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The green synthesis of Ag/ZnO in montmorillonite with enhanced photocatalytic activity

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ABSTRACT

The Ag/ZnO-MMT nanocomposite was prepared using *urtica* dioica leaf extract. To improve the photocatalytic properties of ZnO-MMT nanocomposite, silver metal nanoparticles was deposited over nanocomposite. $Zn(CH_3COO)_2$, $AgNO_3$ and *Urtica dioica* leaf extract were used as a zinc, silver precursor and reducing agent, respectively. The nanocomposite was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and ultraviolet-visible diffuse reflectance spectroscopy (DRS). The powder X-ray diffraction showed that Ag/ZnO nanoparticles located on the surface MMT layers. The diffuse reflectance spectra of nanocomposite indicated a strong surface plasmon resonance (SPR) absorption band in the visible region, resulting from metallic Ag nanoparticles. TEM image demonstrated the presence of silver nanoparticles with an average size of 2–4 nm over both MMT and flower-shape ZnO. The photocatalytic activity of nanocomposite was studied for destructive reaction methylene blue dye under visible light. In addition, the effects of different parameters such as amount of nanocomposite, concentration of the dye and pH of the solution were studied. The results showed that modiffication of ZnO-MMT nanocomposite with silver nanoparticles increased the percentage of discoloration methylene blue (MB) from 38.95 to 91.95. MMT matrix showed an important role in the reduction of recombination of electron-hole in nanocomposite.

1. Introduction

Semiconductor photocatalysis has been widely accepted since 1972 as the most promising method for addressing environmental pollution and energy shortage. Great efforts have been devoted to develop efficient photocatalysts [1]. There are two kinds of semiconductors: (i) UV-light driven semiconductors (UVLD), such as TiO_2 and ZnO. They usually exhibit high photocatalytic activities under UV light, but their application is greatly limited because UV light only accounts 3%–5% of the solar light spectrum [2]. (ii) Visible-light-driven (VLD) semiconductors like the most metal sulfate compounds [3]. Therefore, extending optical absorption of UVLD photocatalysts from the UV region to visible-light region and delaying the recombination of the photoexcited electron-hole pairs are the two main challenges for improving the photocatalytic efficiency of UVLD photocatalysts with different morphologies and sizes.

Zinc oxide is a well known n-type semiconductor with the band gap energy of ~3.37 eV. ZnO is employed for a variety of important potential applications, including sensors, memory devices, UV-light emitting diodes, solar cells, piezo- electric transducers, photodiodes, photodetectors and photocatalysts [4,5]. However, pure ZnO phase exhibits relatively low photocatalytic activity owing to its low utilization of visible light and the rapid recombination of photogenerated electron-hole pairs, which largely limited its practical applications in normal light condition.

Plasmonic photocatalysis has recently emerged as a promising technology for developing high performance VLD photocatalysts. The term "plasmonic photocatalysis" was first created by Awazu et al. in 2008 [6]. The noble metal nanoparticles (NPs) have attracted considerable interest due to their surface plasmon resonance (SPR), which accelerates the separation process of the photo-generated electrons and holes in the semiconductor catalyst under visible light [7]. Many researchers have demonstrated that the Ag NPs deposited on semiconductor show efficient plasmon resonance in the visible region [8,9]. The coupling of ZnO nanostructures with various metallic nanocrystals, including Au [10], Pt [11], and Ag [12], was found to possess improved UV and visible-light photocatalytic activity. It is known the decreasing of particle size is one effective way to increase the surface area of

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photocatalyst, but the agglomeration of nano-sized particles and difficulty of their recovery from the reaction system after photocatalysis reduces their application in this field. For overcoming these problems, semiconductor NPs can be assembled into micro-size materials or different matrices [13,14]. Smectite clays have excellent swelling and adsorption ability, which is especially interesting for the impregnation of nano-size metals and compounds in the interlamellar space of clay [15,16]. Montmorillonite (MMT) as lamellar clay has intercalation, swelling, and ion exchange properties. Its interlayer space has been used for the synthesis of material and biomaterial nanoparticles [17]. ZnO nanoparticles (ZnO NPs) are commonly synthesized by wet chemical route [18], vapour phase process [19], hydrothermal method [20], precipitation, ultrasonic spray pyrolysis [21] and sonochemical method [22]. However, these methods always involve utilization of toxic reagents and expensive instruments along with the tedious process control. Thus, to develop a simple and green approach to synthesize ZnO NPs is of considerable necessary. Using plants for nanoparticle synthesis can be advantageous over other biological processes such as microbial route, because it eliminates the elaborate process of maintaining cell cultures.

