Journal of Colloid and Interface Science 534 (2019) 357–369

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

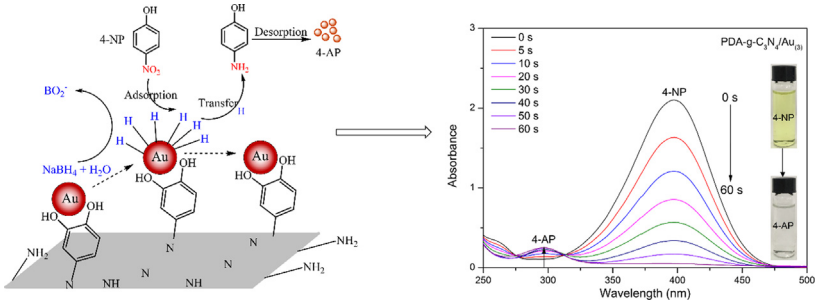
In-situ deposition of gold nanoparticles onto polydopamine-decorated g-C_3N_4 for highly efficient reduction of nitroaromatics in environmental water purification

Lei Qin [1], Danlian Huang [1], Piao Xu [1], Guangming Zeng *, Cui Lai *, Yukui Fu, Huan Yi, Bisheng Li, Chen Zhang, Min Cheng, Chengyun Zhou, Xiaofeng Wen

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, PR China

GRAPHICAL ABSTRACT

Efficient reduction of nitroaromatics by PDA-g-C_3N_4/Au catalyst.



ARTICLE INFO

Article history:
Received 31 July 2018
Revised 12 September 2018
Accepted 15 September 2018
Available online 17 September 2018

Keywords:
Au catalysts
Polydopamine
g-C_3N_4
Nitroaromatics
Reduction

ABSTRACT

A green synthesized gold-catalyst (PDA-g-C_3N_4/Au) for highly efficient reduction of nitroaromatics by $NaBH_4$ was proposed. Polydopamine (PDA) served as the reductant and stabilizer for AuNPs reduction, avoiding the use of chemical reductant and stabilizer that may result in secondary contamination. g-C_3N_4 not only acted as the support but also provided compatibility for AuNPs deposition, enhancing the stability and deposition of AuNPs, which improved the catalytic activity. Different experimental parameters including the amount of Au loading, concentration of $NaBH_4$, and dosage of catalyst were studied. Results showed that PDA-g-C_3N_4/$Au_{(3)}$ revealed higher catalytic activity with a rate constant of 0.0514 s^{-1} and TOF of 545.60 h^{-1} for 4-NP reduction. In addition, the catalyst was highly efficient in reduction of other nitroaromatics and the reduction rates of these compounds were found as the sequence: methyl orange > 2-nitrophenol > 2, 4-dinitrophenol > Erichrome Black T > Congo red. Moreover, the PDA-g-C_3N_4/$Au_{(3)}$ catalyst kept high stability and excellent conversion efficiency over ten reduction cycles. The practical application on different real water samples suggests that this Au catalyst has promising application in environmental water purification. The simple and green synthetic Au catalyst expands the range of application and provides potential application on environmental remediation.

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, PR China.
E-mail addresses: zgming@hnu.edu.cn (G. Zeng), laicui@hnu.edu.cn (C. Lai).
[1] These authors contribute equally to this article.

https://doi.org/10.1016/j.jcis.2018.09.051
0021-9797/

1. Introduction

In recent years, the noble nanoparticles like gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) have gained tremendous application in the generation of chemicals and fuels [1,2]. They are important for environmental protection because of the unique optical and electronic properties, as well as the potential application as an alternative class of efficient catalysts [3–5]. Among them, gold nanoparticles (AuNPs) have been demonstrated as one of high-efficiency catalysts in a great number of redox reactions even at low temperature, because they are proven to have large surface-to-volume ratio and more negative Fermi potential [6,7]. As for the reactions catalyzed by AuNPs, the reduction of nitroaromatics is of great significance in the fields of environment and chemical industry due to the pollutant nature of these compounds and the practical value of the reduction products [8–11]. For example, 4-aminophenol (4-AP), the reduction product of 4-nitropheol (4-NP), is found applications as drying agent, corrosion inhibitor, and precursor for the fabrication of some drugs [12,13]. In addition, compared with other noble nanoparticles, AuNPs have the unique properties of strongly size-dependent property. Smaller size, higher catalytic activity shows at mild conditions, even at low temperature [14]. However, free AuNPs are easy to aggregation because of the high surface energy, thus leading to a certain decay of catalytic activity, poor durability, and low recyclability [15]. In this case, researchers tend to immobilize AuNPs on the supports dispersedly.

