Gold nanoparticles–graphene hybrids as active catalysts for Suzuki reaction

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ABSTRACT

Graphene was successfully modified with gold nanoparticles in a facile route by reducing chloroauric acid in the presence of sodium dodecyl sulfate, which is used as both a surfactant and reducing agent. The gold nanoparticles–graphene hybrids were characterized by high-resolution transmission electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, X-ray diffraction and energy X-ray spectroscopy. We demonstrate for the first time that the gold nanoparticles–graphene hybrids can act as efficient catalysts for the Suzuki reaction in water under aerobic conditions. The catalytic activity of gold nanoparticles–graphene hybrids was influenced by the size of the gold nanoparticles.

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1. Introduction

Graphene is a flat monolayer of carbon atoms tightly packed into a honeycomb lattice. It continues to attract immense interest in fundamental physics and for its potential applications after experimentally isolated in 2004, mostly due to the unusual electronic properties and effects that arise from its one-atom thickness [1]. It may be a promising alternative to carbon nanotubes in polymer nanocomposites [2,3]. It could also be applied in nanoelectronics as an insulating material or semiconductor [1,4]. In addition, due to its low-cost, large specific surface area and strong interactions with metal clusters, graphene is a promising material for catalytic applications [5,6]. The dispersion of metal nanoparticles on graphene sheets potentially provides a new way to develop catalytic materials [7]. However, only a few metal nanoparticles–graphene hybrids have been reported [8,9], and fewer studies have investigated their catalytic properties.

Gold (Au) nanoparticles have attracted considerable attention in recent years. Their catalytic applications in heterogeneous organic reactions are particular attractive. These reactions are traditionally carried out with homogeneous transition metal catalysts [10–16]. The Suzuki reaction, which is predominately catalyzed by palladium (Pd) catalysts, is a powerful and convenient synthetic method in organic chemistry for the generation of biaryls, conducting polymers, and liquid crystals [17–21]. Considering Au(I) is isoelectronic with Pd(0), Au nanoparticles may also catalyze the Suzuki reaction.

Previously, we found that deoxygenation of graphene oxide (GO) occurred under alkaline conditions, providing a green and cost effective way to prepare graphene on a large-scale [22]. Here, we developed a facile route to homogeneously disperse Au nanoparticles with a small size distribution on chemically modified graphene in water. We also demonstrated for the first time that Au nanoparticles (as Au–graphene hybrids) can be used as efficient catalysts for the Suzuki reaction of aryl halides with arylboronic acids.

2. Experimental

2.1. Synthesis of Au–graphene hybrids

Graphite oxide was prepared by Hummer method [23] and exfoliated into GO by sonication in water [24]. The prepared GO was heated in a sodium hydroxide (NaOH) solution to obtain a suspension of reduced graphene. Then, 40 mL sodium dodecyl sulfate (SDS, 0.1 M) aqueous solution was added into 15 mL of the reduced graphene suspension ($\sim$6 mg mL^{-1}) and sonicated for 5 min. Subsequently, chloroauric acid (HAuCl$_4$) (0.02 M) was added to this mixture, and it was refluxed at 100 °C with magnetic stirring for 6 h. After cooling to room temperature, the mixture was then washed extensively with deionized water and centrifuged several times, in order to remove excessive surfactants.

2.2. Suzuki reaction catalyzed by Au–graphene hybrids

Iodobenzene (204 mg, 1.0 mmol) was added into a stirred mixture of NaOH (160 mg), phenylboronic acid (146 mg, 1.2 mmol) and deionized water (H$_2$O) (20 mL). This was followed

