



Synthesis of Ni nanoparticles decorated SiO₂/TiO₂ magnetic spheres for enhanced photocatalytic activity towards the degradation of azo dye



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ABSTRACT

Highly photocatalytic active Ni magnetic nanoparticles-decorated SiO₂ core/TiO₂ shell (Ni-SiO₂/TiO₂) particles have been prepared by the simultaneous hydrolysis and condensation of titanium tetraisopropoxide on SiO₂ sphere of ~300 nm in size followed by the reduction of nickel chloride using hydrazine hydrate as a reducing agent. The crystalline nature, surface morphology, electrochemical impedance spectra and UV–vis diffuse reflectance spectra of the Ni-SiO₂/TiO₂ magnetic spheres were characterized by PXRD, FE-SEM, TEM, EIS and UV–vis DRS. The Ni-SiO₂/TiO₂ magnetic photocatalyst was used for the degradation of Acid Black 1 (AB 1) dye under UV irradiation. The effects of different concentrations of the Ni nanoparticles deposited on the SiO₂/TiO₂ composite spheres for the photo-mineralization of AB 1 dye were analyzed. The results showed the Ni-SiO₂/TiO₂ magnetic photocatalyst to be efficient and reusable.

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1. Introduction

The environment is contaminated by various organic compounds that are commonly used in industrial, agricultural and domestic applications. Among these most of the organic compounds are non-biodegradable and some of them are biodegradable at low concentration and they produce non-biodegradable intermediates. The conventional treatment methods could not mineralize the pollutants to harmless products by flocculation, adsorption and membrane separation. The heterogeneous semiconductor photocatalysts are capable of mineralizing organic pollutants into harmless products like CO₂, H₂O and mineral acids [1–5].

Semiconductor photocatalysis is a topic of current interest mainly in view of its potential application in wastewater purification [6–9]. In our previous work, we have used Ag-SiO₂/TiO₂ spheres for the photodegradation of AB 1 dye [10–12]. In this study, the sub-micrometer-sized SiO₂ is used as a substrate and TiO₂ nanoparticles were coated on it to increase the active surface area. The Ag nanoparticles helped to suppress the recombination of electron–hole pairs. After photodegradation experiment, it is

very difficult to remove the photocatalyst because those are in the nanopowder form. Separation and purification of catalyst consumes money and time. The catalyst needs long time to settle or needs centrifugation to be removed from the solution. In order to overcome the above-mentioned difficulties, the magnetism is introduced into the SiO₂/TiO₂ composite spheres with the help of magnetic nanoparticles. Once the catalyst gets magnetic behavior, it could be easily separated by magnet or the magnetic particles join together and settle at the bottom without using separation technique.

The metal oxide catalysts are modified with the transition-metal nanoparticle that increases their catalytic efficiency and reduces the recombination of electron–hole pair as well as easy separation of catalyst after photocatalytic experiment [13–15]. Recently, the magnetic nanoparticles have attracted great attention for easy separation of catalysts. TiO₂-Ni magnetic nanoparticles for several applications have been investigated. For example, Guo et al. introduced the magnetic nickel particles to the porous silica core by using electroless plating followed by coating of titania on the outer layer and the multilayer-coated spheres were investigated under external electric and magnetic fields [16]. Zhang et al. prepared the Ni/TiO₂-SiO₂ catalyst by simultaneous mixing of nickel, titania and silica precursors followed by calcination at different temperatures and then tested the catalyst for the reaction of CO₂ reforming of methane to synthesis gas [17]. Stefanov et al. modified the titanium dioxide (Degussa P25) with Ni nanoparticles which

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were dip coated on microscope slides for the degradation of methylene [18]. Zhu et al. synthesized the Ni/TiO₂ core/shell nanorod arrays by one-step electrodeposition technique [19]. Pang et al. synthesized TiO₂ film-coated one-dimensional Ni nanostructures by hydrothermal method and their photocatalytic and biocompatibility results showed the outstanding photocatalytic activities for the decomposition of organic pollutants and great biocompatibility [20]. Mohamed and Aazam reported the nano-sized Ni particles deposited on TiO₂-SiO₂ by two methods of photo-assisted deposition and impregnation for enhanced H₂ production [21]. Rodriguez et al. synthesized the Ni/TiO₂ catalysts that were used for the degradation of the herbicide 2,4-dichlorophenoxy acetic acid in aqueous solution in the presence of ozone and the initial activity of Ni/TiO₂ catalysts was 26% higher when comparing the conventional ozonation [22]. Olya et al. reported the mixing of TiO₂ sol with nickel sol to get the Ni/TiO₂ nanocomposite photocatalyst for the degradation of Acid Red 88 in aqueous solution [23]. Casados et al. reported the different concentrations of Ni nanoparticles incorporated into the TiO₂ then coated on the glass substrate to form catalytic thin films for the degradation of Malachite Green solutions [24]. Cui and Lu investigated the surface electron transfer and the enhancement on hydrogen evolution under visible light irradiation using Ni@NiO core/shell cluster on TiO₂ surface (Ni@NiO/TiO₂) [25]. The reported Ni nanoparticles were only deposited on the agglomerated SiO₂/TiO₂ nanocomposite or Ni-SiO₂/TiO₂ thin films. None of the above studies had synthesized the core-shell structure of Ni-SiO₂/TiO₂ composite spheres with uniformity in shape and size.

To the best of our knowledge, we report for the first time the synthesis of Ni magnetic nanoparticle-deposited SiO₂/TiO₂ (core-shell) composite spheres with uniform in size and shape. This was done without the assistance of template and surfactant. Transmission electron microscopy (TEM) and field-emission scanning microscopy (FE-SEM) were used to study the surface morphologies of the Ni-SiO₂/TiO₂. Its ability in the degradation of AB 1 dye under UV light illumination was also demonstrated.

