clay with organic surfactants, are extremely attractive in both science and industries. The Acrylic acid coated ZnO particles were successfully synthesized by a two-step chemical method, which were prepared by the polymerization of ZnO nanoparticles and followed by coating of acrylic acid nanolayer. The synthesized Zinc Oxide/Polyacrylic acid (ZnO/PAA) core-shell nanoparticles, consist of zinc oxide as the core and polyacrylic acid as the shell. The SEM study reveals that the ZnO/PAA nanoparticles with average diameters of ~40 nm. The UV-Visible spectroscopy indicates that the core-shell ZnO/PAA nanoparticles reduces the absorbance and act as a good photoabsorber.

Keywords: Acrylic Acid; Core-shell Nanoparticles; SEM-EDX; ZnO

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1. Introduction

Nano-shells, which are thin coatings deposited on core particles of different material have gained considerable attention. Nano-shell particles constitute a special class of nanocomposite materials. They consist of concentric particles, in which particles of one material are coated with a thin layer of another material using specialized procedures. These materials show novel properties which are different from their single-component counterpart. By simply tuning the core to shell ratio, the properties can be altered. The versatility of core-shell nanoparticles compared to those fabricated from a single source also makes them an increasingly interesting subject of research such as an efficient photocatalyst [1]. With emerging new techniques, it is now possible to synthesize these nanostructures in desired shape, size and morphology [2]. In the core-shell structure, the core size dependent magnetic susceptibility at room temperature combined with the chemical stability of the silica coatings suggests that, the resulting nanocomposites may be a good candidate for biomedical applications, such as magnetic separation, drug targeting, image contrast in magnetic resonance imaging and hyperthermia therapy. Core-shell nanoclusters have recently received considerable attention owing to their physical and chemical properties that are strongly dependent on the structure of the core, shell and interface. This structure dependence opens possibility for tuning properties by controlling their chemical composition and relative size of the core and shell. Core-shell magnetic nanoparticles have received significant attention recently and are actively investigated owing to their large potential for a variety of applications [3]. The core-shell magnetic nanoclusters are of special interests since the heterogeneous nanostructures offer opportunities for developing devices and cluster assembled materials with new functions for magnetic recording, bio, and medical applications [4]. In fact, super paramagnetic nanoparticles with suitable biocompatible coatings have important implications in biology, biotechnology and other biomedical disciplines. Core-shell magnetic nanoparticles comprise a magnetic core (e.g. cobalt, iron oxide etc.) and a shell that can provide not only a hydrophilic layer to the Nanoparticles but also a platform for the surface functionalization of the Nanoparticles [5].

So, in the present paper attempt were made to synthesis the ZnO/PAA core-shell nanoparticles with varying concentration and evaluated the UV-Visible absorbing properties.

2 Experimental

2.1 Materials

Zinc acetate dehydrate [$(CH_3COO)_2$ $Zn.2H_2O$] (90.9%), ethyl alcohol (C_2H_5OH) 99.5%, Ammonium hydroxide (NH_4OH) 99.5% were purchased from Sigma Aldrich. Acrylic Acid (99.9%), Benzoyal per oxide (99.8%) etc. was purchased from Alfa Asser, Germany. All chemicals were used as received.

2.2 ZnO/PAA Core-shell Nanoparticles

ZnO nanoparticles prepared by sol-gel method, 5.5 gm zinc acetate was dissolved in 50 ml distilled water followed by addition of 2 ml ethanol, after then ammonium hydroxide (6 ml) was added with continuous stirring for 30 minutes at 70^0C. After dry in oven at 90^0C zinc oxide nanoparticles were obtained [6, 7]. Zinc oxide (0.1 g) was dispersed in 200 ml of deionized water by magnetic stirrer for 30 min. Then 1 ml of acrylic acid monomer was injected into the mixture. After stirring for 30 min, 10 ml of 1 mM benzoyl peroxide aqueous solution was dropped slowly into the mixture. The polymerization was performed under 80^0C for 8h with constant mechanical stirring. The prepared core-shell nanocomposites were washed several times with distilled water and ethanol, and dried at 50^0C for 6 h in air. The influence of benzoyal peroxide was carried out by keeping the reactions and varying the benzoyl peroxide, (0.1, 0.5 and 2.0 mg) have also been carried out.