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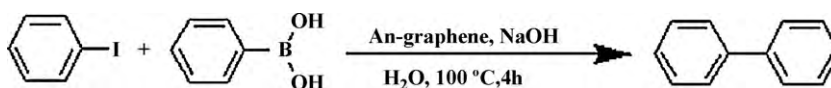
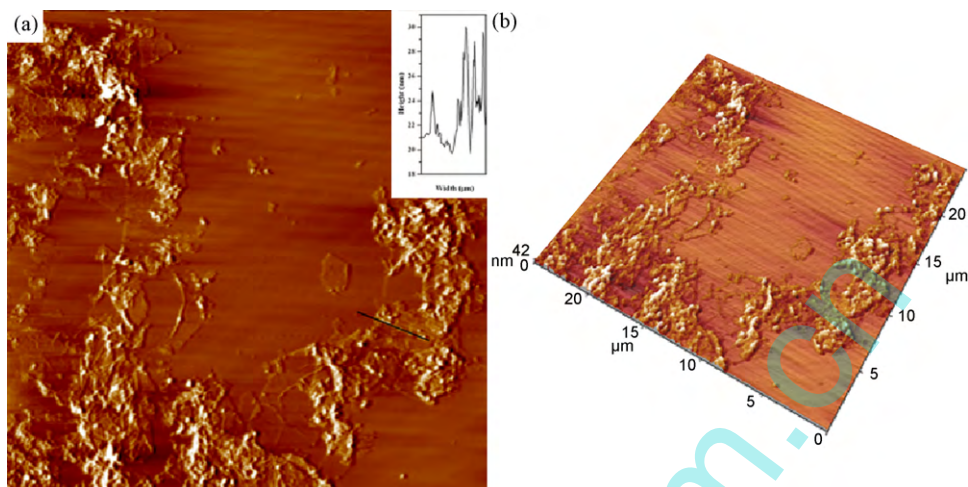**Scheme 1.** Suzuki reaction using Au–graphene as the catalyst.

Fig. 1. AFM image (a) of modified graphene, deposited on freshly cleaved mica substrates, the bright "spots" are the Au nanoparticles deposited on the graphene, and the insert image of cross-section analysis, as well as corresponding 3D image and (b) of Au–graphene hybrids.
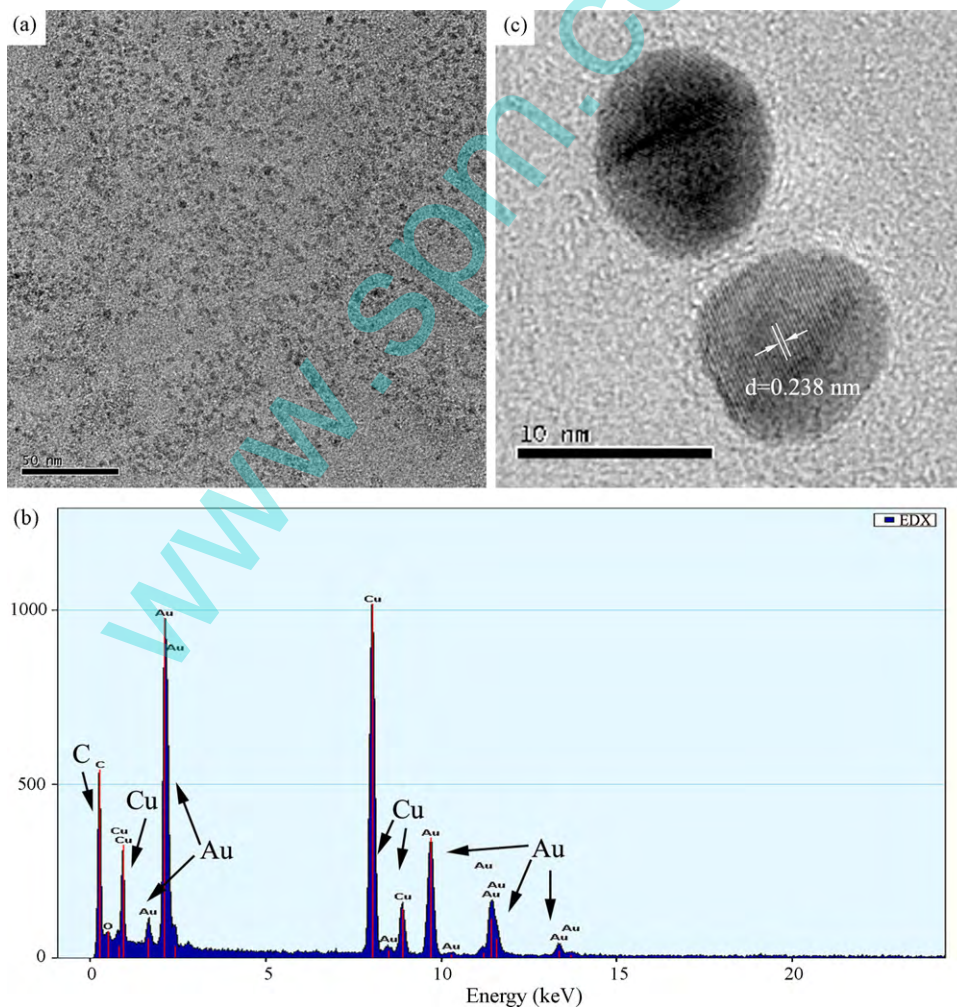

