



Controlled Green Synthesis of Polymer Functionalized Zinc Oxide Nanoparticles

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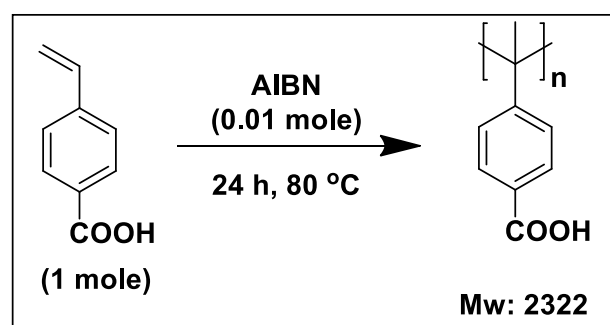
Abstract: Synthesizing metal nanostructures with uniform sizes have received great attention in recent times due to their potential applications in the fields of plasmonics, catalysis, photocatalysis and renewable energy. Indeed, the controlled synthesis of zinc oxide nanoparticles (ZnONPs) with uniform sizes is always a challenging task. In the present study, we introduced a simple green strategy for the preparation of ZnONPs with uniform size. Initially, poly(4-vinylbenzoic acid) (PVBA) was prepared from the polymerization of vinyl benzoic acid and used as capping agent to control the size of ZnONPs. The resultant polymer grafted ZnONPs (p-ZnONPs) was characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), high resolution transmission electron microscopy (HRTEM), and nuclear magnetic resonance (NMR) analysis. The successful formation of polymer grafted ZnONPs (p-ZnONPs) was confirmed by NMR and XPS analysis. The TEM results confirmed the formation of uniform size of p-ZnONPs. The average particle size of p-ZnONPs was calculated to be ~5 nm. We presume that the resultant p-ZnONPs would be useful in various catalytic and energy applications.

