Enhancing catalytic performance of Au catalysts by noncovalent functionalized graphene using functional ionic liquids
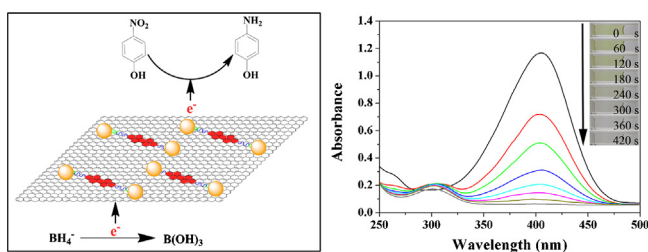
Shuwen Li, Shujing Guo, Honglei Yang, Galian Gou, Ren Ren, Jing Li, Zhengping Dong, Jun Jin, Jiantai Ma *

State Key Laboratory of Applied Organic Chemistry, Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

HIGHLIGHTS

- The new catalyst was fabricated by a facile and environment-friendly approach.
- The catalyst has excellent activity and reusability due to the synergistic effect.
- The approach provides a green way to synthesize low cost Au-based catalysts.

GRAPHICAL ABSTRACT

ABSTRACT

New catalyst, prepared through Au nanoparticles anchored on the Ionic Liquid of 3,4,9,10-perylene tetracarboxylic acid-noncovalent functionalized graphene (Au/PDIL-GS), was fabricated using a facile and environment-friendly approach. The information of the morphologies, sizes, dispersion of Au nanoparticles (NPs) and chemical composition for the as-prepared catalysts was verified by systematic characterizations, including transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Raman spectra, X-ray diffraction (XRD) and X-Ray photoelectron spectroscopy (XPS). As a new catalyst, the resulting Au/PDIL-GS exhibited excellent catalytic activity in the reduction of 4-nitrophenol because of the synergistic effect between the PDIL-GS and Au NPs. The facile and environment-friendly approach provides a green way to effectively synthesize low cost Au-based catalysts for 4-NP reduction and is promising for the development of other useful materials.

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1. Introduction

Considering its fundamental scientific interests and technological importance in various applications, the metal nanostructures have attracted great attention over several decades [1–4]. Among various noble metals, gold nanoparticles (Au NPs) have been the subject of intense investigation due to their unique physical and chemical properties and broad applicability in biomedicine, catalysis and biosensing [1,5]. Unfortunately, smaller Au NPs aggregate very easily to minimize their surface area owing to their higher surface energy, resulting in a remarkable reduction in their catalytic activity although Au NPs exhibit highly efficient catalytic activity [6]. In addition, the high cost and limited supply further hinder its practical application as a facile catalyst for recovery and recycling. An effective approach to treat the above problems is to anchor Au NPs on the surface of solid supports [7]. Not only the maximizing loading of catalysts can be achieved and the catalytic activity may be enhanced by tuning the surface functionality of supports, but also the strong synergistic interaction between noble metal NPs and support can greatly enhance the catalytic

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* Corresponding author. Tel.: +86 931 8912577; fax: +86 931 8912582.
E-mail address: majiantai@lzu.edu.cn (J. Ma).

activity and stability [6,8,9]. Graphene sheets (GS), as an atomic-layer-thick two-dimensional material, have recently received significant attention in various fields of science and engineering because of their unique electrical, optical, thermal and mechanical properties [10–13]. As a good supporting substrate for active species on account of its good conductivity, high chemical stability, low manufacturing cost and large surface area, the combination of GS and Au NPs may open up a new avenue for designing the next generation catalysts [6,14]. However, the pristine GS is hard to disperse in aqueous solution and has a lack of binding sites for metal NPs to immobilize on them, usually resulting in poor dispersion and large metal particles. In order to overcome these problems, the functionalization of GS by covalent or noncovalent method is considerably investigated [15–17]. The functionalization of GS through covalent method (including graphene oxide, GO) cannot avoid the structural damage of graphene which adversely affects the electrical, mechanical, and stabile properties of the material because of the transformation of carbon atoms from a planar sp^2-hybridized geometry to a distorted sp^3-hybridized geometry [18]. Non-covalent method by supermolecular interactions such as $\pi-\pi$ stacking has advantages of operating and preserving the intact electronic structure of GS compared with covalent functionalization [19,20]. Moreover, GS will be endued with other properties when it is combined with functionalized molecules through non-covalent methods [21,22]. Ionic liquids (IL) are finding increasing applications in various diverse fields for their unique properties like high ionic conductivity, wide temperature liquid range, environment-friendly green nature, wide electrochemical stability window and good thermal stability [23–25]. The problems of leakage and impossible miniaturization for IL limit their use in actual devices, but IL grafted onto the supports is a good strategy to break out the limitations. Additionally, the microenvironment of IL can facilitate a number of reactions [26,27].