Fig. 2. TEM image (a) and corresponding EDX result (b) of Au nanoparticles (average diameter of ~3 nm) homogeneously deposited on graphene. The Cu peaks in EDX come from the copper grid. Enlarged HRTEM image (c) of Au nanoparticles with a clear lattice of 0.238 nm.

by the addition of Au–graphene hybrids at a mole fraction of 1%. This reaction is illustrated in Scheme 1. The mixture was then stirred at 100 °C in an oil bath for 4 h and extracted with ethyl acetate (3 × 20 mL). The combined organic extract was dried over anhydrous sodium sulfate (Na$_2$SO$_4$), and the resulting mixture was analyzed by gas chromatography (GC).

2.3. Characterization

The Au–graphene hybrids were characterized by high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20), atomic force microscopy (AFM) (CSPM 5000), energy X-ray spectroscopy (EDX) (Philips Tecnai G2 F20), X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, PHI 1600 spectrometer) and Raman spectroscopy (NT-MDT NTEGRA Spectra). The catalytic activity of the Au–graphene hybrids was measured by gas chromatography (GC) on an Agilent 6890N GC-FID system.

3. Results and discussion

3.1. Synthesis of Au–graphene hybrids

The purified Au–graphene hybrids show impressive stability in water, as no precipitation is observed in the suspension for months (Fig. 2S, Supporting Information). The stability of the hybrids in water can be attributed to the resulted dodecanoic acid, which is generated from thermally decomposed SDS and acts as an excellent stabilizer. Dodecanoic acid and the sulfonic groups not only provide stability, but also contribute to the homogeneous and sufficient dispersal of Au nanoparticles on graphene sheets. The residual sulfonic groups of SDS (Fig. 3S, Supporting Information) adsorbed on the Au–graphene hybrids should extend to the solution and provide electrostatic repulsions, which stabilize the suspension [25]. They also behave as active sites for the adsorption of Au ions and as the nucleation centers for Au nanoparticles. Additionally, the pH of the reaction solution in our experiment is 8.5, and the alkalinity facilitates formation of smaller particles with a faster nucleation rate [26].

An AFM image of the Au–graphene hybrids (Fig. 1) shows that monodispersed nanoparticles are homogenously deposited on the surface of most graphene sheets. No free nanoparticle is observed outside the graphene sheets even after intensive sonication during the preparation of the sample for AFM characterization. It may demonstrate the strong interaction between the sheets and the nanoparticles (cross-section analysis in Fig. 2S, Supporting Information). The homogenous deposition of Au nanoparticles on graphene is further confirmed by HRTEM (Fig. 2(a)). The corresponding EDX result (Fig. 2(b)) shows that Au nanoparticles are abundant in the hybrids. An enlarged image of the Au nanoparticles clearly shows the typical lattice of crystalline gold (Fig. 2(c)). The measured regular d-spacing of about 0.238 nm in this image corresponds to the {1 1 1} planes of gold [27]. The XRD pattern also confirms the formation of the Au nanoparticles (Fig. 4S, Supporting Information).

