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Au nanoparticles embedded on urchin-like TiO_2 nanosphere: An efficient catalyst for dyes degradation and 4-nitrophenol reduction

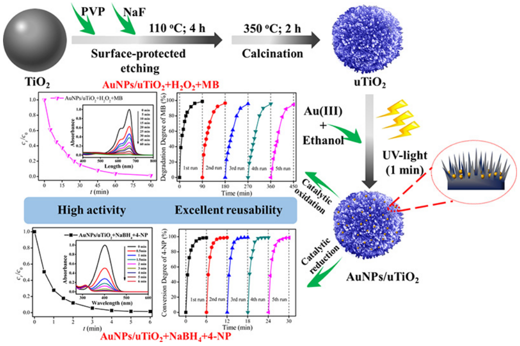
Zheng-Hui Ren [a,1], Hai-Tao Li [a,1], Qiang Gao [a,*], Hao Wang [a], Bo Han [b], Kai-Sheng Xia [b], Cheng-Gang Zhou [b,*]

[a] *Department of Chemistry, Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China*
[b] *Sustainable Energy Laboratory, Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, PR China*

HIGHLIGHTS

- $AuNPs/uTiO_2$ was prepared via photoreduction deposition of Au nanoparticles (AuNPs) on urchin-like TiO_2 nanosphere ($uTiO_2$).
- $AuNPs/uTiO_2$ showed high surface area (147.5 $m^2 \cdot g^{-1}$), large pore volume (0.52 $cm^3 \cdot g^{-1}$), and high dispersity of AuNPs.
- $uTiO_2$ support could prevent leaching or aggregation of AuNPs, while allowing guest molecules to diffuse in and out easily.
- $AuNPs/uTiO_2$ exhibited superior catalytic efficiencies for dyes degradation and 4-nitrophenol reduction.
- Catalytic activity of $AuNPs/uTiO_2$ could remain almost unchanged after being recycled for several times.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient heterogeneous catalysts for degrading organic pollutants or converting them into harmless and even useful products is of vital significance for environmental remediation. Herein, we reported the facile synthesis of a highly active and stable nanocatalyst ($AuNPs/uTiO_2$) via a simple photoreduction deposition of Au nanoparticles (AuNPs) on urchin-like TiO_2 nanosphere ($uTiO_2$), and demonstrated its excellent performances as a catalyst for oxidative degradation of organic dyes and reductive conversion of 4-nitrophenol (4-NP). The $AuNPs/uTiO_2$ nanocomposite showed high surface area (147.5 $m^2 \cdot g^{-1}$), large pore volume (0.52 $cm^3 \cdot g^{-1}$), and high dispersity of AuNPs. In particular, the $uTiO_2$ support could combine AuNPs strongly and serve as a shield to prevent leaching or aggregation of AuNPs, while allowing guest organic molecules to diffuse in and out easily. Benefiting from the excellent characteristics, the $AuNPs/uTiO_2$ exhibited superior catalytic properties for dyes degradation and 4-NP reduction with significantly higher catalytic efficiencies than many previously reported heterogeneous catalysts. Moreover, the catalytic activity of $AuNPs/uTiO_2$ could remain almost unchanged after being recycled for several times, demonstrating its long-term stability. The $AuNPs/uTiO_2$, combining the advantages of high activity, favorable kinetics, and excellent durability for dye degradation and 4-NP reduction, should be very promising for wastewater treatment.

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[*] Corresponding authors.
E-mail addresses: gaoqiang@cug.edu.cn (Q. Gao), cgzhou@cug.edu.cn (C.-G. Zhou).

[1] The two authors contributed equally to this work.

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1. Introduction

The contamination of water supplies by organic compounds has become an issue of serious international concern due to the extensive industrialization and consequently the massive discharge of various types of organic toxicants, including chlorinated solvents, fertilizers, dyes, phenols, and nitro aromatic compounds etc. [1]. Among them, the organic dyes and nitro aromatic compounds are biologically and chemically stable, which makes them difficult to eliminate by natural degradation processes [2]. Such contaminants once released can adversely affect aquatic organisms and pose serious threats to human health [3,4]. Thus, removing these organic contaminants or converting them into harmless and even useful products before discharge is of utmost practical importance [2]. Organic dyes can be removed by various techniques including biodegradation, chemical oxidation, and adsorption etc. [5,6]. Among these techniques, Fenton oxidation degradation, based on the catalytic decomposition of H_2O_2 to yield highly reactive •OH, is very promising for dyes removal [7]. By contrast, the preferred way of detoxificating nitro aromatic compounds is to convert them into industrially valuable aromatic amines via catalytic reduction in the presence of $NaBH_4$ as the reducing agent [8–10].

