



Robust Au–Ag/graphene bimetallic nanocatalyst for multifunctional activity with high synergism



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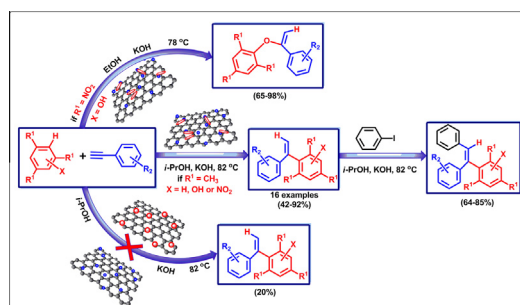
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HIGHLIGHTS

- Hydroarylation, C-arylation and hydrophenoxylation are performed over Au–Ag/SLG.
- Salmon milt DNA stabilizes the AgNPs and also obliging in producing AuNRs.
- Mixture of monometallic Au/SLG and Ag/SLG is inadequate for hydroarylation.
- Nature of substituent determines the hydroarylation or hydrophenoxylation.
- Consecutive C-arylation of hydroarylated products is achieved using Au–Ag/SLG.

GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanorods (AuNRs) and silver nanoparticles (AgNPs) were fastened over single layer graphene (SLG) and successfully designated using microscopic (TEM and SEM–EDX) and spectroscopic (Raman, XRD, XPS and ICP) techniques. Salmon milt DNA stabilized the AgNPs and was also obliging in producing AuNRs. Bimetallic nanocatalyst (Au–Ag/SLG) was tremendously exerted as a versatile catalyst for hydroarylation, C-arylation and hydrophenoxylation reactions under mild and ligand-free conditions. But the mixture of monometallic nanocatalysts (Au/SLG and Ag/SLG) was unsuccessful in exposing their catalytic performance towards hydroarylation reaction. Initially the reaction conditions were optimized. 16 examples were fruitfully demonstrated for hydroarylation reaction in *i*-PrOH solvent with KOH. High synergistic effect was experienced with Au–Ag/SLG bimetallic nanocatalyst. Electron releasing group at the phenyl ring lead to the formation of 1,1-diphenylethylenes whereas the arenes with electron withdrawing functional group preferred hydrophenoxylation rather than hydroarylation. Consecutively C-arylation of hydroarylated products (1,1-diphenylethylenes) was achieved with iodobenzene by means of the same bimetallic nanocatalyst (Au–Ag/SLG). Leaching of metal nanoparticles during the course of the catalytic reaction was examined using heterogeneity test and ICP analysis. Reusability results confirmed the chemical stability of the proposed bimetallic Au–Ag/SLG nanocatalyst.

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1. Introduction

Graphene served as a miscellaneous solid support for metal nanoparticles (MNPs) because of its high thermal and chemical inertness, high surface to volume ratio and high dispersion in reaction medium [1]. In recent years, MNPs anchored graphene is widely used in the fields of energy and environment. In evidence to this, MNPs supported on graphene have been found to be effective materials for the designing of renewable solar energy converting devices. Wang et al. constructed indium tin oxide (ITO) and fluorine tin oxide (FTO) over the transparent and conductive solid state graphene electrode for dye-sensitized solar cells [2]. Similarly, mono-crystalline ZnO nanorods (NRs) electrochemically deposited on reduced graphene oxide (rGO) were used to fabricate inorganic-organic hybrid solar cells [3]. Choi et al. have summarized the utility of MNPs-graphene composites for the development of fuel cells and capacitors [4]. CdS/graphene was found to be an efficient catalyst for water splitting reaction [5]. SnO₂/rGO [6], ZnO/rGO [7], ZnFe₂O₄/rGO [8] and ZnSe/N-doped graphene (NG) [9] were utilized as effective nanomaterials for photodegradation of pollutants.

In addition to all these, because of its high stability under harsh chemical and thermal conditions, graphene can be effectively used as a solid support for MNPs to catalyze organic conversions. Co₃O₄, MnCo₂O₄, Mn₃O₄, Fe, Ru or Pt NPs were supported over rGO or PDDA-rGO or N-rGO and were utilized as effective catalysts for industrially important reactions such as oxygen reduction reaction (ORR) [10], methanol oxidation reaction (MOR) [11–13] and oxygen evolving reaction (OER) [14,15]. Hydrogen evolving reaction (HER) has been successfully demonstrated using MoS₂/rGO [16]. Hemoglobin/GO nanocatalyst was extensively exploited for peroxidatic reaction [17]. Oxidation of HCOOH was greatly achieved by Pt-Au/PDDA-rGO nanocatalyst [18]. Soybean oil was victoriously transesterified with methanol using CaO/GO catalyst [19]. Pd/rGO nanocatalyst was used to generate C–C bond via Suzuki–Miyaura coupling [20] and Heck reactions [21]. Graphene was successfully modified with AuNPs and can act as efficient catalyst for the Suzuki reaction in water under aerobic condition [22]. Recently, we have illustrated the catalytic utility of GNPs-RuO₂NRs towards the transfer hydrogenation of carbonyl compounds [23], and GNS-RuNPs for aerial oxidation of alcohols and transfer hydrogenation of ketones [24]. Bimetallic NPs decorated on solid matrix always have high versatility and efficiency as compared to the monometallic NPs [8,9,18]. For example, Au–Pt core-shell NPs have been synthesized on rGO surface and its catalytic activity was investigated towards ORR and MOR [25].

