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Physicochemical and photocatalytic studies of Ln^{3+}- ZnO for water disinfection and wastewater treatment applications

Marwa M. Ibrahim*, Saad Asal

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, 11711, Cairo, Egypt

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In the present work, x mol Ln^{3+} modified ZnO Nano-particles (Ln = Sm^{3+}, Eu^{3+} and Gd^{3+} ions; x = 0.008, 0.015, 0.025, 0.03 and 0.05) were synthesized by precipitation method. These Nano-particles are characterized by different advanced techniques; such as X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive spectroscopic (EDX), UV–Visible diffuse reflectance, and fluorescence (FL) spectroscopy. Doping by lanthanides improves the crystal, surface area, porosity, morphology, as well as the optical adsorption and emission of UV light properties of the prepared photo-catalysts. Photocatalytic activity for the prepared Nano-materials was determined using both, fluorescent probe and dye methods. Results showed that the highly active Nano-particle is 0.025 Gd^{3+}-ZnO. The highly active sample (0.025 mol Gd^{3+}- ZnO) successfully mineralized textile dye and real refractory wastewater samples under sunlight illumination using CPC photo-reactor. Prepared photo-catalysts were also applied for water disinfection.

1. Introduction

Wastewater, nowadays, is a major problem which faces humankind due to population growth and technology development. Discharge of different wastes into the environment such as synthetic dyes, detergents, and herbicides has a massive effect on the environment, and, consequently, on human life [1]. The removal of wastewater and reusing it, hence, became main targets to protect the environment over the word.

Heterogeneous photo-catalysis is regarded as the promising effective method used to overcome the environmental pollution. This is due to its low energy, environment-friendly nature, as well as being unselective in degradation of various pollutants [1–3]. Metal oxide Nano-semiconductor with wide-band gap is the basic material in heterogeneous photo-catalysis method. It can accelerate the degradation of any pollutant under solar illumination [4–6]. Among these semiconductors, zinc oxide (ZnO) is considered one of the most powerful photo-catalysts. ZnO has several advantages; low cost, biocompatibility, and it enjoys an excellent physical, chemical, mechanical, and thermal stability. Despite the advantages of ZnO, it was merely used in limited applications. This is due to the high recombination rate between photo-generated electron hole and poor exploitation of solar energy [1,7–12].

Doping of ZnO with various metal ions is applied to overcome the above limitations [13–17]. Lanthanide metal ions are promising dopant cations for any semiconductors. Lanthanide doped Nano-particles have low toxicity, high resistance to photobleaching, sharp emissions, long fluorescence lifetimes, and superior physicochemical properties (magnetic, chemical, and optical) as well as stable intra-4f shell transitions in their ions. Red shift takes place in the band gap absorption, due to the introduction of localized electronic energy levels by lanthanide dopants within the band gap states of semiconductor Nano-particles like ZnO [18–20]. In addition, lanthanides doped Nano-particles enhance the absorption capacity due to lanthanide ions having a strong ability to form complexes with various Lewis bases, like alcohols, acids and, aldehydes [5,6,21]. Doping of ZnO with low percentage of lanthanide elements, moreover, forms biocompatible Nano-materials with highly efficient impact in different things. This includes dye-sensitized solar cells, catalysis, devices, solid-state laser, optical tele-communication, fingerprint detection, and non-destructive materials in diagnosis of various diseases; as atherosclerotic plaques, which can lead to strokes and heart diseases [18–21].

Several methods were applied for the determination of photocatalytic activity of semiconductors including stearic acid method,

* Corresponding author.
E-mail addresses: marwamohamed@edu.asu.edu.eg, marwa_chem_83@yahoo.com (M.M. Ibrahim).

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dye method, contact angle method, and fluorescent probe method [4–6,22].

Though a wide range of lanthanide doped ZnO compounds have been synthesized and studied from a structural and luminescence point of view from Refs. [18,23–25], the photocatalytic studies for Ln^{3+} doped ZnO are still limited [26–29]. Yet, the use of lanthanide doped ZnO for water densification and real water treatment under solar illumination is notably unexplored.

Taking the previously mentioned into consideration, the preparation of high quality RE Nano-particles doped ZnO with different sizes and shapes appears to be important for modern research and application fields. In this work, we focused on applying different prepared lanthanides (Ln = Sm^{3+}, Eu^{3+} and Gd^{3+}) doped ZnO with various sizes and morphology in photo water disinfection and wastewater treatment using sunlight.

2. Experimental

2.1. Preparation of Ln^{3+}-ZnO nano-particles (Ln = Sm^{3+}, Eu^{3+} and Gd^{3+})

For typical synthesis of lanthanide ions doped ZnO Nano-particles using precipitation method, 2 gm of Zn $(acetate)_2$ obtained from loba Chemie 99.5%pure grade were added to 100 ml of distilled water and stirred for 30 min. Then 0.008, 0.015, 0.025, 0.03, and 0.05 mol of each lanthanide nitrate dopant [Aldrich (99.9% pure grade] were added with further stirring for 10 min. In the prepared solution, 15 ml of 4 M NaOH solution were introduced to adjust pH range (pH10-11) as a white precipitate was produced and stirred for 1 h at room temperature. The resulting products were taken out and removed along with some existing impurities and ions by washing with deionized water till being neutral. The final products were dried at 80 °C and calcined at 450 °C for 30 min. Pure ZnO was also prepared in the same way without doping for comparison. All chemicals employed were of analytical grade and were used as received.