3 Results and Discussion

3.1 FTIR Spectroscopy

FTIR studied were carried out in appropriate liquid sample using Bruker, FTIR spectrometer within a range of 450-4400 cm^{-1} using resolution of 4 cm^{-1}. FTIR spectroscopy was employed to characterize the formation of (Zinc Oxide/Polyacrylic acid) core-shell nanocomposites. **Table 1** FTIR Spectra of ZnO and ZnO/PAA Core-Shell Nanocomposites

Sample	**Vibrations (υ) (cm^{-1})**	**Inference**
ZnO Nanoparticles	679-488	Zn-O stretching
Zinc Oxide/Polyacrylic Acid Nanocomposites	1194	C-O stretching
	1575	COO stretching
	1576, 1421	C-C asymmetric, symmetric stretching
	1420	CH_2 bending
	3420	O-H stretching

The band at 3419 cm^{-1}, 1575-1420cm^{-1}, 1194 cm^{-1}, and 678-488 cm^{-1} were all characteristic absorption band of polyacrylic acid which are well according with that reported literature [8], in which characteristic peak of the acrylic acid including the CH_2 bending vibration at 1420 cm^{-1}, C-C asymmetric and symmetric stretching vibrations at 1575cm^{-1} and 1420 cm^{-1} respectively and the COO- stretching vibration at 1194 cm^{-1}, O-H broad band peak at 3419 cm^{-1}, clearly observed. There is a peak near the 678 cm^{-1} which clearly indicate that the ZnO nanoparticles incorporated on the surface of acrylic acid, which was confirmed according the Alam, et al. [9], in which, the IR spectra of zinc oxide show absorption in 450-1400cm^{-1} in ZnO/polyacrylic acid nanocomposites. The experimental FTIR data is shown in table 1.

3.2 UV-Visible spectroscopy

The UV–Vis. absorption spectra of nano composites was obtained in DMSO using double beam spectrophotometer, within the range of 200-800 nm. UV-Vis. spectroscopy was employed to characterize the electronic excitation behavior of ZnO/polyacrylic acid nanocomposites. Increase in Polyacrylic Acid (PAA) concentration were checked, at various wavelength viz., 248, 251, 367 and 734 nm and their absorbance intensity were studied. It was found that, the absorbance get decreases from the ratio 1:1 to 1:2 (ZnO/PAA) concentration because of the concentration of PAA increases, which decrease the absorbance activities of the zinc oxide. At 248 nm wavelength, in the ZnO/PAA (1:1 to 1:2) ratio, the absorbance got decreased from 2.096 to 2.092, which is about ≈ 0.004 (0.2%). And the ratio 1:2 to 1:5 decrease in the absorbance from 2.092 to 2.065, it means that the decrease absorbance is about 0.27 (1.3%) approx. At the wavelength 251 nm, the ratio 1:1 to 1:2 (ZnO/PAA), the absorbance decreases from 2.092 to 2.086, which is 0.006 (0.30%) approx., and in the ratio 1:2 to 1:5 (ZnO/PAA) absorbance decrease from 2.086 to 2.069 which is 0.006 (0.81%) approx. Likewise, the wavelength at 367 nm the ratio of (ZnO/PAA) 1:1 to 1:2, the absorbance decrease from 0.189 to 0.169, it decrease to 0.020 (10%) approx., and in the ratio (ZnO/PAA) 1:2 to 1:5 absorbance decrease from the 0.169 to 0.140 (0.029) 17% which was maximum during the study of the UV-Visible spectroscopy. At wavelength 734 the ratio of (ZnO/PAA) 1:1 to 1:2 absorbance get decrease from 0.077 to 0.057, it means that the absorbance decrease (0.020) 26% approx., and the ratio of (ZnO/PAA) 1:2 to 1:5 get the absorbance decrease from 0.057 to 0.054, it means decrease the absorbance (0.003) 5% approximately. The overall trend is followed in all UV spectra, that at various wavelength increases, and in increase in the PAA concentration, the absorbance intensity is decreases as shown in the table 2.

3.3 Scanning Electron Micrograph (SEM-EDX)

The SEM image of the ZnO/Poly acrylic acid (ZnO/PAA) nanocomposites shows in figure 1(a), and compositional data using EDX. SEM micrograph of the ZnO/PAA nanocomposites

