



Highly efficient reduction of 4-nitrophenol by heterostructured gold-magnetite nanocatalysts



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ABSTRACT

In this study, the catalytic reduction of 4-nitrophenol by heterostructured Au-Fe₃O₄ nanocatalysts using NaBH₄ as the reducing agent was investigated under various environmental conditions. The electron behaviors at the interface of Au and Fe₃O₄ nanoparticles were examined to elucidate the reaction mechanisms for 4-nitrophenol reduction. The transmission electron microscopic images show that the average particle size of Au-Fe₃O₄ heterostructures increases slightly from 14 to 18 nm after phase transfer from oil phase to aqueous solution. The X-ray photoelectron and X-ray absorption near edge spectroscopic results show the electron flow from Au seeds to Fe₃O₄, resulting in the formation of positively charged Au surface to accelerate the catalytic reduction efficiency and rate of 4-nitrophenol. In addition, the reduction of 4-nitrophenol is a surface-mediated reaction and the catalytic efficiency and rate of 4-nitrophenol is highly dependent on the initial 4-nitrophenol concentration, pH, and reaction temperature. The increase in pH lowers the reduction efficiency and rate of 4-nitrophenol and a 2.4-fold decrease in the pseudo-first-order rate constant is observed when pH increases from 5 to 9. In addition, the Au-Fe₃O₄ nanocatalysts show a good separation ability and reusability which can be repeatedly applied for complete reduction of 4-nitrophenol for at least six successive cycles without the loss of morphology and saturation magnetization. Results obtained in this study clearly demonstrate that the Au-Fe₃O₄ heterostructures are excellent nanocatalysts which can be applied in heterogeneous catalysis, water treatment, and green chemistry.

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1. Introduction

Nitrophenols are one of the most often used chemicals in production of explosives, pharmaceuticals, pesticides, dyes, and rubber chemicals [1,2]. These compounds are suspected carcinogens and have been promulgated as the priority pollutants by the US Environmental Protection Agent [2]. Due to the highly stable and biorefractory characteristics, the removal of nitrophenols by traditional biological and physicochemical treatment methods are usually strenuous. Therefore, the development of an effective strategy for rapid and efficient removal of nitrophenols from the wastewater and contaminated aquifers is highly demanded.

Several advanced treatment methods including ozonation, Fenton processes, and photodegradation have been developed for the removal of nitrophenols in aqueous solutions [3–5]. More recently, metal-based catalysts including gold (Au), silver (Ag), platinum (Pt), nickel (Ni), and cobalt (Co) nanoparticles have been employed for the reduction of nitrophenols [6–10]. Au-based nanoparticles have

been found to be effectively catalysts for low temperature CO oxidation [11], reductive catalysis of chlorinated hydrocarbons [12–14], and organic synthesis [15]. The catalytic ability of Au nanoparticles usually decreased with time because of the aggregation of nanoparticles. Several materials including polymers, resins, TiO₂, SiO₂, and carbon have been used as the supports to stabilize the nanocatalysts as well as to enhance the catalytic activity by well-tuning the surface functionality [6,7,16,17]. However, these catalysts are usually recycled by tedious and time-consuming processes including centrifugation and re-dispersion cycles, thus hampering the reusability of recycled catalysts in aqueous solutions.

Magnetic nanoparticles (MNPs), another alternative material for catalyst support, have recently been received much attention because of their environmentally benign and superparamagnetic nature [18,19]. The MNP-based nanocatalysts have been designed in various morphologies including core-shell, yolk-shell, and core-satellite for reduction of organic compounds [20–22]. Different from the core-shell nanoparticles, the Au-Fe₃O₄ heterostructures, which the Au seeds are interfacially linked to Fe₃O₄ nanoparticles, are novel nanomaterials with high magnetic property and excellent catalytic activity because of their unique physicochemical and catalytic properties [23–28]. Several studies have depicted

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that Au–Fe₃O₄ can effectively decompose nitrophenols in the presence of sodium borohydride [24,26]. However, the role of electronic behaviors at the interface between Au and Fe₃O₄ nanoparticles in the catalytic activity of Au–Fe₃O₄ remains unclear. In addition, the influence of environmental parameters on the catalytic reduction of 4-nitrophenol by Au–Fe₃O₄ has received less attention. This gives a great impetus to develop a systematic study to elucidate the reduction of 4-nitrophenol by Au–Fe₃O₄ heterostructures in aqueous solutions.

In this study, the catalytic reduction of 4-nitrophenol by Au–Fe₃O₄ heterostructures using NaBH₄ as the reducing agent was investigated under various environmental conditions. The morphology, particle size, crystallinity, optical property, and magnetic property of Au–Fe₃O₄ nanocatalysts were determined by transmission electron microscopy (TEM), X-ray diffractometry (XRD), UV–visible spectroscopy (UV–Vis), and superconducting quantum interference device (SQUID), respectively. The change in chemical species and electron behaviors at the interface of Au and Fe₃O₄ nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES). The effect of several environmental parameters including initial 4-nitrophenol concentration, pH, and reaction temperature on the reduction efficiency and rate of 4-nitrophenol were investigated. In addition, the recyclability of Au–Fe₃O₄ for 4-nitrophenol reduction was evaluated and the possible reaction mechanism was proposed.