In general, a crucial issue for both Fenton oxidation degradation of organic dyes and catalytic reduction of nitro aromatic compounds is the design and fabrication of catalysts [11]. During the past two decades, a great deal of research on Fenton oxidation degradation of dyes has been conducted over various heterogeneous catalytic systems with the metal oxides or hydroxides (e.g., Fe_2O_3, Fe_3O_4, Co_3O_4, FeOOH, MnOOH, and Mn_3O_4) as catalysts [12]. Practically speaking, however, since the catalytic processes take place only at the solid–liquid boundary, the heterogeneous catalysts commonly show much lower efficiencies as compared to the homogeneous analogues [13]. Introduction of external energies such as ultrasound, UV light, microwave, and electricity, can largely promote heterogeneous Fenton oxidation process, but it also results in the need for specific equipment [14]. To investigate the possibility of facilitating the heterogeneous Fenton reaction without external energy input, some studies have recently been done on the nanoscaled noble metals [12,15]. Fortunately, it has been discovered that Au nanoparticles (AuNPs), dispersed on a suitable solid support, have a powerful potential in catalytically decomposing organic pollutants [16–20]. In essential, AuNPs can act as excellent electron-donor or acceptor, so they can significantly promote the decomposition of H_2O_2 to •OH via a redox cycle process without aid of external energy [19]. Moreover, AuNPs have a great advantage in catalytic durability over conventional heterogeneous Fenton catalysts because Au is rather “inert” and highly resistant to chemical attacks under various reaction conditions [19]. But it should be also noted that the support of AuNPs can affect the surface area, pore size, pore volume, exposed active sites, stabilization of AuNPs, which all have significant impacts on the overall catalytic performance [21]. To date, only a limited number of solid materials such as hydroxyapatite, carbon, diamond, titania, and hematite have been used as the supports of AuNPs to construct AuNPs-based Fenton catalysis systems for organic pollutants degradation [16–20]. Even though these supports can disperse homogeneously AuNPs on their surfaces, they either have low surface areas or lack of abilities to prevent AuNPs from migrating and even leaching.

On the other hand, AuNPs have attracted great attention as one of the most promising catalysts for reduction of nitro aromatic compounds in recent years [22]. In these applications, AuNPs are generally immobilized on the supporting materials, such as polymer, carbon, silica, and metal oxides, to prevent particle aggregation [23]. Among them, the immobilization of AuNPs on TiO_2 is of particular interest because the TiO_2 support is chemically/mechanically stable and highly effective for the dispersion of AuNPs in a catalytically active form [24–27]. However, in the majority of cases, the used TiO_2 supports have low porosities and cannot provide sufficient surfaces for adsorbing and activating reagents, and therefore, high activities are often hard to achieve [28]. Encapsulation of AuNPs in porous TiO_2, though relatively scarcely reported, may be an effective way to alleviate the above problem [23,29,30]. For example, a mesoporous AuNPs/TiO_2 nanocomposite was synthesized recently by Ismail et al., exhibiting a high catalytic activity for 4-NP reduction [29]. More recently, a macro-/meso-porous AuNPs/TiO_2 composite was developed by Li et al. as the catalyst of 4-NP, which also showed a favorable catalytic ability [30]. Nonetheless, these porous composites usually possess randomly aligned mesopore channels and a large part of AuNPs stay deeply inside the mesopores, so the guest molecules would be difficult to diffuse through the pores to react with the active sites on the internal surface, resulting in a relatively slow reaction kinetics as compared to exposed catalysts [31]. In addition, the immobilization of AuNPs on TiO_2 usually requires multiple processes (e.g., impregnation followed by high-temperature reduction), which is somewhat tedious, time-consuming, and probably limits the wide applications of these catalysts. Therefore, a facile and efficient route to fabrication of porous AuNPs/TiO_2 catalyst with highly accessible active sites and further superior catalytic properties is still a challenge and of particular significance.

In the present work, we reported a facile synthesis of AuNPs embedded on urchin-like TiO_2 spheres (AuNPs/uTiO_2) and demonstrated its superior catalytic performances for Fenton degradation of organic dyes and reduction of 4-NP (Fig. 1). The uTiO_2 support with highly opened structure was facilely fabricated by a combination of surface-protected etching and calcination with the use of TiO_2 solid spheres as precursor [32]. Then, the AuNPs were successfully deposited on the uTiO_2 by a simple one-step photoreduction process under room temperature over a short period of time (only 1 min). It was confirmed that the resulting AuNPs/uTiO_2 showed a high surface area (up to 147.5 $m^2 \cdot g^{-1}$), large pore volume (up to 0.52 $cm^3 \cdot g^{-1}$), and high dispersity of AuNPs. In particular, the uTiO_2 support could combine AuNPs strongly and serve as a shield to prevent leaching or aggregation of active AuNPs, while allowing guest molecules to diffuse in and out easily. As a consequence, this AuNPs/uTiO_2 nanocomposite was demonstrated to be a highly efficient catalyst for both dyes degradation and 4-NP reduction, simultaneously fulfilling the important requirements of high activity, favorable kinetics, and excellent durability in the two kinds of reactions.

2. Experimental

2.1. Chemicals and reagents

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 4H_2O$), polyvinylpyrrolidone (PVP, 10 k), ammonium hydroxide ($NH_3 \cdot H_2O$, 28 wt%), ethanol, acetonitrile, hydrogen peroxide (H_2O_2, 30 wt%), methylene blue (MB), auramine O (AO), basic red 5 (BR), and basic blue 17 (BB), sodium tetraborohydrate ($NaBH_4$), 4-nitrophenol (4-NP) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Titanium isopropoxide (TTIP, $Ti(OC_3H_7)_4$, 98%) was obtained from J&K Scientific Ltd. (Beijing). All chemicals and regents used in this study were commercially available and used without further purification. Distilled water was used throughout our experiments.

2.2. Preparation of AuNPs/uTiO_2

The uTiO_2 support was synthesized by surface-protected etching and sequential calcination processes, according to a reported method with a minor modification [32]. First, amorphous TiO_2 nanosphere precursor was synthesized through a controlled hydrolysis of TTIP. In detail, 0.38 g of $NH_3 \cdot H_2O$ (28 wt%) and 0.91 g of water were added into a mixed solution containing 150 mL ethanol and 100 mL acetonitrile. Afterwards, TTIP (5 mL) was promptly injected into the above solution under vigorous stirring. A milky suspension was formed immediately. After further stirring for 7 h, the product was centrifuged and washed with ethanol for several times. Second, the TiO_2 precursor powders