Raman spectra of GO, graphene and the Au–graphene hybrids are shown in Fig. 3. The two bands at about 1358 cm^{-1} and 1622 cm^{-1} correspond to the disorder-induced D band and the in-phase vibration of the graphene lattice (G band), respectively [28]. In line with other research groups' studies on chemically reduced graphene [29], the $I(D)/I(G)$ intensity ratio of graphene ($I(D)/I(G)^{graphene}$ = 2.06) in Fig. 3(b) is slightly higher than that of GO ($I(D)/I(G)^{GO}$ = 1.99) (Fig. 3(a)). This result may reflect the reduction in size of the graphene [29]. The $I(D)/I(G)$ intensity ratio of Au–graphene ($I(D)/I(G)^{Au-graphene}$ = 2.22, Fig. 3(c) is much larger than that of graphene. Such an enhancement is also observed when other metal nanoparticles are deposited on GO [30] and carbon
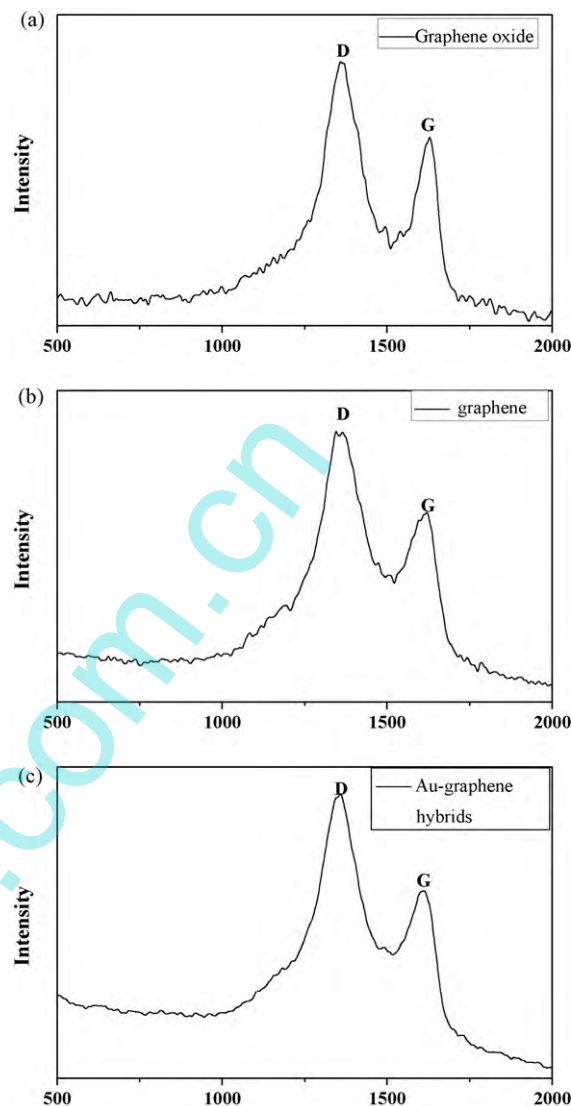
Fig. 3. Raman spectra of graphene oxide (a), graphene (b) and Au–graphene hybrids (c).

nanotubes [31,32]. This result therefore suggests a chemical interaction or bond between the Au nanoparticles and graphene [30,31]. As the graphene sheets in this study are obtained by chemical reduction of GO, they likely contain many carbon vacancies and defects [9], which may enhance the interaction between Au nanoparticles and graphene [33,34]. Moreover, the G bands of graphene and Au–graphene hybrids (1622 cm^{-1}) are shifted to lower frequency compared with that of GO (1629 cm^{-1}). This could probably be explained by an alternating pattern of single-double carbon bonds within sp^2 carbon ribbons during the reactions [35].