Graphitic carbon nitride (g-C_3N_4), an easy-gained sustainable and environmentally friendly material, has attracted growing interest as graphene-like structure that reveals good electrical, thermal, and mechanical properties [16–21]. Abundant amine groups on the surface of g-C_3N_4 provide compatibility for anchoring metal nanoparticles [22]. The presence of nitrogen groups on the surface of carbon support can reduce the size and enhance the stability of nanoparticles [23–27]. These characteristics allow g-C_3N_4 an ideal support for anchoring AuNPs as gold-based catalyst. For example, Wang et al. [28] have prepared an Au/g-C_3N_4 hybrid for bacteria killing and wound disinfection by catalyzing the decomposition of H_2O_2 to $^{\bullet}OH$ radicals, in which g-C_3N_4 possess intrinsic peroxidase-like activity and plays the role on a synergetic nanozyme with AuNPs. With the excellent electron transfer ability of g-C_3N_4, Fu et al. [29] have used the Au/g-C_3N_4 contact system for reduction of 4-nitrophenol (4-NP) in the dark and under visible light irradiation. The synergistic effect of Au and g-C_3N_4 makes charge-transfer effect, which contributes to negative shift in Fermi level of Au. Besides, the N-contaning structure renders g-C_3N_4 possess strong proton (H^+) adsorption ability, which may be beneficial to H^+ transfer of nitroaromatics reduction [30–32]. Nevertheless, the deposition of AuNPs on g-C_3N_4 always needs precipitant or reducing agent whether using the deposition precipitation method or traditional AuNPs reducing method (e.g. Turkevich–Frens method or Brust–Schiffrin strategy) [33–35]. Most of these chemical reagents raise environmental concerns, which limits the biocompatibility and biomedical application [36]. Therefore, a reliable and bio/eco-friendly "green" chemical process for deposition AuNPs on g-C_3N_4 support is of great importance.

Dopamine (DA), a neurotransmitter, widely exists in the animal brain. It has drawn great attention since it contains plenty of amine and catechol functional groups and has the ability to adhere to the surface of many materials [37,38]. Especially, it can be self-polymerized to form polydopamine (PDA) under mild conditions (weakly alkaline pH) [39,40]. This process is simple, green, and low-cost. Moreover, numerous catechol groups of PDA are believed an alternative for synthesis of AuNPs due to the obvious reductive and stabilizing ability [38,41–43]. In view of this, PDA decorated g-C_3N_4 for Au catalyst synthesis shows the potential to improve the inherent property of Au catalyst and provide high catalytic activity. In this work, a PDA-g-C_3N_4 supported Au catalyst was prepared for highly efficient reduction of various nitroaromatics. The AuNPs were obtained via in-situ reduction of chloroauric acid by PDA. The effects of some experimental parameters on the catalytic performance were discussed in detail. To investigate the catalytic performance of described Au catalyst, some typical nitroaromatics like 2-nitrophenol (2-NP), 4-NP, 2, 4-dinitrophenol (2, 4-DNP), methyl orange (MO), Congo red (CR), and Erichrome Black T (EBT) were used as the targets. Additionally, reduction of 4-NP was used as the model reaction throughout the experiment and the catalytic performance on real water samples was proposed as well.

2. Experimental

2.1. Chemicals

Chloroauric acid hydrated ($HAuCl_4{\cdot}4H_2O$), melamine, sodium borohydride ($NaBH_4$), 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), hydrochloric acid (HCl), and 4-Nitrophenol were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The ultrapure water (18.2 Ω, Milli-Q Millipore) was used in whole experimental process. Dopamine hydrochloride was gained from the Aladdin Bio-Chemical Technology Co., ltd (Shanghai, China). 2-nitrophenol, 4-nitrophenol, 2, 4-dinitrophenol, methyl orange, Congo red, and Erichrome Black T were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All of the chemicals were used as obtained without further purification.

2.2. Characterization

The UV–Vis spectra were measured by a UV-2007 spectrometer (Shimadzu corporation, Kyoto, Japan) to obtain the absorption spectra with a quartz cuvette (1-cm pathlength). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were measured on a TECNAI G2 F20 high-resolution transmission electron microscope with an accelerating voltage of 200 kV (FEI Company, Hillsboro, USA). The morphologies were recorded by scanning transmission electron microscopy (SEM, JSM-5600, Japan). The crystal structure of samples was realized in an X-ray diffraction analyzer with scan rate of 6° min^{-1} (XRD, radiation Bruker Smart-Apex-II, Cu Kα, λ = 0.1541 nm, Bruker, Germany). The elements and chemical state analyses were carried out by the X-ray photoelectron spectra (XPS) performed on a multifunctional imaging electron spectrometer using Al Kα radiation (Thermo ESCALAB 250XI, Thermo Scientific, USA). The Chemical transformation on the samples surface was performed on Fourier transform-infrared spectra (FT-IR, NICOLET 5700, Thermo Nicolet, USA). The contents of Au in different catalysts were measured by the inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 725 ICP-OES, USA).

2.3. Preparation of PDA-g-C_3N_4/Au catalyst

2.3.1. Preparation of g-C_3N_4

The bulk g-C_3N_4 was obtained by direct polymerization under high temperature. Typically, 10 g of melamine was carefully placed in an alumina crucible with cover and then kept into the center of the muffle furnace. The alumina crucible was first heated at 600 °C with a heating rate of 5 °C min^{-1} and maintained at 600 °C for 2 h and finally cooled down to room temperature naturally. The fabricated bulk g-C_3N_4 was further triturated for use.