Graphene oxide supported Au–Ag alloy nanoparticles with different shapes and their high catalytic activities

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2013 Nanotechnology 24 125301
(http://iopscience.iop.org/0957-4484/24/12/125301)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 202.113.13.10
The article was downloaded on 05/03/2013 at 06:44

Please note that terms and conditions apply.
Graphene oxide supported Au–Ag alloy nanoparticles with different shapes and their high catalytic activities

Tao Wu¹, Junkui Ma¹, Xingrui Wang¹, Yue Liu¹, Han Xu², Jianping Gao¹, Wei Wang², Yu Liu¹ and Jing Yan¹

¹ School of Science, Tianjin University, Tianjin, 300072, People’s Republic of China
² School of Chemical Engineer and Technology, Tianjin University, Tianjin, 300072, People’s Republic of China

E-mail: jianpinggao2012@126.com and yanjingls2012@163.com

Received 16 November 2012, in final form 3 February 2013
Published 4 March 2013
Online at stacks.iop.org/Nano/24/125301

Abstract
A simple method was developed to fabricate Au–Ag nanoparticle/graphene oxide nanocomposites (Au–Ag/GO) by using simultaneous redox reactions between AgNO₃, HAuCl₄ and GO. The Au–Ag/GO was characterized by x-ray photoelectron spectroscopy, transmission electron microscopy and energy dispersive x-ray spectroscopy. The GO nanosheets acted as the reducing agent and the support for the Au–Ag alloy nanoparticles. In addition, Au–Ag alloy nanoparticles with different shapes including core–shell-like, dendrimer-like and flower-like were obtained by simply modifying the concentration of the reactants and the reaction temperature. With no reducing or stabilizing agents added, the Au–Ag/GO nanocomposites show superior catalytic performance for the reduction of 4-nitrophenol and for the aerobic homocoupling of phenylboronic acid.

(Some figures supplementary data available from stacks.iop.org/Nano/24/125301/mmedia)

1. Introduction

The synthesis, characterization and assembly of different types of nanoparticles have dramatically advanced over the last 20 years [1, 2]. However, the incorporation of multiple metals into a single system is more useful for most applications than single metal systems. Therefore, the fabrication of alloy nanoparticles has become a major challenge. The optical and catalytic properties of Ag and Au nanoparticles are useful for a diverse range of applications, such as photonics [3], catalysis [4], information storage [5], chemical and biological sensing [6, 7] and surface enhance Raman scattering (SERS) [8]. By combining these two metals into a single entity, the catalytic performance of the material can be enhanced [9] and the surface plasmon absorption of Au–Ag alloy nanoparticles can be varied continuously between the absorptions of monometallic Au and Ag nanoparticles by changing the ratios of the precursors of Au and Ag [10].

Several physical and chemical techniques have been developed to fabricate Au–Ag alloy nanoparticles, such as evaporation–condensation [11], co-reduction [12–15] and galvanic replacement reactions [16–18]. Chen et al used hydrazine as a reducing agent to prepare Au–Ag alloy nanoparticles with mean diameters of 4–22 nm in water-in-oil microemulsions [19]. Mallin and co-workers used borohydride and sodium citrate as reducing and stabilizing agents respectively to prepare Au–Ag alloy nanoparticles with average diameters of 5–7 nm [20]. Zhang et al reported that the shape and composition of Au–Ag alloy nanoparticles with diameters of less than 10 nm can be tuned by very complex methods [21].

Nanoparticles are often deposited onto supporting materials to form catalytic systems. For example, TiO₂ supported Cu–M (M = Pt, Pd, Ru or Rh) bimetallics have
been prepared and used as catalysts for the hydrogenation of nitrites [22]. To date, many materials have been chosen as support materials, such as aluminum [23], carbon nanotubes [24] and polymers [25].