2. Materials and methods

2.1. Materials

For this study, analytical grade chemicals were used as received without further purification.

2.2. Synthesis of SiO₂ spheres and SiO₂/TiO₂ composite spheres

The synthesis procedures for the SiO₂ spheres and SiO₂/TiO₂ composite spheres have been described in our previous study [26]. The SiO₂ spheres were prepared by mixing 2 mL TEOS, 0.6 mL dodecane, 10 mL anhydrous ethanol, 2 mL water, 0.4 mL ammonia solution, and 6 mL anhydrous ethanol in sequence and the mixture was allowed to stir at room temperature for 2 h. The SiO₂ spheres were separated by centrifugation and washed three times with ethanol. The SiO₂ spheres in ethanol were rotovaped to remove ethanol and dried in a vacuum oven at 60 °C for 6 h. The SiO₂ spheres (1 g) were uniformly dispersed in anhydrous 2-propanol (50 mL) by ultrasonication for 30 min, followed by the addition of 1 mL titanium tetra-isobutoxide (Ti(iOBu)₄), 0.2 mL dodecane, and 0.1 mL water. The mixture was allowed to stir at room temperature for 4 h. The TiO₂-coated SiO₂ spheres were separated by centrifugation and washed three times with ethanol and dried in a vacuum oven at 60 °C for 6 h. To obtain the anatase TiO₂, the prepared SiO₂/TiO₂ composite spheres were calcined at 450 °C for 4 h. The total amount of TiO₂ nanoparticles coated on the SiO₂ spheres, analyzed by energy dispersion spectrometer (EDS) under a FE-SEM microscope, was 4 at%.

2.3. Deposition of magnetic Ni nanoparticles on SiO₂/TiO₂ composite spheres

The Ni nanoparticles deposited on SiO₂/TiO₂ composite spheres with magnetic behavior were obtained by the reduction of nickel chloride using hydrazine hydrate as a reducing agent [27]. The synthesis process of Ni-deposited SiO₂/TiO₂ magnetic spheres is as follows: 0.1 g nickel chloride was dissolved in a mixture of 60 mL ethylene glycol and 0.1 mL hydrazine hydrate. The SiO₂/TiO₂ composite spheres (0.5 g) were ultrasonically dispersed in the above mixture for 30 min followed by the addition of 0.4 mL of 1 M sodium hydroxide solution and stirred at 60 °C for 1 h. Ni-coated SiO₂/TiO₂ magnetic spheres were separated using magnet and washed three times by ethanol and dried in a vacuum oven at 60 °C for 6 h.

2.4. Measurements

Powder X-ray diffraction (PXRD) data was obtained on a Bruker D2-phasex diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the magnetic Ni-SiO₂/TiO₂ spheres was observed by FE-SEM (JSM 6500F, JEOL, Tokyo, Japan) and TEM (H-7000, equipped with a CCD camera, Hitachi, Tokyo, Japan). The UV-vis diffuse reflectance spectra (DRS) were evaluated by a Jasco V-670 UV spectrophotometer. Electrochemical impedance spectroscopy (EIS) was carried out using an IM6ex Zahner (Kroanach, Germany). A glassy carbon electrode (GCE) was used as a working electrode and an Ag/AgCl electrode (Sat. KCl) and platinum wire were used as reference and counter electrodes, respectively.

2.5. Photodegradation experiments

A specially designed apparatus was used for the photocatalytic reaction under identical conditions. A 550 W Hg-Xe lamp with a cut-off filter used for blocking light (infrared and visible) with the wavelength above 420 nm. The distance between the top of the sample bottle and light source was kept at 1 m. In each experiment, 10 mg of prepared SiO₂/TiO₂ and Ni-SiO₂/TiO₂ photocatalysts were charged into 50 mL of 5 ppm AB 1 dye aqueous solution. To ensure the adsorption and desorption equilibrium between the photocatalyst and AB 1 dye, the reaction solutions were kept in the dark and stirred for 30 min. Then the reaction solution was kept under UV illumination for complete degradation of dye. At certain intervals of time, 5 mL aliquots were sampled out and the photocatalyst was separated from the aqueous solution by centrifugation. Further, the concentration of AB 1 was monitored by UV absorbance intensity at 615 nm that corresponds to the maximum absorption wavelength of AB 1 dye.

3. Results and discussion

Powder X-ray diffraction patterns of the prepared SiO₂ sphere, TiO₂ nanoparticle, SiO₂/TiO₂ composite spheres, and Ni-SiO₂/TiO₂ magnetic spheres are shown in Fig. 1. There was no diffraction peaks observed for SiO₂ spheres, which were in an amorphous state. The TiO₂ appears to be in an anatase phase after calcination of the SiO₂/TiO₂ composite spheres at 450 °C for 2 h. The PXRD pattern of the prepared SiO₂/TiO₂ composite spheres showed the diffraction peaks in good agreement with the reference profile, PDF #21-1272, for TiO₂ of the anatase phase [28]. After depositing Ni on SiO₂/TiO₂, new characteristic peaks were appeared at 44.5° and 51.8° that were contributed from the (111) and (200) diffraction planes of pure face-centered cubic Ni with the reference profile of PDF #04-0850 [27]. There is no Ni oxide peaks found in the PXRD patterns of Ni-SiO₂/TiO₂ magnetic spheres.

In our previous work, we reported the FE-SEM images of the SiO₂ spheres and SiO₂/TiO₂ composite spheres and their sizes were 310

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