The size of the Au nanoparticles deposite on the surface of graphene sheets can be adjusted by varying the [Au]/[graphene] mass ratio. Because no free metal nanoparticle appeares outside the graphene sheets in the AFM and HRTEM images obtained from different regions of samples, the amount of reactants used in the synthesis could be used to calculate the mass ratio of [Au]/ [graphene]. The result from this calculation is similar to that from EDX elemental analysis. Fig. 4 shows the HRTEM images and the associated nanoparticle size distributions. When the mass fraction of Au nanoparticles is 8%, the average diameter of the Au nanoparticles deposited on the graphene is 2–3 nm with a relatively small distribution (Fig. 4(a) and (b)). In comparison,
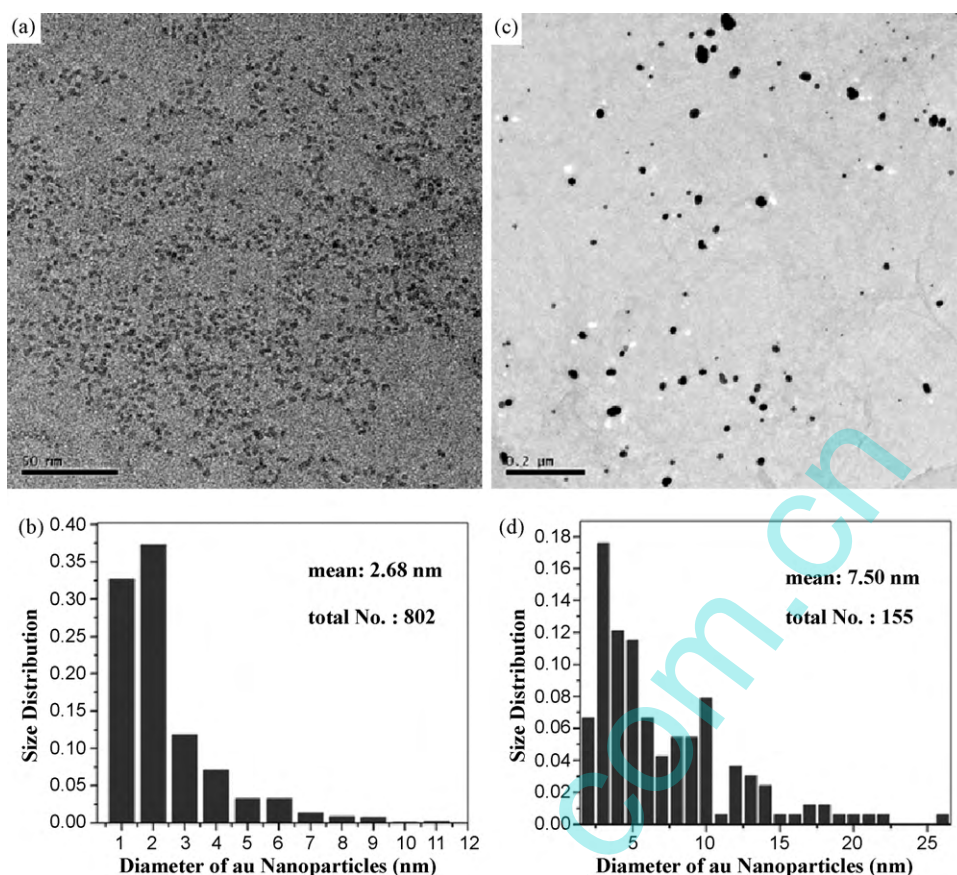
Fig. 4. HRTEM image (a) and size distribution (b) of Au nanoparticles (average diameter is ∼3 nm) on graphene, produced using a mass fraction of 8%. HRTEM image (c) and size distribution (d) of Au nanoparticles (average diameter is 7.5 nm) on graphene, produced using a mass fraction of 21%. The scale bars in (a) and (c) are 50 nm and 0.2 μm, respectively.

the average diameter of the Au nanoparticles increases to about 7.5 nm when the mass fraction is 21% (Fig. 4(c)). This result is consistent with previous studies on metallic nanoparticles, where nanoparticle size was easily controlled by the amount of corresponding precursors [36]. The sizes distributions of the Au nanoparticles are further confirmed by UV–vis analysis (Fig. 7S, Supporting Information).

