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Research paper

In-situ construction of novel silver nanoparticle decorated polymeric spheres as highly active and stable catalysts for reduction of methylene blue dye

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ABSTRACT

A facile strategy has been developed for the preparation of novel silver/poly(styrene-N-isopropylacrylamide-methacrylic acid) (Ag/PSNM) nanocomposite spheres with high catalytic activity and good storage stability. Silver (Ag) nanoparticles are successfully deposited on poly(styrene-N-isopropylacrylamide-methacrylic acid) (PSNM) spheres surfaces via *in situ* reduction and simultaneously protected by polyvinylpyrrolidone (PVP). The prepared Ag/PSNM nanocomposite spheres show good temperature/pH responsive property and improved thermal property. Moreover, they also exhibit high catalytic activity and good recyclability for the catalytic reduction of methylene blue (MB) to leuco methylene blue (LMB). The result of clock reaction indicate that the redox reaction generates a colorless (LMB) solution which easily reverts back to blue (MB) in air. The catalytic activity increase with the increasing of temperature and the reaction rate constant (k) follows the typical Arrhenius-type dependence on temperature. In addition, the prepared Ag/PSNM nanocomposite spheres show good storage stability and the catalytic activity remains almost unchanged after storage for 90 days at room temperature. Therefore, the prepared Ag/PSNM nanocomposite spheres can have a highly potential use in the catalytic degradation of organic dyes in wastewater treatment applications.

1. Introduction

Over the past decade, noble metal nanoparticles have received widespread attention in many fields because of their unique chemical, biological, and physical property when compared to their bulk counterparts [1–5]. Among these noble metal nanoparticles, Ag nanoparticles have been widely used as one kind of highly effective catalyst for catalytic degradation of organic dyes because Ag nanoparticles, with high specific surface area, enable a lot of atoms on their surfaces so as to be accessible to the environment's media [6]. Unfortunately, Ag nanoparticles with small size tend to aggregate, and reduce their specific surface area, which will cause a remarkable deterioration of their catalytic property [7]. To overcome these shortcomings, it is vital to find a proper substrate to load Ag nanoparticles [8,9]. For instance, polymeric colloids [9–11] and inorganic oxides (such as titanium oxide [12], silica [13], ferroferric oxide [14], and zinc oxide [15]) have been commonly used as substrates to load Ag nanoparticles. Among these supporting materials, functional polymeric spheres (such as sulfonated polystyrene spheres [16], and polystyrene-methyl acrylic acid spheres [17]) is an interesting and promising matrix for the preparation of Ag nanocomposites because it has abundant functional groups. These functional groups can provide an excellent platform to adsorb silver precursor [18]. Moreover, these functional polymeric spheres can also effectively impede Ag nanoparticles aggregation and thus enhancing their thermal and chemical stability [19,20].

Poly(styrene-N-isopropylacrylamide-methacrylic acid) (PSNM) spheres are a fairly ideal and novel matrix for the preparation of Ag nanocomposites because not only can the PSNM spheres provide abundant active functional carboxyl groups to adsorb silver precursor but also the preparation process of PSNM spheres is simple and mild (PSNM spheres can be prepared by emulsifier-free emulsion polymerization) [21]. Moreover, PSNM spheres are a stimuli-responsive (temperature/pH responsive) polymeric spheres [22], when Ag nanoparticles are loaded onto the surface of PSNM spheres, the temperature/pH responsive property of PSNM spheres may be retained. The Ag nanoparticles wil be strongly fixed on the surface of PSNM spheres due to the strong electrostatic attraction which make the Ag nanoparticles possible to fully contact with the reactants. This result will make it exhibits high catalytic activity and good storage stability.

In general, the preparation process of this kind of Ag/PSNM

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nanocomposite spheres consists of two steps. First, the surface of PSNM spheres is activated by the abundant functional carboxyl groups. Then Ag nanoparticles are loaded onto the surface of PSNM spheres. In this case, additional reagents (such as reducing agent, surfactant, stabilizer, *etc*) must be added to reduce silver precursors to Ag nanoparticles and prevent the Ag nanoparticles from aggregating [23]. However, these additional reagents will be retained as impurities in the final system and potentially cause environmental pollution and biological hazards. Therefore, an environmentally friendly method is highly desired. Polyvinylpyrrolidone (PVP) has been proved to be a good reducing agent and stabilizing agent for the preparation of Ag nanocomposites by Deng's group [16,24–26]. Moreover, it also has many superior property such as low toxicity, good initial tack, chemical and biological inertness, *etc* [27]. Thus, PVP will be a fairly ideal choice for the preparation of Ag/PSNM nanocomposite spheres.

Herein, we present a simple, mild, green, and controllable method to prepare a novel Ag/PSNM nanocomposite spheres through using PSNM spheres as polymeric substrates and PVP as reducing agent and stabilizing agent. In this way, first, PSNM spheres are prepared by emulsifier-free emulsion copolymerization of styrene, N-isopropylacrylamide, and methylacrylic acid. Next, PSNM spheres are used as polymeric substrates and silver precursor-$[Ag(NH_3)_2]^+$ ions are adsorbed onto the surfaces of PSNM spheres. Finally, $[Ag(NH_3)_2]^+$ ions are reduced to Ag nanoparticles and simultaneously protected by PVP on the surface of PSNM spheres. The prepared catalyst are characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis. Besides, the temperature/pH responsive property, thermal stability, catalytic activity, and storage stability of the prepared catalyst are also studied detailedly.

