



# Investigating the effect of ultrasonic irradiation on preparation and properties of conductive nanocomposites

Hashem Ahmadizadegan<sup>a,\*</sup>, Sheida Esmailzadeh<sup>b</sup>

<sup>a</sup> Department of Chemistry, Darab Branch, Islamic Azad University, Darab, 7481783143-196, Islamic Republic of Iran

<sup>b</sup> Young Researchers and Elite Club, Darab Branch, Islamic Azad University, Darab, Islamic Republic of Iran



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## ABSTRACT

In the present study, the ultrasonic irradiation technique was employed as a new approach to prepare 0-3-dimensional polyaniline/ZnO shell-core composite particles. By taking advantage of the multiple effects of ultrasound, one can break down the aggregates of nanocrystalline ZnO particles. The polymerization of aniline proceeded while the nanoparticles were redispersed by ultrasound, and the synthesized polyaniline deposited on the ZnO particle, which formed polyaniline-coated nanocrystalline composite particles. The material was characterized by using transmission electron microscopy, XRD, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA). With increased ZnO content, the H-bonding interaction is strengthened and the characteristic peaks of benzoid and quinoid are shifted. X-ray photoelectron spectroscopy (XPS) shows that the ratio of the number of Zn and N atoms (Zn/N) on the surface is lower than that in the bulk. This is strong evidence for a PANI-encapsulated ZnO nanoparticles structure. The conductivity of the composites obtained through ultrasonic irradiation decreases with increasing ZnO content. Ultrasonic irradiation contributes to the increase in the conductivity compared with conventional stirring. Photocatalytic properties of PANI/ZnO nanocomposites were examined by degrading Reactive Black 5 (RB5) dye under visible light irradiation.

## 1. Introduction

In recent years, developments of inorganic–organic hybrid materials on nanometer scale have been receiving significant attention due to a wide range of potential applications and high absorption in the visible part of the spectrum and high mobility of the charge carriers [1–5]. Polyaniline is the most attractive conductive polymer because of the presence of the reactive –NH– groups in polymer chain [6–8], and used in broad applications such as batteries [9], sensors [10,11], electronic devices [12], supercapacitors [13] and corrosion protection in organic coatings [14–17] due to its physical and chemical properties, good electrical conductivity (p-type), high environmental stability, low cost [18,19], light weight, flexibility, facile fabrication and possibility of both chemical and electro-chemical syntheses [20–22]. Electrical conductivity of polyaniline is a very important parameter and it could be modified by the addition of inorganic fillers [23]. Additionally, electrical conductivity of polyaniline depends on dopant ions [24–26].

Among inorganic nanoparticles, Zinc oxide (ZnO) is a wide band gap semiconductor (3.37 eV) with a 60 meV exciton binding energy, which permits laser emission at room temperature. ZnO is a nontoxic

material, n-type semiconductor with a good photocatalytic activity [27]. The structure and morphology of ZnO have an important effect on its properties and applications; thus, several parameters such as reaction time, rate of evaporation and precursor concentration are found to determine the growth of ZnO nanostructures like nanoparticles, nanorods and nanospheres. The one dimensional nanostructure such as nanorod, nanowire and nanotube has obtained more attention in various applications due to its potential as a building block for other structures especially in paints and coatings. Further-more, its electrical and optical properties are better due to the reduced carrier scattering in one dimensional structure [28–31].

This one dimensional nanostructure has gained enormous attention due to its extraordinary characteristics in photonics, optics and electronics, and therefore has been used in various industries such as rubber, medical and dental, pigments and coatings, catalysts, ceramic, concrete and in chemical synthesis [32–34].

Azo dyes are manmade chemical with a double bond between two nitrogen atoms (–N=N–), and it is still being widely used in textile, printing, and food industry 1-2 for example, Reactive Black 5 (RB5). Dye with N-substituted aromatic biotransformation products is toxic,

\* Corresponding author.

E-mail addresses: [h.ahmadizadegan.2005@gmail.com](mailto:h.ahmadizadegan.2005@gmail.com), [h.ahmadizadegan@ch.iut.ac.ir](mailto:h.ahmadizadegan@ch.iut.ac.ir) (H. Ahmadizadegan).

mutagenic and carcinogenic, therefore, the dyes are considered as important environmental pollutants. There is a need to develop the strategies to degrade toxic organic compound to less toxic material. Photocatalytic degradation is an efficient and economical method that attracted increasing attention [35]. This is because it is particularly useful for cleaning biologically toxic or nondegradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in waste water. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization [36].

Ultrasonic irradiation, as a new technology, has been widely used in chemical synthesis. When an ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow, and collapse in a very short time of about a few microseconds, an effect that is called ultrasonic cavitation. Sonochemical theory calculations and the corresponding experiments suggested that ultrasonic cavitation can generate local temperatures as high as 5000 K and local pressures as high as 500 atm, with heating and cooling rates greater than  $10^9$  K/s, a very rigorous environment [37–39]. Therefore, ultrasound has been extensively applied in dispersion, emulsifying, crushing, and activation of particles [40–42].