All these results motivated us to develop a bimetallic nanocatalyst anchored over single layer graphene (SLG) for some of the important organic transformations such as hydroarylation, C-arylation and hydrophenoxylation. These conversions were chosen because hydroarylation of alkynes is a kind of Friedel–Crafts alkenylation reaction in which C–H bond activation takes place followed by C–C coupling [26,27], which is one of the prominent processes in organic synthesis [28,29]. Similarly, C-arylation of 1,1-diphenylethylenes produce β,β -diarylalene derivatives which are valuable intermediates for the synthesis of natural products and pharmaceuticals [30,31]. In the same way, hydrophenoxylation of alkynes involves formation of the O–C (sp²) bond which is of fundamental interest in synthetic organic chemistry [32,33]. So herein we report Au–Ag/SLG bimetallic nanocatalyst for hydroarylation of alkynes, C-arylation of 1,1-diphenylethylenes and hydrophenoxylation of alkynes under mild and ligand-free conditions.

2. Experimental

2.1. Materials and methods

Industrial quality single layer graphene nanosheets (SLG, purity: >98 wt%, surface area: ~600 m²/g, average thickness: \leq 3 nm, Electrical resistivity: \leq 0.30 Ω cm⁻¹) were purchased from ACS materials, US. Ag/DNA was provided by Nissei Bio Co., Ltd. H₂SO₄ (98%) and HNO₃ (70%) were purchased from Wako pure chemicals, Japan. H₂AuCl₄·xH₂O and all other chemicals were purchased from Aldrich and used as received.

Transmission electron microscopic images were recorded on JEM-2100 JEOL instrument with accelerating voltage of 200 kV. The weight percentage of MNPs over SLG was confirmed by scanning electron microscopy-energy dispersive spectrum [SEM–EDS, Hitachi 3000H]. Raman spectrometer (Hololab 5000, Kaiser Optical Systems Inc., USA) was used to investigate the interaction of MNPs with SLG using argon laser at 532 nm with a Kaiser holographic edge filter. X-ray diffraction (XRD) studies were performed on a Rotaflex RTP300 (RigakuCo., Japan) diffractometer at 50 kV and 200 mA. Nickel-filtered Cu K α radiation was used for this measurement, with an angular range of 10–80°. The chemical state of MNPs in nanocatalysts was confirmed by X-ray photoelectron spectroscopy (XPS) using Kratos Axis-Ultra DLD model instrument. The samples were irradiated under Mg K α ray source before XPS analysis. NMR spectra were recorded on a 400 MHz Bruker spectrometer in CDCl₃ using tetramethylsilane as a standard.

2.2. Functionalization of SLG

SLG was functionalized as per the literature procedure [34]. 1.0 g of SLG was sonicated with a mixture of conc. H₂SO₄ and conc. HNO₃ (3:1) at 40 °C for 3 h. The mixture was poured into de-ionized H₂O (1 L) then filtered through a Millipore filter paper (0.65 μ m). The precipitate was washed several times with de-ionized H₂O until the pH of the filtrate reached 7. The residue was dried at room temperature to obtain functionalized graphene (*f*-SLG).

2.3. Preparation of Au/SLG

Aqueous solution of H₂AuCl₄·xH₂O (0.001%, 30 mL) was sonicated with *f*-SLG (150 mg) for 3 h at 27 °C. Then the mixture was centrifuged and washed thoroughly with de-ionized H₂O. The precipitate (Au–SLG) was calcinated at 700 °C for 3 h (with the increasing rate of 5 °C per minute) under N₂ atmosphere.

2.4. Preparation of Ag/SLG

Colloidal suspension (250 μ L) of AgNPs (~2–4 nm size) in Salmon milt DNA (5.3 \times 10⁻² mol L⁻¹) was diluted with 30 mL of H₂O. *f*-SLG (150 mg) was added to this solution and sonicated at 27 °C for 3 h. The mixture was centrifuged and washed with de-ionized H₂O. Then Ag/SLG was dried and calcinated at 700 °C for 3 h (with the increasing rate of 5 °C per min.) under N₂ atmosphere for the complete removal of Salmon milt DNA.

2.5. Preparation of Au–Ag/SLG

Mixture of H₂AuCl₄·xH₂O (30 mL of 0.001% aqueous solution) and colloidal Ag/DNA (250 μ L) was sonicated for 1 h at 27 °C. Sonication was continued for another 3 h at 27 °C after the addition of *f*-SLG (150 mg). Then the mixture was centrifuged to recover the

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