2. Materials and methods

2.1. Materials

Styrene (St, > 99.7%) and methacrylic acid (MAA, 98%) was bought from Aladdin Reagent Inc., Shanghai, China, and the inhibitor was removed by vacuum distillation. Polyvinylpyrrolidone (PVP, M_w = 40000 mol/g), absolute ethanol, N-isopropylacrylamide (NIPAM, 99%), silver nitrate ($AgNO_3$, ≥99.8%), potassium persulfate (KPS, ≥99%), aqueous ammonia solution (concentration, 28%), and methylene blue (MB, ≥97%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water from a Milli-Q water system was used throughout the experiments.

2.2. Preparation of monodisperse PSNM spheres

Monodisperse PSNM spheres were prepared by emulsifier-free emulsion polymerization method according to our group previous research [28–30]. In brief, St (5 g), NIPAM (0.5 g), MAA (0.25 g), and KPS (0.1 g) were dispersed in 100 mL of deionized water, and then sonicated for 20 min. Next, the mixture was added into a 250 mL four-necked flask equipped with mechanical stirrer, reflux condenser, nitrogen inlet, and temperature controller. The mixture solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. Finally, polymerization (Fig. S1) proceeded for 6 h at 78 °C under the atmosphere of nitrogen. The obtained product was dialyzed for 5 days and then was a stable dispersion in deionized water with ca. 2 wt% solid content.

2.3. Preparation of Ag/PSNM nanocomposite spheres

The typical strategy to prepare Ag/PSNM nanocomposite spheres was based on our group former reported method [17,31]. In detail, PSNM dispersion (4 g), PVP (1 g), and deionized water (30 mL) were added into a 100 mL three necked flask. Then, 10 mL of freshly prepared aqueous solution of $[Ag(NH_3)_2]^+$ (0.2–0.4 M) was quickly added into the above mixture. Next, this mixture was stirred for 1 h at room temperature. Finally, this mixture was kept at 70 °C and stirred for 7 h. The final products were separated by centrifugation and washed with an excess amount of deionized water and absolute ethanol several times and then dried in vacuum at 50 °C for 24 h. Herein, three Ag/PSNM nanocomposite spheres with different concentrations of $[Ag(NH_3)_2]^+$ ions were prepared; the concentrations of $[Ag(NH_3)_2]^+$ ions were 0.2, 0.3, and 0.4 M, marking Ag/PSNM-1 nanocomposite spheres, Ag/PSNM-2 nanocomposite spheres, and Ag/PSNM-3 nanocomposite spheres, respectively.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) analysis of the samples was taken on a Spectrum One FTIR spectrometer (Perkin-Bhaskar-Elmer Co., USA), and the dried samples were pressed with KBr into compact pellets. The morphology of the samples was determined by transmission electron microscopy (TEM, Tecnai G20, USA FEI Corp.). All samples were diluted with deionized water and dried on the silica wafer at room temperature before observation. A crystallinity study of the samples were performed on an X-ray diffraction (XRD, D/MAX-IIIC, Japan), taken from 5° to 90° with Cu–Kα (λ = 0.154 nm) radiation to the sample at the scanning rate of 10° min^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an AXIS Ultra X-ray photoelectron spectrometer (Thermo Fisher Scientific Escalab 250Xi). The hydrodynamic size and size distribution of the samples were characterized by dynamic light scattering (DLS, Autosize Loc-Fc-963, Malvern Instrument). The point of zero charge (pH_{PZC}) of samples was determined by Zetal potentiometer. Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer TGA-7 thermogravimetric analyzer (Waltham, Massachusetts, USA) at the heating rate of 20 °C min^{-1} from 30 to 800 °C under nitrogen atmosphere. Differential scanning calorimeter (DSC) was performed using a PerkinElmer DSC-7 at a heat rate of 20 °C min^{-1} from 80 to 130 °C under nitrogen atmosphere. Inductively coupled plasma-atomicemission spectrometric (ICP-AES) was used for testing the amount of Ag in supernatant.

2.5. Catalytic activity of Ag/PSNM nanocomposite spheres

The catalytic activity of Ag/PSNM samples were quantitatively investigated by using a typical catalytic model reaction: the reduction of methylene blue (MB) to leuco methylene blue (LMB) through adding catalysts with an excess amount of $NaBH_4$ [32]. In a typical catalytic experiment, 2.0 mg Ag/PSNM samples were well dispersed into 2.0 mL MB dye solution (0.03 mM), and then 0.5 mL of $NaBH_4$ solution (60 mM) was added. In the recycling study, the catalysts were separated from the solution by centrifugation when the reduction reaction was completely finished. Similar to the above reduction process, the obtained product was redispersed in 0.2 mL of deionized water, and then mixed with 0.5 mL of $NaBH_4$ (60 mM) aqueous solution and 2.0 mL of MB dye solution (0.1 mM). The completion time of the reaction is strictly limited. The catalytic experiment was repeated 10 times.

3. Results and discussion

3.1. Preparation process of Ag/PSNM nanocomposite spheres

The detailed preparation process of Ag/PSNM nanocomposite spheres has been illustrated in Fig. 1. In this way, monodisperse PSNM spheres were firstly prepared by emulsifier-free emulsion polymerization. Then, $[Ag(NH_3)_2]^+$ aqueous solution was added into PSNM dispersion. $[Ag(NH_3)_2]^+$ ions were easily adsorbed onto the surfaces of the PSNM spheres due to the strong electrostatic attraction between