Graphene has attracted a great deal of attention since a monolayer of graphene was successfully fabricated in 2004 [26–29]. Recently, graphene oxide (GO), a derivative of graphene, has been widely studied because of its convenient preparation on a large scale and its unique properties [30–32]. Since GO has a large surface area and abundant functional groups on its surface, it has been used to provide anchoring sites for nanoparticles, such as gold (Au) [33], TiO₂ [34] and ZnO [35], and these nanocomposites display good photocatalytic and electrochemical properties. Many monometallic nanoparticles, such as Pd [36], Au [37], Pt [38] and Ag [39], have been successfully attached to graphene. Most recently, graphene supported bimetallic catalysts have been successfully fabricated, such as a Au–Pt alloy supported on graphene [40]. This material had a high electrocatalytic activity and stability for the oxidation of formic acid. Nanoparticles are often deposited onto supporting materials to form catalytic systems.

In our previous work, a simple method to prepare Au/GO nanocomposites by a redox reaction between HAuCl₄ and GO nanosheets was developed [33]. Here, Au–Ag alloy nanoparticles supported on GO nanocomposites (Au–Ag/GO) were easily fabricated by simultaneously reducing Ag⁺ and AuCl₄⁻ with GO without the use of any additional reductant. In addition, we also determined the factors that affect the shape of the nanoparticles including the reaction temperature, the Au and Ag precursor ratio and the mass ratio of GO to metals. The high catalytic activity for the reduction of 4-nitrophenol and for the aerobic homocoupling of phenylboronic acid were also investigated in this paper.

2. Experimental details

2.1. Materials

The graphite was from Huadong Graphite Factory, China. The chloroauric acid (HAuCl₄) was from Sigma; all other reagents were from Tianjin Chemical Reagent Co. All the chemicals were used as received.

2.2. Preparation of GO

GO was prepared from purified natural graphite by a modified Hummers method. Experimental details are given in the literature [32].

2.3. Preparation of Au–Ag/GO, Au (Au/GO) or Ag (Ag/GO) nanoparticles supported on GO

One milliliter of AgNO₃ aqueous solution (9.4 × 10⁻⁴ M) and 1 ml of aqueous solution of HAuCl₄ (9.4 × 10⁻⁴ M) were mixed with 0.25 ml of aqueous GO suspension (8 mg ml⁻¹). The mixture was stirred with a mechanical stirring bar for 20 min at 84°C. During this process, Au–Ag alloy nanoparticles were formed and deposited on the surfaces of the GO nanosheets to form Au–Ag/GO. The Au/GO and Ag/GO were prepared using the same method except that 2 ml of the desired salt solution was used instead of the mixture of both ions.

2.4. Characterization

Ultraviolet–visible (UV–vis) absorption spectra were recorded with a TU-1901 UV–vis spectrophotometer. Photos of the GO materials were recorded with a digital camera (Coolpix S260, Nikon, Japan). Transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDX) measurements and scanning transmission electron microscopy (STEM) were performed using a Philips Tecnai G2F20 microscope at 200 kV. The x-ray diffraction (XRD) patterns of the samples were measured using an x-ray diffractometer (BIX3300) with a reference target, Cu Kα radiation (λ = 1.54 Å), voltage, 30 kV, and current, 30 mA. The samples were measured from 30° to 80° (2θ) with steps of 4° min⁻¹. X-ray photoelectron spectroscopy (XPS) was conducted on an x-ray photoelectron spectrometer (PHI1600 ESCA System, Perkin Elmer, USA). Atomic force microscopy (AFM) images were obtained with a Nanoscope Multimode and an Ex-plore atomic force microscope (Veeco Instruments, USA).

2.5. General procedure for the reduction of 4-NP

First, 2.5 ml of aqueous 4-NP solution (1.54 × 10⁻³ M) was mixed with 0.5 ml of freshly prepared aqueous NaBH₄ solution (0.88 M) and a deep yellow solution was formed. Then, 150 µl of catalyst (for example, Au–Ag/GO with mGO/mAu-Ag = 6.99, bAu-Ag/GO = 0.11 mg ml⁻¹; b represents the mass concentration) was added to the solution and when the solution became colorless it indicated that the reaction was finished.