Keywords: Zinc oxide; nanoparticles; polymerization; grafting; XPS

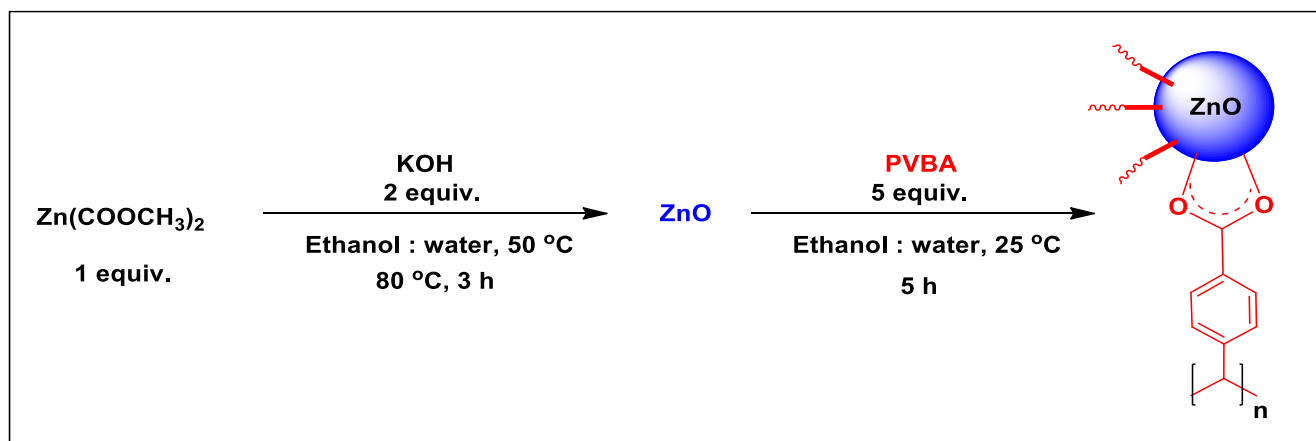
1. Introduction

Zinc oxide nanoparticles (ZnONPs) are one of the very important metal oxides employed in various fields due to their peculiar physicochemical properties.^[1-2] The ZnONPs and its derived materials have played crucial role in various applications for the last 40 years. As a wide-band gap semiconductor, ZnONPs is used as additive in the preparation of numerous materials and commercial products such as rubbers, plastics, ceramics, glass, etc.^[3] The ZnONPs is indeed low-cost and low-toxicity nanomaterial, have played significant role in various biomedical fields, including anticancer, antibacterial, antioxidant, antidiabetic, and anti-inflammatory activities, as well as for drug delivery and bioimaging applications.^[4] In native doping experiment, the ZnONPs semiconductor plays a promising role because of its oxygen vacancies or zinc interstitials is used as n-type semiconductor.^[5] Those properties lead to emerging applications for: transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, and electronics as thin-film transistors and light-emitting diodes. Promisingly, ZnO NPs have a remarkable potential in biomedicine studies, interestingly in the fields of anticancer and antibacterial fields, grasping their potent ability to trigger excess reactive oxygen species (ROS) production, release zinc ions, and induce cell apoptosis.^[6] Moreover, the increasing number of publications based on ZnONPs and its applications clearly shows the urgency of the wide-band gap

semiconductor, ZnONPs.^[7-8] In general, the ZnONPs occurring in a very rich variety of size and shape will provide a wide range of properties. Widely used synthetic methods for the preparation of ZnONPs are chemical precipitation method, sol-gel method, solid-state pyrolytic method, solution-free mechanochemical method, and biosynthesis method. Bhuyan et al.,^[9] prepared ZnONPs via biosynthesis method using *Azadirachta indica* plant extract. They found that the resultant ZnONPs is highly suitable for biomedical and catalytic applications. Shaikh et al.,^[10] developed ultrasonication-assisted synthetic procedure for polymer (3-substituted indoles) grafted ZnONPs catalyst. Similarly, several synthetic methods are available in the literature for the controlled and simple preparation of polymer grafted ZnONPs.^[11-14]



Scheme 1. Synthesis of PVBA using AIBN.



Scheme 2. Synthesis of functionalised ZnONPs using PVBA.

In spite of that the preparation of ZnONPs with uniform size is still a challenging task. In order to obtain the uniform size of ZnONPs, several reaction or preparation parameters to be controlled or toxic/expensive reagents should be used. Hence, in the present work, we have focussed on synthesis of ZnO in situ polymer capping to control the growth of the ZnONPs. Among the several other functionalization methods using organic molecules, grafting of polymer has its own merits because of the high stability factor. Most of the functionalization units contain amines, alcohols, acids group which facilitates high electron cloud towards the electron deficient metal or metal-oxide centres. The acid group in the polymer chain stimulates the cross-linking behaviour towards the metal oxide, which leads the stronger interaction corresponds to the control growth. We have experimented the above hypothesis in order to prove the materialistic property of ZnONPs. Initially, ZnONPs were synthesized and characterized using NMR and gel permeation chromatography. Then polymer was grafted on ZnONPs by a simple green method the resultant polymer was characterized by NMR, SEM-EDAX, XPS and HRTEM analysis.

2. Experimental Section

2.1. Materials and characterization

All chemicals used were of analytical grade. All the commercial grade solvents were distilled as per the standard procedures and dried over molecular sieves before use. Nuclear magnetic resonance (NMR) spectra were recorded using DMSO- d_6 as solvent and tetramethylsilane as an internal standard on a Bruker 500MHz spectrometer. X-ray photoelectron spectroscopic (XPS) analyses were done on a Kratos Axis-Ultra DLD instrument. During the analyses, samples were irradiated with Mg $K\alpha$ X-ray source. The scanning electron microscopic (SEM-EDAX) images were obtained by using Bruker microscope. The high resolution transmission electron microscopic (TEM) images were seen by using JEOL JEM 2100 microscope.

2.2. Synthesis of polyvinyl benzoic acid (PVBA)

Monomer vinyl benzoic acid (1 mol) and azobisisobutyronitrile AIBN (0.01 mol) were taken in a schlenk flask under inert atmosphere

(Scheme 1). To the above mixture, 15 mL of tetrahydrofuran dry solvent was added under nitrogen atmosphere. In order to remove oxygen from the reaction mixture, several rounds of freeze-thaw cycles (3 cycles) were conducted with N_2 purging. The reaction mixture was allowed to stir for 24 hours at 80°C. After the completion of the reaction, the resulting crude product was dissolved in ethanol and then re-precipitated using diethyl ether (100 mL, 2 times). Finally, the separated white product was filtered off and dried in a temperature controlled hot air oven at 50°C for 1 day. ^1H NMR (500 MHz, DMSO- d_6) δ 11.99 (1H, br peak, COOH), 7.10-7.14 (4H, br peak, ArH), 0.8-1.6 (5H, br m peak, aliphatic protons).