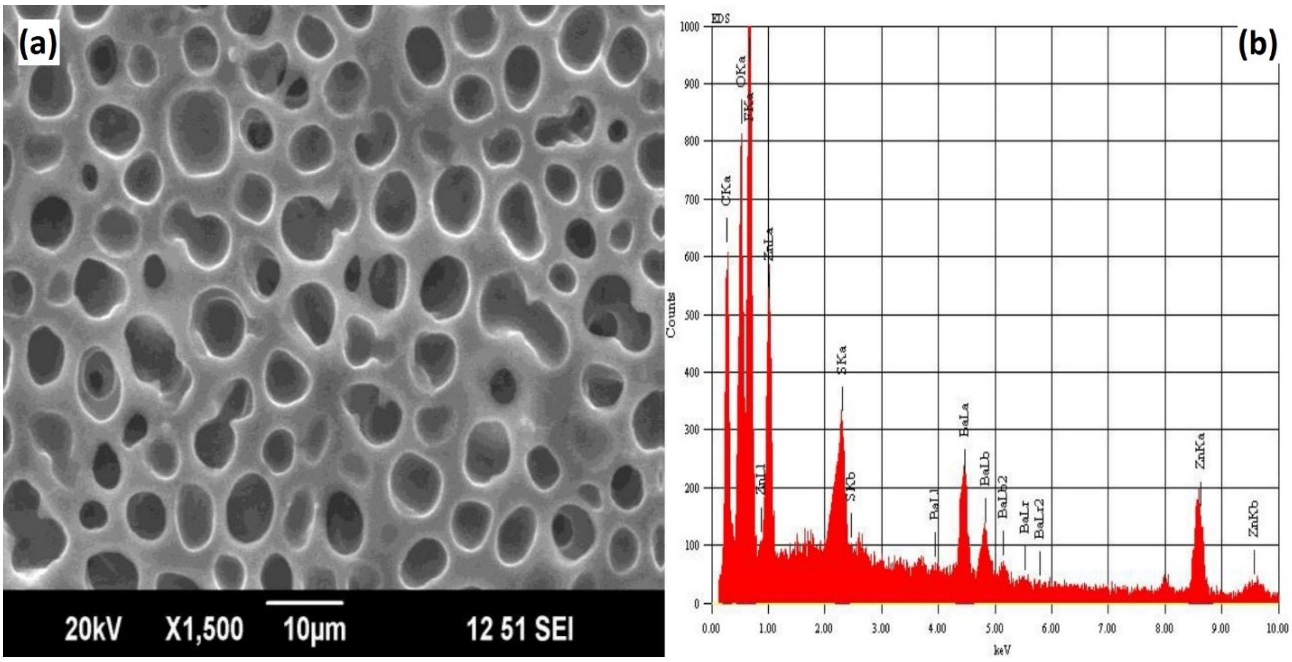

Fig. 1 (a) SEM Image of ZnO/PAA core-shell nanocomposites, (b) SEM-EDX spectrum of ZnO/PAA core-shell nanocomposites

show, that the ZnO nanoparticles are spherical in shape and the surface of ZnO/PAA nanocomposites is smooth and edge is not uniform [10, 11]. As observed from the SEM micrograph, the particle size near about 40 nm as per the calculation performed through the given scale of 10 µm. The nanoparticles of ZnO are deeply seated inside the polymer matrix, confirms the formation of ZnO core-shell nanocomposites.

Table 2 Experimental UV-Vis Data of ZnO/PAA in Various Ratios

Sr. No.	Wavelength	Absorbance ZnO/AA (1:1)	Absorbance ZnO/AA (1:2)	Absorbance ZnO/AA (1:5)
1	248.00	2.096	2.092	2.065
2	251.00	2.092	2.086	2.069
3	367.00	0.189	0.169	0.140
4	734.00	0.077	0.057	0.054

Also, as confirmed from the EDX results in figure 1(b), the particle is composed of ZnO and acrylic acid. The EDX spectrum of nanoparticles of ZnO/PAA shows that prominent presence of zinc, oxygen and carbon peaks in this spectrum.

4. Conclusion

Polymeric core-shell nanocomposites, which are hybrid of polymer and modified inorganic clay with organic surfactants, are extremely attractive in both science and industries. The Acrylic acid coated ZnO particles were successfully synthesized by a two-step chemical method, which were prepared by the polymerization of ZnO nanoparticles and followed by coating of acrylic acid nanolayer. Zinc oxide nanoparticles were prepared by the sol-gel method, and nanoparticles prepared by the reacting zinc acetate with ethanol using NH_4OH, the whitish colour nanoparticles. Their solubility were observed and found that most of the nanocomposites are soluble in DMSO and DMF in most of the core-shell nanocomposites. The FTIR shows characterized peaks in the region, from 400-700 cm^{-1} which shows the probability of existence of bonding between ZnO nanoparticles and acrylic acid. The UV-Vis. spectrophotometer shows results of various ratios of ZnO/PAA, in which the increases concentration of acrylic acid decreases the absorbance of the ZnO/PAA nanocomposites and the SEM image of ZnO/PAA core-shell nanocomposites shows the irregular size and heterogeneously disperse of ZnO nanoparticles in Acrylic acid matrix and also indicating the formation of core-shell nanoparticles. The uniform porous formation of the film was due to the effect of ZnO nanoparticles, which could be a material for industrial applications such as a membrane for water purification.

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