2.6. The aerobic homocoupling of phenylboronic acid catalyzed by Au–Ag/GO

Phenylboronic acid (61 mg, 0.5 mmol) and NaOH (32.0 mg, 0.8 mmol) were added to an aqueous solution of Au–Ag/GO, Au/GO or Ag/GO and the reaction mixture was allowed to react for 12 h at 90°C with stirring. The mixture was cooled to room temperature and centrifuged. The Au–Ag/GO then settled to the bottom during the centrifugation. The supernatant solution was collected and 0.6 ml of ethyl acetate was added to it. The organic layer was collected and the ethyl acetate was removed with a rotary evaporator to obtain the final product (a white solid). Gas chromatography—mass spectrometry (GC–MS) was used to purify the products and to calculate the conversion yield. The Au–Ag/GO that settled on the bottom of the centrifuge tube was added to new reactants to begin another cycle of reaction and treatment.
3. Results and discussion

Exfoliated GO is readily dispersed in water with mild ultrasonic treatment to form a transparent suspension that is stable for several months (see figure S1(A) available at stacks.iop.org/Nano/24/125301/mmedia). According to the TEM image and the AFM photo (see figures S1(B) and (C) available at stacks.iop.org/Nano/24/125301/mmedia), the GO nanosheets consist of one to several layers.

AgNO$_3$ and HAuCl$_4$ were chosen as the Ag and Au nanoparticle precursors respectively. The Au–Ag alloy nanoparticles were produced and deposited on the GO nanosheets by heating a mixed aqueous solution of HAuCl$_4$, AgNO$_3$ and a GO suspension at 84°C for 20 min. The Au–Ag/GO can also be dispersed in an aqueous solution to form a stable suspension, as shown in figure S1(A) (available at stacks.iop.org/Nano/24/125301/mmedia). The TEM images of the Au–Ag/GO are shown in figure 1 and the images indicate that there are many nanoparticles on the GO nanosheets.

Figure 1(E) is the energy dispersive x-ray (EDX) spectrum of some of the nanoparticles in figure 1(B). The strong elemental gold and silver peaks in this spectrum indicate the co-existence of Au and Ag on the GO. Interestingly, the supported nanoparticles show a dark core and a comparatively pale shell (figures 1(C) and (D)), indicating that these alloy nanoparticles have a core–shell-like structure. A typical STEM image of the sample is shown in figure S2 (available at stacks.iop.org/Nano/24/125301/mmedia) and its corresponding EDX line-scan spectrum (figure 1(G)) suggests that the Au is distributed uniformly in the whole particle whereas the Ag is concentrated in the outside region. These results are consistent with Au–Ag core–shell-like alloy nanoparticles forming on the GO nanosheets.

X-ray photoelectron spectroscopy (XPS) is an effective method to investigate the elemental composition of materials. Figure 2 shows the XPS spectra of GO and Au–Ag/GO. The surface atomic ratio of Au to Ag is only 9:36 (figure 2(B)), which is significantly less than that from the TEM–EDX analysis (6:4). Since XPS can only penetrate a few nanometers of the surface, the signal from the Au core is significantly shielded by the Ag shell during the XPS analysis. Therefore, this result strongly supports the formation of a Au–Ag core–shell-like alloy structure. XPS is also a convenient method to trace changes in the GO since all the carbon and oxygen are from the GO in the Au–Ag/GO. The oxygen content decreased from 24.2% in the GO to 21.76% in the Au–Ag/GO.

The reduction potential of AuCl$_{4}^{-}$ is 0.76 V versus SCE and that of Ag$^{+}$ is 0.79 V versus SCE, and the oxidation potential of GO is 0.48 V versus SCE. Therefore, redox reactions between the GO and the Ag$^{+}$ and AuCl$_{4}^{-}$ probably contributed to the formation of the Au–Ag core–shell-like alloy nanoparticles. In addition, the growth of the Au–Ag nanoparticles after nucleation may involve a galvanic-like process, in which the reduction of Au$^{3+}$ occurs on a Ag nuclei by the electrons transferred from the GO.
Figure 2. XPS spectra of GO (A) and Au–Ag/GO (B). The XPS signature of the Ag 3d doublet (3d_{5/2} and 3d_{3/2}) and the Au 4f doublet (4f_{7/2} and 4f_{5/2}) for the Ag and Au supported on Au–Ag/GO (C).