In this paper ultrasonic irradiation, was used to prepare polyaniline/nanocrystalline ZnO composite particles. Polymerization of aniline proceeded under ultrasonic irradiation in the presence of ZnO. The aggregation of nano ZnO can be reduced under ultrasonic irradiation, and the nanoparticles can be redispersed in the aqueous solution. The polyaniline deposits on the surface of the nanoparticle, which leads to a core-shell structure. The resulting polyaniline/ZnO nanocomposite particles are spherical, and the sizes vary with the content of ZnO. The polyaniline/nano ZnO composite particles prepared by the conventional stirring method have a “raspberry” aggregate structure, which is different from that obtained through ultrasonic irradiation. The presence of nanocrystalline ZnO strengthens the UV absorption of polyaniline and leads to a blue shift of the  $\pi$ -polaron absorption of polyaniline. Ultrasound can enhance the doping level. When polyaniline deposits on the surface of nano ZnO, the crystalline behavior of polyaniline is hampered and the degree of crystallinity decreases. With increased ZnO content, the H-bonding interaction is strengthened and the characteristic peaks of benzoid and quinoid are shifted. X-ray photoelectron spectroscopy (XPS) shows that the ratio of the number of Zn and N atoms (Zn/N) on the surface is lower than that in the bulk. This is strong evidence for a polyaniline-encapsulated ZnO structure. The conductivity of the composites obtained through ultrasonic irradiation decreases with increasing ZnO content. Ultrasonic irradiation contributes to the increase in the conductivity compared with conventional stirring. When the content of polyaniline decreases to  $\sim 10\%$ , the conductivity of composite still remains at  $10^{-1} \text{ S cm}^{-1}$ .

## 2. Experimental

### 2.1. Materials

Aniline (ANI) (AR, Beijing Chemical Reagent Co., China) was distilled twice under reduced pressure and stored below  $4^\circ\text{C}$  under nitrogen atmosphere. Nano-sized ZnO powder was purchased from Neutrino (Tehran, Iran) with an average particle size of 25–30 nm, sodium lauryl sulfate (SLS) (CP, Shanghai Xiangde Chemical Factory, China), sodium dodecyl benzene-sulfonate (SDBS) (CP, Shanghai Xiangde Chemical Factory, China), cetyl trimethylammonium bromide (CTAB) (AR, Beijing Chemical Reagent Co., China), sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) (Acros Organics, New Jersey), poly(ethylene glycol) mono-4-octylphenyl ether (OP-10) (CP, Beijing Chemical Reagent Co., China), 38% hydrochloric acid, and ammonium peroxydisulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (APS) were used as received.

### 2.2. Characterization

X-ray diffraction (XRD) analysis was carried out by Shimadzu XRD-6000 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) the operating conditions were 40 kV and 30 mA in the scanning range from  $10^\circ$  to  $70^\circ$  at rate of  $2^\circ/\text{min}$ . The morphology of the synthesized products was carried out using a JEOL/JSM-6335F-EDS SEM. The TEM images of the ZnO nanoparticles were performed using JEOL 2100 HRTEM at 300 kV. The optical absorption spectra of all the samples were obtained using an Ocean Optics HR4000 UV–visible spectrophotometer and the FTIR spectra of all materials were recorded by a Perkin Elmer 1725 spectrophotometer. The equipment employed in this research was 20 kHz ultrasonic generator, Fisher Sonic Dismemberator Model 550 (Fisher Scientific Co.) or VC-1500 (Sonic & Materials). Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture emulsion system. During the polymerization thermostated water was circulated to maintain the temperature constant, and  $\text{N}_2$  purging rate keeps constant.

X-ray photoelectron spectroscopy (XPS) was performed on a XSAM 800 X-photoelectron spectrometer with a  $\text{Mg K}\alpha$  X-ray source. In the data analysis, the binding energy (BE) of the core level C1s was set at 284.8 to compensate for surface-charging effects. The surface elemental stoichiometries were determined from the ratios of peak areas corrected with the empirical sensitivity factors. The electrical conductivity measurements were made by the conventional four-point method on pressed pellets of composite particles prepared at ambient temperature ( $15^\circ\text{C}$ ).

Misonix Inc S-3000 Misonix Sonicator 3000 Ultrasonic Cell Disruptor with Temperature Control 04711–81. Watts 600Max, Sample Size (mL) 40000, Power (VAC) 100, Power (Hz) 50/60, Height (in) 10.5, Width (in) 8.5, Depth (in) 19, Height (cm) 26.67, Width (cm) 21.59, Depth (cm) 48.26 and Description Misonix Sonicator 3000 Ultrasonic Cell Disruptor with Temperature Control 04711–81.

### 2.3. Measurement of photocatalytic activities

The photocatalytic activities of polyaniline/ZnO nanocomposites were evaluated in the degradation of model compound RB5. A 150W Xe lamp was used as a light source with UV filter. The photocatalytic degradation of RB5 was measured at ambient pressure and room temperature in a photoreactor set up. RB5 aqueous solution with an initial concentration  $10 \text{ mg L}^{-1}$  was mixed with 15 mg of prepared nanocomposite powder. Before irradiation, suspension was left in dark condition for 3 h to achieve adsorption-desorption equilibrium between photocatalyst and RB5. The photocatalytic reaction was then started by irradiating the suspension with 150W Xe lamp. Air was supplied to the suspension during adsorption desorption and irradiation of light. Then, 5 mL of the dye suspension was withdrawn at regular time interval and filtered using microfiltration membrane unit, utilizing a  $0.22 \mu\text{m}$  from Millipore Millex-GP. The concentration of remaining RB5 were analysed using a UV–visible spectrometer and the percentage of degradation was calculated.

### 2.4. Preparation of polyaniline/ZnO nanocomposites through ultrasonic irradiation

The polyaniline/ZnO nanocomposites were prepared as follows. Typically, 2 g of ZnO particles, 1 mL of aniline, 2.5 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , 100 mL of 2.4 M concentrated HCl aqueous solution, 4 g of SLS, and 90 mL of deionized, distilled water were introduced into the reaction vessel. Deoxygenation was done by bubbling with oxygen-free nitrogen for 2 min in the reaction vessel, and then cooling water was circulated. The APS:ANI molar ratio was 1:1 in all experiments in this study. Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture emulsion system [37]. A thermometer probe was immersed in the solution to measure the temperature

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