In this paper, we fabricated a new catalyst (Au/PDIL-GS), which was prepared through Au NPs was anchored on the IL derived from 3,4,9,10-perylene tetracarboxylic acid (PDIL)-noncovalent functionalized GS *via* $\pi-\pi$ stacking, by a facile and environment-friendly synthetic approach. Systematic characterizations, including transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Raman spectra, X-ray diffraction (XRD) and X-Ray photoelectron spectroscopy (XPS) were used to obtain the information such as the morphologies, dispersion of Pd nanoparticles (NPs) and chemical composition for the as-prepared catalysts. With the development of chemical engineering, nitroarenes are typically found in industrial production and agricultural waste water. 4-nitrophenol (4-NP) is one of the most common organic pollutants in industrial and agricultural waste water, which are very harmful and hazardous for the environment. At present, varieties of physical, biological and chemical methods have been developed for the removal of nitrogenous organic matter, such as adsorption, microbial degradation, photo degradation, electrochemical treatment and catalytic reactions [28–33]. Among them, selective hydrogenation of nitroarenes to the corresponding aminoarenes is considered as an effective measure and a nice choice, not only because the treatment process is simple and fast but also the products (aminoarenes) are very useful and important in synthetic organic chemistry and many industrial applications. Therefore, the excellent catalytic activity of the resulting nanohybrid Au/PDIL-GS was exploited toward the reduction of 4-NP, owing to 4-NP is one of the most common organic pollutants in industrial and agricultural waste water, while the product (4-aminophenol, 4-AP) is very useful and important in many applications [34].
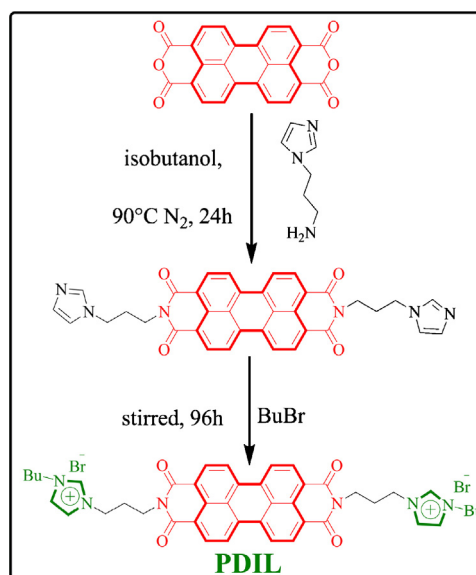
Scheme 1. Synthetic route of PDIL.

2. Experimental

2.1. Materials

Graphene sheets (pristine GS, 95%) prepared by physical method were purchased from Nanjing XFNano Materials Tech Co., Ltd., China. HAuCl$_4$·3H$_2$O (99%), NaBH$_4$, 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA, 98%) and *N*-(3-Aminopropyl)-imidazole were purchased from Alfa Aesar. All other reagents were purchased from the Tianjin Guangfu Chemical Co. Ltd. Water used in the experiments was deionized and doubly distilled.

2.2. Synthesis of PDIL

The synthesis route of PDIL molecular was summarized in Scheme 1 and the specific steps of synthesis were shown in supplementary information.

2.3. The fabricated route of the Au/PDIL-GS

The fabricated route of the Au/PDIL-GS was summarized in Fig. 1.The following specific steps of preparation were shown.

PDIL-GS: The GS (50 mg) were ultrasonicated in deionized water (50 mL) containing PTCA (30 mg) for 12 h. After that, the mixture was filtered through membrane and washed repeatedly with absolute ethyl alcohol and distilled water for several times. The final products were dried in vacuum oven at room temperature overnight.

Au/PDIL-GS: The PDIL-GS (20 mg) was dissolved in H$_2$O (20 mL) with ultrasonic treatment to form a uniform suspension. Then, HAuCl$_4$·3H$_2$O solution (0.01 M, 1.15 mL) was added into the suspension under stirring and the mixture was stirred for 30 min in room temperature. Subsequently, the fresh, ice-cooled NaBH$_4$ solution (1.15 mL 0.1 M) was delivered by drops into the above suspension under continuous stirring. After reacting for 1 h at room temperature, the solid material was separated by centrifugation, washed repeatedly with water and ethanol several times, and dried in a vacuum at 25 °C for 12 h.

The Au/GS was also prepared in the same procedure except that the PDIL-GS was replaced by the GS.