Figure 3. TEM images of Au–Ag/GO prepared at different reaction temperatures: 0°C (A) and (B), 50°C (C) and (D) and 84°C (figures 1(A)–(D)). Reaction conditions: 20 min, n_{Au}/n_{Ag} = 1:1, m_{GO}/m_{Au–Ag} = 6.99.

The complete reduction of Au and Ag in Au–Ag/GO can be confirmed by the XPS spectra of the Ag 3d doublet (3d_{5/2} and 3d_{3/2}) and the Au 4f doublet (4f_{7/2} and 4f_{5/2}). These are shown in figure 2(C). The Ag 3d_{5/2} and Ag 3d_{3/2} peaks are at 367.8 and 373.5 eV, respectively, and the Au 4f_{7/2} and Au 4f_{5/2} peaks are at 83.7 and 87.5 eV, respectively. All peaks shifted to lower binding energies compared with the standard characteristic metallic Ag^0 peaks at 368.2 and 374.2 eV and Au^0 peaks at 84.0 and 87.7 eV [41, 42]. The negative shift arises from the electron transfer from the GO nanosheets to the Au–Ag alloy [42], which further confirms that the Au–Ag core–shell-like alloy nanoparticles were anchored onto the surface of the GO.

In order to obtain the best reaction conditions for the redox reactions between AgNO_3, HAuCl_4 and GO, the impact of the reaction temperature, the reaction time, the ratio of the precursors of Au and Ag, and the mass ratio of GO to metal precursors on the shape and composition of Au–Ag/GO was investigated. Figures 3(A)–(D) show the TEM images of Au–Ag/GO materials made at different reaction temperatures. Au–Ag alloy nanoparticles can be deposited on GO nanosheets over a wide range of temperatures from 0 to 84°C. The formation of large spherical and flower-like particles at 0°C (figures 3(A) and (B)) may be a result of the aggregation of small metal nanoparticles and the weak stabilizing effect of GO. The average diameters of the spherical and flower-like particles are 20 and 200 nm, respectively. The size of the particles decreased greatly and the flower-like particles totally disappeared when the reaction
temperature was 50 °C (figure 3(C)). At 50 °C, there are two different sizes of nanoparticles on the GO nanosheets and the average diameters of the large and small particles are about 20 and 10 nm respectively. Thus, smaller particles can be obtained with higher temperature. Interestingly, when the temperature was further increased to 84 °C, Au–Ag core–shell-like alloy nanoparticles were formed. These are the Au–Ag alloy nanoparticles that were discussed in detail earlier (figure 1). These results suggest that the shapes of the Au–Ag alloy nanoparticles strongly depend on the reaction temperature and the temperature must be kept at 84 °C to fabricate Au–Ag core–shell-like alloy nanoparticles.

In order to determine the formation process for the core–shell-like alloy structure, several Au–Ag/GO samples were prepared with different reaction times. Figure 4 shows the TEM images of Au–Ag/GO prepared at 3, 8, 15 min and 1 h. TEM images of Au–Ag nanoparticles are known to show banding due to the electron density with the dark regions being due to gold and the light regions due to silver [43, 44]. After 3 min of reaction, there are many nanoparticles supported on the GO nanosheets. A few of them are dark spherical particles with diameters of about ten nm and these can be attributed to gold. The rest are, by comparison, pale particles with irregular shapes and these can be attributed to silver. To obtain further information about the composition of these nanoparticles, HRTEM (figure 4(B)) and EDX analysis (figure S3(A) available at stacks.iop.org/Nano/24/125301/mmedia) were conducted and the results indicate the co-existence of Au and Ag in each nanoparticle.