As shown in the XPS spectra (Fig. 5), the binding energy (4f7/2) of the smaller Au nanoparticles (2–3 nm) on graphene (Fig. 5(a)) is obviously blue shifted by 0.6 eV compared with the larger Au nanoparticles (∼7.5 nm) (Fig. 5(b)). This energy shift could be interpreted as the effect of cluster size on core level binding energy [37]. An similar size effect has been also reported in Au nanoparticles on another catalyst carrier [38]. It has been hypothesized that the size-dependent changes in electronic structure may cause unusual catalytic properties [39].

3.2. Suzuki reaction catalyzed by Au–graphene hybrids

The catalytic activity of the Au–graphene hybrids is explored in the Suzuki reaction of iodobenzene with phenylboronic acid to the form carbon–carbon bond of biaryls (Scheme 1). These reactions are generally carried out under an inert atmosphere in a mixture of organic solvent and aqueous inorganic base [40]. However, recent studies have indicated that the presence of water is required for the Suzuki reaction [41,42]. In this study, we investigate the reaction with Au–graphene catalyst in air with water as the solvent, to develop a green and low-cost strategy.

To optimize the reaction condition, a series of experiments with different qualities of Au–graphene catalysts have been carried out as illustrated in Fig. 8S (Surpporting Information).

Optimum conversion and selectivity are both obtained using a mole fraction of 1.0% of Au–graphene catalysts in a reaction for 4 h at 100 °C. The reactions are also carried out under similar condition with Au nanoparticles (synthesis in Scheme 1S, Surpporting Information) as catalysts. The conversion (55.7%) and selectivity (27.3%) are much lower than with Au–graphene catalysts. The graphene sheets can stabilize the supported Au nanoparticles against aggregation, resulting in better catalytic activity than pure Au nanoparticles.

As a comparison, the reaction is also performed with palladium (II) acetate, which is commonly used to catalyze the Suzuki reaction [43]. Its conversion and selectivity under the same conditions are 79.3% and 85.6%, respectively. This result indicates the catalytic activity of the Au–graphene hybrid is comparable to the commercial palladium (II) acetate. Further study should be carried out to improve the catalytic activity of the Au–graphene hybrid.

The Suzuki reactions are carried out with different Au–graphene catalyst samples. Table 1 summarizes the performance of these Au–graphene catalysts in water at 100 °C. The results confirm that the ∼7.5 nm Au nanoparticles supported on graphene

Table 1

Catalytic results of different Au–graphene hybrids in the Suzuki reaction under same reaction conditions.

Catalyst[a]	Conversion (%)	Selectivity (%)
8 wt% Au–graphene (2–3 nm)	76.5	85.8
21 wt% Au–graphene (∼7.5 nm)	59.8	11.2