In our previous work, the Ag/AgCl nanoparticles in the interlayer space of MMT were synthesized according to the physical reduction technique, UV irradiation method as the reducing agent [23]. The nanocomposite indicated high photoactivity for the degradation of methylene blue. There are low data about biosynthesis of metal and metal oxide NPs in supports by utilizing the aqueous leaf extract of plants. In this study *Urtica dioica* leaf extract was chosen as a reducing agent for the synthesis of Ag nanoparticles and flower-shaped ZnO from $AgNO_3$ and $Zn(CH_3COO)_2$ solutions, respectively. *Urtica dioica*, often called common nettle or stinging nettle, is a herbaceous perennial flowering plant, native to Europe, Asia, northern Africa, and North America, and is the best-known member of the nettle genus Urtica. The leaves contain triterpenoids, alkaloids, polyphenols and tannins [24], hence this plant is chosen as reducing agent for the green synthesis. Therefore, a simple and effective strategy were developed to synthesis Ag NPs doped flower-shaped ZnO nanoparticles over MMT support using green synthesis process. Therefore, deposition of Ag doped ZnO flowers in MMT clay is an efficient way to construct a composite photocatalyst to improve the properties of ZnO by utilizing the unique properties of MMT and silver. The fix attachment of NPs on the surface of MMT clay and the presence of aluminium atoms in MMT structure not only prevents from the loss of photocatalyst during recovery but also assists electron–hole separation during the photocatalytic process.

2. Experimental

2.1. Materials

The commercial sodium montmorillonite clay (NaMMT), <25 μm montmorillonite, cation exchange capacity ((CEC) = 92.6 meq/100 g) was purchased from Southern Clay Products (Gonzales, TX). Zinc acetate dehydrated ($Zn\,(CH_3COO)_2{\cdot}2H_2O$) and $AgNO_3$ were purchased from Merck, Germany. *Urtica dioica* leaves were collected from one of the cities around Tehran, Iran, and were cleaned with double distilled water and shade-dried for a week at room temperature away from sunlight and further *Urtica dioica* leaves were ground to powder and stored for further study.

2.2. Preparation of leaf extract

A 10 g of this plant leaf was stirred with 100 mL de-ionized water at 60 °C for 24 h, and filtered to get the extract. The filtrate is used as reducing agent and stabilizer.

2.3. Synthesis of ZnO and Ag nanoparticles

An aqueous 0.1 M zinc acetate dehydrate solution was prepared with 60 mL water. Then 20 mL *Urtica dioica* leaf extract was added to above solution and kept under continuous stirring at 80 °C for 4 h. The pale white precipitate was obtained through centrifugation and washed with ethanol and water. The ZnO NPs were then collected with annealing the sample in a furnace at 200 °C for1 h. The color of ZnO NPs was yellow.

For synthesis of Ag NPs, 1.0 mL of leaf extract was added to 2.0 mL of 1.0×10^{-2} M $AgNO_3$ and the volume was adjusted to 10 mL with double distilled water for the green reduction process.

2.4. Synthesis of ZnO-MMT nanocomposite

20 mL of leaf extract was added to 60 mL of 0.1 M $Zn(CH_3COO)_2{\cdot}2H_2O$. In order to establish the role of MMT in the green biosynthesis of ZnO nanoparticles, synthesis of ZnO NPs was done the presence of 1.0 g MMT. Then the suspension was kept under continuous stirring at 80 °C for 4 h. The buff precipitate was obtained through centrifugation and washed with ethanol and water and dried at room temperature. The buff precipitate was located in a furnace at 200 °C for 1 h until obtained of ZnO-MMT nanocomposite.

2.5. Synthesis of Ag nanopaerticles in ZnO-MMT nanocomposite

10 mL of leaf extract was added to 20 mL suspension of 1.0×10^{-2} M $AgNO_3$ and 0.5 g ZnO-MMT nanocomposite. Then volume was adjusted to 100 mL with double distilled water for the green reduction process. The brown precipitate was obtained through centrifugation and washed with ethanol and water. The Ag/ZnO-MMT nanocomposite was then collected and dried at room temperature.

2.6. Characterization

Powder X-ray diffraction patterns of the samples were recorded using an X-ray diffractometer (Bruker D8 Advance) with Co Kα radiation ($\lambda = 1.789$ A°) under the conditions of 40 KV and 30 mA, at a step size of $2\theta = 0.02°$. X-ray diffraction (XRD) patterns were recorded between 2° and 70° 2θ at a scanning speed of 2° min^{-1}. All samples were analyzed in random orientation. The UV–vis diffused reflectance spectra (UV–vis DRS) were obtained with a UV–vis Scinco 4100 spectrometer with an integrating sphere reflectance accessory. $BaSO_4$ was used as reference material. UV–vis absorption spectra were recorded using a Shimadzu 1600 PC in the spectral range of 190–900 nm. The infrared spectra were measured on a Bruek spectrophotometer using KBr pellets. For each sample, 128 scans in the 4000–400 cm^{-1} spectral range were recorded with a resolution of 2 cm^{-1}. Samples of 0.5 mg were dispersed in 200 mg of KBr. The transmission electron micrographs (TEM) were recorded with a Philips CM10 microscope, working at a 100 kV accelerating voltage. Samples for TEM were prepared by dispersing the powdered sample in acetone by sonication and then drip drying on a copper grid coated with carbon film. Samples were sonicated for 15 min.

2.7. Photocatalytic activity

Photodegradation experiments were performed with a photocatalytic reactor system. This bench—scale system consisted of cylindrical Pyrex–glass cell with 250 mL capacity, 10 cm inside diameter and 15 cm height. A 100 w tungsten filament Philips lamp ($\lambda > 400$ nm) was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stop the lamp and the tube were then