2.3. Synthesis of functionalized ZnONPs with PVBA

A total of 0.5 g of $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ was completely dissolved in ethanol:water (1:1) mixture, at 100 mL at 50°C until solution returns clear. Then slow addition of KOH (0.255 g) was added and the mixture was stirred for 10 min. Then the mixture was stirred for 3 h at 80°C with vigorous stirring and stopsit. Then cool the mixture to room temperature in order to precipitate ZnO particles slowly. To the above solution, add the solution of PVBA (0.5 g) in ethanol drop wise and stirred for 5h at room temperature (Scheme 2). The resulting product was washed with ethanol 3 times to remove unreacted PVBA by centrifugation and ultra-sonication.

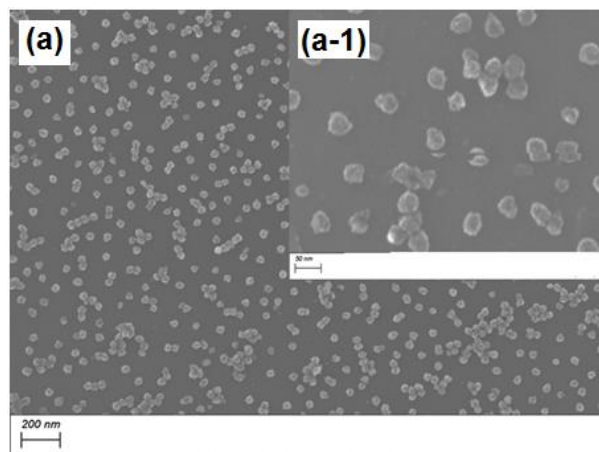


Fig. 1. (a, a-1) SEM images of ZnONPs without capping.

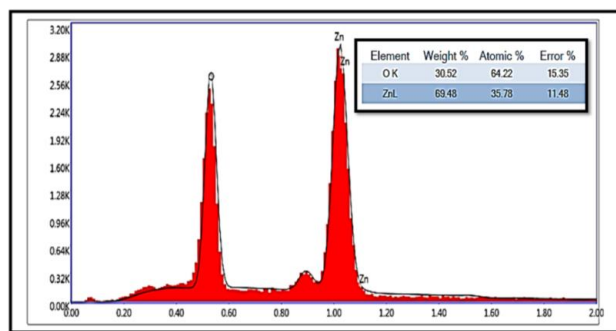


Fig. 2. EDAX image of ZnONPs without capping.

3. Results and Discussions

3.1. Synthesis and Characterization of the PVBA

Nucleobase-containing polymers are the most widely studied materials in various fields such as biosensors and drug therapies because of the complementary hydrogen bonding.^[15] In the present work, the PVBA was synthesized by using vinyl benzoic acid monomer and azo bisisobutyronitrile (AIBN). Dry tetrahydrofuran was used as solvent and the complete reaction was performed under nitrogen atmosphere at 80°C for one day. Finally, in order to obtain the PVAB with high purity, the resulting crude product was dissolved in ethanol and then re-precipitated using diethyl ether. Scheme 1 shows the synthesis of PVBA using AIBN. The resultant PVBA was characterized by GPC and NMR. The GPC spectrum of the synthesized PVBA has been provided in supporting information (Fig. S1). The weight average molecular weight (Mw) and poly-dispersity indices (PDI) of the PVBA calculated from the GPC analysis were 2322 g/mol⁻¹ and 1.69 respectively. The high value of Mw (2322 g/mol⁻¹) clearly shows the merit and suitability of the present method for the preparation of PVBA. 1H NMR spectrum of PVBA was recorded in (500 MHz, DMSO-d₆) and the result confirmed the formation of PVBA. The signals at 11.99 (1H, br peak, COOH), 7.10-7.14 (4H, br peak, ArH), 0.8-1.6 (5H, br m peak, aliphatic protons) confirm the structure of PVBA. Yang et.al.,^[16] prepared A series of poly-vinyl benzoic acid (PVBA) and UiO-66 materials (PVBA-UiO-66). The resultant materials are proved to be an efficient adsorbent toward methylene blue (MB). Similarly, the present material may be suitable for the adsorbent of dye pollutants.