[a] Iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (4 mmol), H_2O (20 mL), Au–graphene hybrids (1 mol%), 100 °C, 4 h.
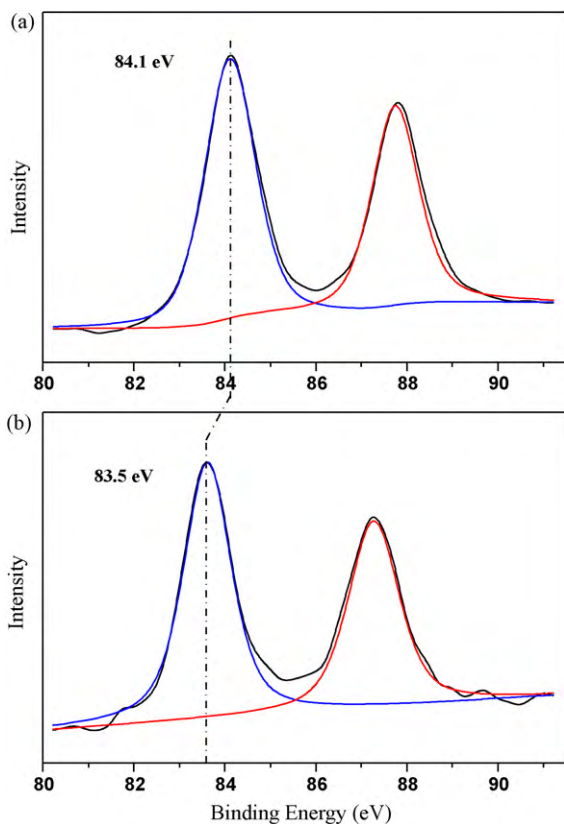
Fig. 5. Au 4f electron region of the X-ray photoelectron spectrum of Au–graphene hybrids produced with a mass fraction 8% (a) (average diameter of Au nanoparticles is 2–3 nm) and the corresponding spectrum of large Au nanoparticles (about 7.5 nm) on graphene (b). The binding energy of the smaller Au nanoparticles (2–3 nm) on graphene shows an obvious blue shift of 0.6 eV compared with the result for the larger Au nanoparticles.

(mass fraction of 21%) are less catalytically active than ~3 nm Au nanoparticles (mass fraction of 8%). The increased catalytic activity of the smaller nanoparticles deposited on graphene may be attributed to more active sites on their surfaces. This result is consistent with previous studies [44,45], which highlighted the important role that the size of metal catalysts plays in C–C bond forming reactions such as the Suzuki reaction. The ability to precisely control the size of the Au nanoparticles formed on graphene is therefore an advantage of our method.

The recyclability of Au–graphene catalyst is also investigated. The catalysts are recovered by simple centrifugation and washing with deionized water. The Au–graphene hybrids are reused without obvious loss of their catalytic activity, and the conversion loss was within 3% for five cycles (Table 2).

Bromobenzene and allyl iodide are also used in the Suzuki reaction with phenylboronic acid to produce the corresponding biaryls and allyl–aryls. The results are summarized in Table 3. The reactivities decrease when these reactants are used instead of iodobenzene. This decrease may be attributed to the differences in the strengths of C–I bond and C–Br bond, as well as to the different electron-withdrawing abilities within the halogen substrates [46].

Table 2

Reuse of Au–graphene hybrids (2–3 nm Au nanoparticles) catalysts for Suzuki Reaction at 100 °C for 4 h.

Use	1st	2nd	3rd	4th	5th
Conversion (%)	76.5	76.7	76.2	74.9	73.4

Table 3

Suzuki coupling of allyl iodide and bromobenzene with phenylboronic acid
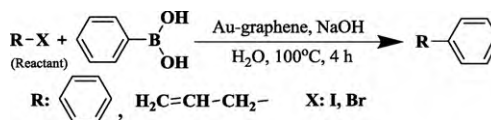
Reactant[a]	Conversion (%)	Selectivity (%)
Bromobenzene	54.2	26.1
Allyl iodide	40.3	26.0

[a] Reactant (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (4 mmol), H_2O (20 mL), Au–graphene hybrids (2–3 nm Au nanoparticles, 1 mol%), 100 °C, 4 h.

4. Conclusion

A simple, economical and environmentally friendly process was developed to homogeneously deposit Au nanoparticles with controlled sizes on graphene sheets. The catalytic activity of the hybrids was investigated in the Suzuki reaction for the first time. The Au–graphene catalyst showed impressive performance even when the reaction was carried out in water under aerobic conditions. This study suggests graphene, as an economical substitute for carbon nanotubes, could act as a prominent support in heterogeneous catalysis. These catalysts were easily recovered. Furthermore, this study could be extended to other type of graphene hybrids.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.materresbull.2010.06.041.

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