2.2. Characterization

XRD measurements (X-ray diffraction) were conducted using a "Philips" diffractometer equipped with a CuKα1 radiation (k = 1.54056 Å) as X-ray source. The data collection was conducted in air, at room temperature. Transmission electron microscope (TEM) microanalysis system, equipped with energy dispersive spectroscopic (EDS) microanalysis system, (JEM- 2100CX (JEOL)) was used. The surface analysis of Nano-particles prepared by precipitation method was measured by a "Quantachrome NOVA 3200" automated gas-sorption apparatus model 10 (USA). UV–Vis absorbance and diffuse reflectance spectroscopy (UV–Vis/DR) was measured on "JASCO V-550" spectrometer (Japan). This spectrometer has an integrating sphere accessory for diffuse reflectance spectra using barium sulfate as a reference. Photoluminescence spectra were measured using "LS55" spectrofluorometer (Perkin Elemr, USA). UV photoreactor (Photon Co., Egypt), air cooled, was used to illuminate the prepared Nano-particles. UV photoreactor lamps emitted photons in the range from 320 to 410 nm and the intensity was found to be 0.9 mW/cm^2. Mineralization of commercial textile dye (Remazol Red RB-133, RR) and real wastewater from highly active doped ZnO was followed by measuring multi-parameter bench photometer with COD, accompanied with COD test tube bench heater model "C-99" from "HANNA" Company.

2.3. Photocatalytic activity

Photo-catalytic activity of all Nano-particles was evaluated by two different methods; fluorescent probe and dye methods.

2.3.1. Determination of •OH radicals using fluorescent probe method

Evaluation of the photo-catalytic activity of prepared photo-catalysts using fluorescent probe method was carried out as follows: 1 g/L from different prepared photo-catalysts was immersed in coumarin solution (1.0×10^{-3} M) and illuminated with UV light under vigorous magnetic stirring. The fluorescence spectra (λ_{ex} = 332 nm) of the solution were measured every 5 min after illumination. The blank experiments without ZnO were conducted and showed that the coumarin without ZnO was totally inactive under UV illumination.

2.3.2. Dye method

The photo-catalytic activity of all Nano-particles was evaluated by degradation of organic dye Remazol Red RB-133 (RR) using dye method. This method was executed as follows: 0.1 g of photo-catalyst into 100 ml dye solution (5×10^{-5} M, pH = 6.5–7). The dye solution is stirred in the dark for 15 min after the addition of catalyst to establish an adsorption/desorption equilibrium. Samples of suspension are withdrawn every 10 min from illumination and are immediately centrifuged at 4500 rpm for 15 min to complete the elimination of catalyst particle.

2.4. Applications

2.4.1. Solar energy for textile dye and real wastewater treatment application using compound parabolic collector (CBC) photoreactor

Highly active Ln^{3+}-doped ZnO (0.025 mol Gd^{3+}- ZnO) Nano-particle was applied for degradation of textile dye (Remazol Red RB132) and real factory wastewater at pH = 6–7 in sun light as a light source using "CPC" photoreactor.

CPC photoreactor (supplement 1) is composed of four borosilicate tubes (90 cm in length and 50 mm inner diameter) mounted on the focal axis of four parabolic trough collectors, made from high quality stainless steel. The four glass tubes are connected in series through high density polyethylene connectors. A centrifugal pump is used to circulate the water though the tubes from bottom to top, leading finally to a re-circulating tank of 40 L capacity. Water flows ($3.7\ m^3\ h^{-1}$) directly from one module to the other, and finally to the reservoir tank. The solar ultraviolet radiation was determined during the field experiments by means of an UV radiometer (YK-35 UV power-meter), mounted on a 37° (the same angle as the CPC's). It provides data in terms of global UV-solar energy power incident per unit area ($mW_{UV}\ cm^{-2}$). The overall surface collector area is about 0.6 m^2.

Intensity of UV radiation was found to be 2.5 mW/cm^2 visible light 1043 mW/cm^2. The mineralization efficiencies of samples using highly active sample at time t, can be expressed as [6]:

$$\text{Mineralization efficiency} = 100 \times COD_0 - COD_t / COD_0$$

where COD_0 and COD_t are the initial and at time t COD values of the samples solutions.

2.4.2. Photo water disinfection application

Gram positive bacteria cell (*E. coli*) (ATCC 7701 strain) were grown aerobically in 2.5 mL of nutrient broth (NB, Nissui Seiyaku) at 30 °C for 16–18 h. Cells were centrifuged at 3000 rpm for 10 min and suspended in sterilized water. 100-ml aliquot of *E. coli* cell suspension (23105 cells mL21) were pipetted into different photo-catalysts and then illuminated with UV light. The cell suspension was collected in 0.15 M aqueous sodium chloride solution after illumination. To determine the number of viable cells in terms of colony-forming units, the solution was spread onto a nutrient agar