3.2. Synthesis and Characterization of ZnONPs

Dakhlaoui et al.,^[17] prepared monodispersed ZnO nanoparticles using a modified polyol process without any requirement to use a catalyst or calcination step at high temperature. They found that the morphology and the size of the resulting ZnO particles were adjusted by using several synthesis parameters (temperature, alkaline ratio, hydrolysis ratio, etc.). Sathya and co-workers^[18] prepared Pb doped ZnO Nanoparticles by precipitation method. The optical property of Pb doped ZnO nanoparticles was found to be good. In the present study, the ZnONPs without polymer capping was successfully prepared in a sustainable and modern way to avoid toxic solvents like methanol, etc. The resultant ZnONPs was characterized by FE-SEM and EDS analysis. The Zn(OAc)₂·2H₂O was used as Zn sources and a mixture of ethanol : water (1:1) was used as solvent and KOH employed as reducing base. Fig. 1. shows the SEM images of the resultant ZnONPs. The results show that the ZnONPs are spherical in shape with an average size of 40 nm. In addition, the size of ZnONPs is found to uniform in size and shape. Fig. 2. depicts the EDAX spectrum of the resultant ZnONPs showed only Zn and O of 69.48 and 30.52 wt% respectively. The result confirms that the ZnONPs is pure without any impurity.

3.3. Preparation and Characterization of ZnONPs functionalized with PVBA (p-ZnONPs)

Indeed, the applications of ZnONPs-polymer composite have been widely demonstrated. Particularly, the ZnONPs-polymer composite are utilized for semiconductor applications, packing materials, catalysis and biomedical.^[19-23] Kumar et al.,^[24] prepared bionanocomposite films by incorporating ZnO nanoparticles into agar. The resultant ZnONPs-agar composite was efficiently used as an active packaging material for shelf life extension of green grape.

Chemical corrosion and bio-corrosion in water pipelines are the most common problem in the industry worldwide which cause damage to expensive equipment and increase the maintenance costs. Sadek et al.,^[25] prepared CuO/ZnO nanocomposite polymer by a simple green synthesis. The resultant nanocomposite at 150 ppm showed the highest anti-corrosion activity 92.3% in 1 M HCl and exhibited mix-type inhibitor (cathodic and anodic). In addition, the CuO/ZnO polymer nanocomposite can be used as anti-biofilm, bio-corrosion inhibitor and anti-corrosion material. Similarly, polyester/

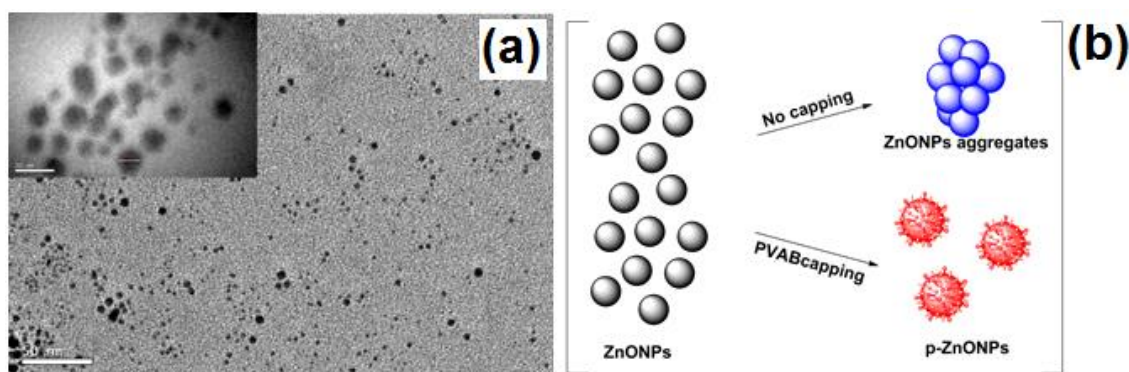


Fig. 3. (a) HRTEM image of polymer functionalised ZnONPs, p-ZnONPs, and (b) schematic illustration for ZnONPs aggregation with and without PVAB capping.