2. Materials and methods

2.1. Chemicals

Iron chloride (FeCl₃·6H₂O, 98%), oleylamine (>70%), oleic acid (90%), 1-octadecene (90%), tert-butylamine-borane complex (97%), and tetramethylammonium hydroxide (25%) were purchased from Sigma-Aldrich. Sodium oleate (95%) was obtained from TCI. Sodium borohydride (95%) and absolute ethanol (99.8%) were purchased from Riedel-de Haën. 4-Nitrophenol was purchased from Fluka. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O) was obtained from Alfa Aesar. Cyclohexane (99.95%) was purchased from TEDIA. All other chemicals were of analytical grade and were used as received without further purification. In addition, all the solutions were prepared using bidistilled deionized water (bdH₂O, 18.3 MΩ cm) unless otherwise mentioned.

2.2. Synthesis of Au seeds in non-aqueous solutions

The Au seeds with particle sizes of ca. 5 nm were prepared in non-aqueous solutions using oleylamine as the capping agent. 40 mg of HAuCl₄·3H₂O were first dissolved in a mixture containing 4 mL of oleylamine and 4 mL of cyclohexane in air followed by the magnetic stirring at 10 °C under a gentle stream of nitrogen gas. 0.2 mmole of tert-butylamine-borane complex dissolving in 0.4 mL of oleylamine and 0.4 mL of cyclohexane were then injected into the precursor solution. The color of solution changed to deep red immediately after injection of borane complex solution. The mixture was aged for 40 min at 10 °C followed by addition of 30 mL of absolute ethanol to precipitate the Au seeds. The Au seeds were harvested by centrifugation at 14,000 rpm for 10 min and then re-dispersed in hexane.

2.3. Synthesis of heterostructured Au–Fe₃O₄ nanocatalysts

The heterostructured Au–Fe₃O₄ nanocatalysts were synthesized by adding 0.5 mmole of oleic acid, 0.5 mmole of oleylamine, 1 mmole of iron-oleate complex, and 0.1 mmole of Au seeds into 5 mL of octadecene. The mixture was heated to 110 °C for 20 min

and then refluxed at 310 °C for 30 min. After cooling down to room temperature, the Au–Fe₃O₄ heterostructures were separated by addition of absolute ethanol, centrifugation at 14,000 rpm for 10 min and re-dispersion in hexane.

The aqueous Au–Fe₃O₄ heterostructures were prepared by washing the organic-capped heterostructures with a mixture of hexane and ethanol (1:2) several times to remove excess capping agents on the surface of Au–Fe₃O₄ heterostructures. The washed Au–Fe₃O₄ heterostructures were then added into an aqueous solution containing 0.2 M tetramethylammonium hydroxide and sonicated for 10 min. The ligand exchange was conducted for several times to ensure the full suspension of Au–Fe₃O₄ heterostructures in de-ionized water.

2.4. Catalytic reduction of 4-nitrophenol

The reduction of 4-nitrophenol catalyzed by aqueous Au–Fe₃O₄ heterostructures was carried out in the presence of NaBH₄ under various conditions. 10–60 μL of 10 mM 4-nitrophenol and 0.05–0.25 mL of 0.1 M NaBH₄ solutions were added into bdH₂O in a quartz cuvette to get the final concentrations of 4.6–27.8 mg/L 4-nitrophenol and 1.7–8.3 mM NaBH₄, respectively. The final volume of reaction mixture in the cuvette was 3 mL. In addition, the final concentrations of added Au seeds and Au–Fe₃O₄ nanocatalyst, determined by inductively optical plasma-optical emission spectroscopy, were 5 and 20 mg/L (5 mg-Au/L), respectively. The change in 4-nitrophenol concentration was monitored by UV–Vis spectrophotometer at 400 nm and the time scan mode was used for UV–Vis measurement. The activation energy of 4-nitrophenol reduction by Au–Fe₃O₄ heterostructures was determined at various temperatures ranging from 10 to 50 °C. All the solutions were incubated in water bath at the desired temperatures. After the addition of reagent solutions into the cuvettes, cells were taken out immediately from the water bath for UV–Vis measurement and the change in temperature was controlled at ±1 °C during the measurement period. The effect of pH on 4-nitrophenol reduction was conducted by adding 0.2 mL of 0.1 M NaBH₄ to solutions at initial pHs of 5–11. The pHs were adjusted to the desired values by 0.1 M HCl or 0.1 M NaOH without the addition of buffer solution. In addition, Au seeds used for the reduction of 4-nitrophenol were obtained by etching Fe₃O₄ away from the Au–Fe₃O₄ NPs in 0.5 M H₂SO₄ solutions to make sure that the comparison between Au–Fe₃O₄ heterostructures and Au seed was on the same basis.

2.5. Characterization

The TEM images were obtained on a JEOL 2011 transmission electron microscope operated at 120 kV. High-resolution transmission electron microscopy (HR-TEM) was carried out on a JEOL JEM-2010 microscope at 200 kV. The samples were prepared by suspension in hexane. Wide-angle XRD patterns were recorded on a Bruker D8 X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 1.5406 Å) and operated at a generator voltage and an emission current of 40 kV and 40 mA, respectively. A Hitachi U-3010 UV–visible spectrophotometer with a 1-cm path length quartz cuvette was used to identify the change in concentration over a wavelength range from 200 to 600 nm. Magnetic measurements were carried out using a superconducting quantum interference device magnetometer (SQUID MPMS5, Quantum Design Inc.) with a maximum applied continuous field of 10,000 Gs at room temperature. The zeta potentials as well as isoelectric point (pH_{IEP}) of pure Au, pure Fe₃O₄, and Au–Fe₃O₄ heterostructures in aqueous solutions were determined by dynamic light scattering (DLS) using the Zetasizer Nano ZS (Malvern Instruments Ltd., UK). The nanoparticles were suspended in the de-ionization water, and the pHs of particle solutions were adjusted to the desired values by

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