When the reaction time was increased from 3 to 8 min, many large spherical particles with diameters of about 25 nm appeared and the number of small particles decreased (figures 4(C) and (D)). EDX analysis of some of the nanoparticles in figure 4(D) showed that the intensity of Au was stronger than that of Ag (figure S3(B) available at stacks.iop.org/Nano/24/125301/mmedia). When the reaction time was increased to 15 min, a clear core–shell-like structure appeared and that structure continued to exist when the reaction time was increased to 1 h (figures 4(E)–(H)).

These results imply that the Au–Ag core–shell-like alloy nanoparticles can be obtained over a large range of reaction times (from 15 to 60 min). Therefore, this is a stable and reproducible method of fabricating core–shell-like alloys as far as the reaction time is concerned. The EDX analysis of some of the nanoparticles in figure 4(E) (reaction time = 15 min) showed that the intensity of the Ag becomes equal to that of the Au (figure S3(C) available at stacks.iop.org/Nano/24/125301/mmedia), which can be attributed to the Au–Ag core–shell-like structure that was discussed earlier. It is interesting to note that the Au–Ag core–shell-like alloy nanoparticles were prepared simply with a one-step reaction that did not use any reducing or capping agents; this is a great advantage over other methods [44, 45].

Next, Au–Ag/GO composites were prepared using different ratios of precursors $n_{Au}/n_{Ag}$ (1/9, 1/3, 1/1 and 3/1), and the TEM images of these materials are shown in figure 5. At a low $n_{Au}/n_{Ag}$ ratio (1/9), the Au–Ag core–shell-like alloy nanoparticles are small spherical particles (figures 5(A) and (B)). Most of the cores are in the centers of the core–shell-like nanoparticles, the average diameter of the cores is 4 nm and the average shell thickness is 3 nm. A few small dark Au nanoparticles are also observed.

When the $n_{Au}/n_{Ag}$ ratio was increased to 1/1, most of the Au cores (figures 5(C) and (E)) were near the periphery of the nanoparticles and more Au spherical particles formed compared to the image in figure 5(A). However, when
Figure 5. TEM images of Au–Ag/GO prepared with different $n_{\text{Au}}/n_{\text{Ag}}$ ratios: 1/9 (A) and (B), 1/3 (C) and (D), 1/1 (E) and (F) and 3/1 (G) and (H); UV–vis absorption spectra of these Au–Ag/GO materials (I). Reaction conditions: 84 °C, 20 min, $m_{\text{GO}} = 2$ mg.

The $n_{\text{Au}}/n_{\text{Ag}}$ ratio was increased to 3/1, the core–shell-like structure disappeared totally and many dark and light nanoparticles could be seen.

Figure 5(I) shows the UV–vis spectra of the above Au–Ag/GO nanoparticles. Au and Ag NPs have special absorption bands called surface plasmon resonance (SPR) bands. Au/GO and Ag/GO were also prepared in order to determine the limits of the SPR for Au–Ag/GO and the corresponding maximum wavelengths ($\lambda_{\text{max}}$) were at 512 and 404 nm respectively. The $\lambda_{\text{max}}$ values corresponding to the adsorption peaks of Au–Ag/GO with $n_{\text{Au}}/n_{\text{Ag}}$ ratios of 1/9, 1/3, 1/1 and 3/1 were 410, 430, 500 and 509 nm respectively. Obviously, the $\lambda_{\text{max}}$ shifts from 410 to 509 with increasing $n_{\text{Au}}/n_{\text{Ag}}$ ratio because the relative contents of Au and Ag change. Only one peak appeared in all the UV–vis spectra, which according to a previous study indicates that the prepared Au–Ag bimetallic nanoparticles have a mixed alloy structure [45]. In order to describe this kind of structure clearly, we called it a core–shell-like alloy nanoparticle. Therefore, the shape of the Au–Ag alloy nanoparticles depends on the ratio of the two metal precursors and Au–Ag core–shell-like alloy nanoparticles only form with a suitable $n_{\text{Au}}/n_{\text{Ag}}$ ratio.