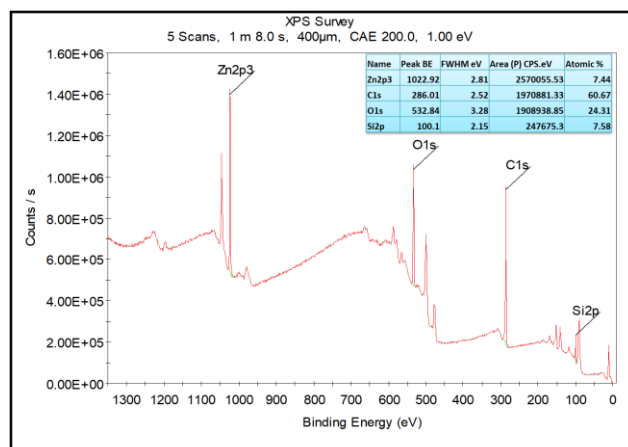


Fig. 4. XPS spectrum of polymer functionalised ZnONPs, p-ZnONPs.

kenaf composites reinforced with ZnONPs were fabricated by Mohammed and co-workers.^[26] The resultant ZnONPs-treated kenaf polymer composites showed good applicability in the weather resistance based on a solar UV radiation.

In the present work, ZnONPs is successfully functionalized with PVBA to obtain ZnONPs-PVBA composite (p-ZnONPs). Scheme 2 shows synthesis of p-ZnONPs. The mixture of ethanol:water (1:1) was used for the synthesis of p-ZnONPs and no toxic reagents are used. The prepared p-ZnONPs has been characterized by TEM, XPS and NMR analysis. The TEM images of p-ZnONPs showed that the ZnONPs are spherical in shape and uniform in size (Fig. 3a). The average size of the p-ZnONPs was calculated to be 5 nm. In comparison to uncapped ZnONPs (40 nm), the size of p-ZnONPs (5 nm) is noticed to be well controlled by the polymer capping. Fig. 3b showed the schematic illustration for ZnONPs aggregation with and without PVBA capping. We conclude that the polymer grafting is the key factor in the controlled preparation of ZnONPs. The XPS analysis is also confirm the functionalization of the polymer with ZnONPs (Fig. 4). The presence of C 1s peak showed the carbon in nanocomposites. Four dominate peaks such as Zn 2p, C 1s, O 1s, Si 2p at binding energy of about 1025, 289, 530, 92 eV respectively were noticed. In addition, the atomic percentage of Zn, C, O and Si were calculated to be 7.44, 60.67, 24.31 and 7.58 % respectively. From the ¹H NMR spectra, the resonance signals due to the aromatic protons of PVBA appearing between 7.10 and 7.14 ppm also remains same in the nanocomposites as a broad singlet. Significantly, the signal belongs to acidic proton from the acid group in the PVBA got disappeared in nanocomposites spectra, which clearly indicates the coordination between the ZnO and deprotonated acidic group (Fig. S2 and S3 in the Supporting Information). Overall, the present predation method is green and the resultant material may be used in various potential applications due to its small size and good polymer and ZnO composition.

4. Conclusions

New methodology was developed to synthesize the ZnONPs with and without capping using polyvinylbenzoic acid (PVBA). The resultant polymer grafted ZnONPs (p-ZnONPs) was characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy

energy dispersive spectroscopy (SEM-EDS), high resolution transmission electron microscopy (HRTEM), and nuclear magnetic resonance (NMR) analysis. The successful formation of polymer grafted ZnONPs (p-ZnONPs) was confirmed by NMR and XPS analysis. The TEM results confirmed the formation of uniform size of p-ZnONPs. The average particle size of p-ZnONPs was calculated to be ~5 nm. We presume that the resultant p-ZnONPs would be useful in various catalytic and energy applications.

Supporting Information

NMR data of PVBA functionalised ZnONPs are provided.

Conflicts of Interest

The authors declare no conflict of interest.

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