The effect of the mass ratio of GO to the metal precursors ($m_{\text{GO}}/m_{\text{Au–Ag}}$) was examined by changing the amount of GO added to the reactants to give a ratio of 2.79 or 6.99. When $m_{\text{GO}}/m_{\text{Au–Ag}}$ was 2.79, many dendrimer-like particles appeared on the GO nanosheets, as shown in figures 6(A) and (B). These particles were composed of small nanoparticles with sizes of about 1.3 µm. The EDX analysis of one of these particles showed the existence of both Ag and Au (figure S5 available at stacks.iop.org/Nano/24/125301/mmedia), which indicates that the dendrimer-like particles are composed of both Ag and Au.

The reason for the formation of dendrimer-like particles is not clear but it probably results from the aggregation of small nanoparticles which occurs because of the weak stabilizing effect of the GO suspension. The metal nuclei first form and deposit on the GO nanosheets and then gradually the Au–Ag alloy nanoparticles form. The number of nuclei that deposit on one single GO nanosheet is high because of the low $m_{\text{GO}}/m_{\text{Au–Ag}}$; therefore, the large number of small nanoparticles can easily aggregate to form large particles like the dendrimer-like particles.

When $m_{\text{GO}}/m_{\text{Au–Ag}}$ was increased to 6.99, no dendrimer-like particles were produced after heating for 20 min. The majority of particles were Au–Ag core–shell-like alloy nanoparticles with an average diameter of 8 nm, although there were some small Ag particles. The small nanoparticles did not aggregate to form large particles due to the stabilizing effect of the GO. Therefore, the nuclei grew into metallic nanoparticles like Au–Ag core–shell-like alloy or Ag nanoparticles.

The above results show that the relative mass of GO to metals strongly affects the shape of the Au–Ag particles. Therefore, XPS was used to investigate what happened to the GO during the formation of the Au–Ag alloy nanoparticles. Compared to the original GO, the relative intensities of
Figure 6. TEM images of Au–Ag/GO with different mGO/mAu–Ag ratios: 2.79 (A)–(D) and 6.99 (E)–(H). Reaction conditions: 84 °C, 20 min, nAu/nAg = 1:1.

The catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-NP) with an excess amount of NaBH₄ has often been used as a model reaction to evaluate the catalytic performance of metal nanoparticles [46–48]. The metal particles start the catalytic reduction by relaying electrons from the donor BH₄⁻ to the acceptor 4-NP which is adsorbed on the Au–Ag/GO. Thus, this reaction was chosen to investigate the catalytic activity of Au–Ag/GO for the reduction of a nitroaromatic compound.

In order to establish an energy saving and environmentally friendly process, room temperature and distilled water were chosen as the reaction conditions. A 2.5 ml aliquot of 1.54 × 10⁻³ M 4-NP solution and 0.5 ml of 0.88 M NaBH₄ solution were mixed in a 3 ml standard quartz cuvette and then a UV–vis spectroscope was used to monitor the absorption maximum of 4-NP at 400 nm. The reduction of 4-NP to 4-AP can be achieved in the presence of NaBH₄ without using any catalyst, but it requires about 430 min. When Au–Ag/GO was added, the reaction was complete in less than 60 s (mGO/mAu–Ag = 6.99).

The reaction kinetics can be monitored easily from the time-dependent absorption spectra, which show the decrease in the intensity of the UV–vis absorption peak at 400 nm with time, and the concomitant development of a new peak ascribed to 4-AP at 300 nm (figure 7(A), mGO/mAu–Ag = 6.99). Since the concentration of NaBH₄ is very high compared with 4-NP, the reaction follows pseudo-first order reaction kinetics [48]. Thus, the pseudo-first order rate constant of the reaction can be calculated from the equation ln(A_t/A_0) = Kt, where A₀ and Aₜ are the absorbance values of 4-NP initially and at time t, respectively, and K is the rate constant. The plot of ln(A_t/A_0) versus time (t) is linear in the presence of the Au–Ag/GO, as shown in figure 7(B). The rate constant calculated from the slope of the plot is 0.05 s⁻¹. In order to compare our results with those reported in the literature, we calculated the ratio of the rate constant k to the total weight of the catalyst, k = K/m, which is called the activity factor. The k of the Au–Ag/GO was 0.05 s⁻¹/(0.0165 mg) = 3 × 10³ s⁻¹ g⁻¹, which is much higher than previously reported ratios [49, 50]. However, the reaction time was 3 min when mGO/mAu–Ag was 2.79.

Dendrimer-like particles have lower surface areas than core–shell-like spherical nanoparticles; this results in longer reaction times. In addition, GO facilitates this reaction because GO has a high affinity for the adsorption of 4-NP via π–π stacking interactions. This increases the concentration of 4-NP near the catalyst which speeds up the reaction. This explanation is supported by the fact that the reduction of 4-NP was complete in about 180 min when only GO was used as the catalyst.

Au–Ag/GO was also used as a heterogeneous catalyst for the homocoupling of phenylboronic acid. In order to establish an environmentally friendly process, distilled water was again chosen as the reaction medium. The influence of Au–Ag/GO with different nAu/nAg ratios and mGO/mAu–Ag ratios on the coupling reaction was investigated. Yields of 85%, 82%, 70% and 55% were acquired respectively when Au–Ag/GO was used as the catalyst.
Table 1. Homocoupling of phenylboronic acid on Au–Ag/GO catalysts. Reaction conditions: 0.5 mmol of phenylboronic acid, NaOH (0.8 mmol), 3 ml of solvent, reaction time 4.5 h. GC–MS yields (GC–MS means gas chromatography—mass spectrometry). The first, second, third and fourth headings in the left hand column refer to cycles with the catalysts being recovered after successive cycles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Au–Ag/GO (mGO/mAu–Ag)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cat¹: 2.79</td>
</tr>
<tr>
<td>First</td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>Second</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>Third</td>
<td></td>
<td>92</td>
</tr>
<tr>
<td>Fourth</td>
<td></td>
<td>91</td>
</tr>
</tbody>
</table>

Figure 7. The UV–vis absorption spectra for the reduction of 4-NP by NaBH₄ in the presence of Au–Ag/GO (mGO/mAu–Ag = 6.99) as the catalyst (A); the natural logarithm of the absorbance at 400 nm versus the reduction time (B).

1:9 was used to catalyze the coupling reaction. Considering the catalytic performance of these four catalysts and the fact that Ag was used to replace Au to reduce the cost, the 1:1 \( n_{Au}/n_{Ag} \) ratio was selected as the typical ratio to discuss. The other three ratios are not discussed further in this paper. Then, when Au–Ag/GO with different \( m_{GO}/m_{Au–Ag} \) (\( n_{Au}/n_{Ag} = 1:1 \)) including 2.79 (Cat¹) and 6.99 (Cat²) was used, yields of 95% and 82% were obtained, respectively (table 1). However, the yields were 90% and 30% respectively when Au/GO and Ag/GO were used. Previous papers have proven that Au nanoparticles have excellent catalytic activity for this reaction [51]. Therefore, the higher yield for Cat¹ is reasonable since there is more Au content in the exterior of Cat¹ compared to Cat². The Au–Ag alloy without GO was also prepared and used to catalyze the reaction. The yield was 45%; therefore, the GO acted as the support and stabilizing agent to effectively avoid aggregation of Au–Ag nanoparticles, and the \( \pi–\pi \) interaction between the GO and the phenylboronic acid concentrated the reagents in the surroundings of the catalyst to improve the catalytic activity. In addition, the catalyst Au–Ag/GO is easily recovered by centrifugation so its recyclability was investigated. The data in table 1 show that the yield was over 91% after four recycles. These results indicate that the Au–Ag/GO catalyst is highly active and has excellent recyclability. According to previous studies, the origin of the catalytic activity of Au–Ag/GO may contribute to the interfacial regions between the nanoparticles and the GO [52–54].

4. Conclusions

In conclusion, a simple method to fabricate Au–Ag/GO by simultaneous redox reactions between AgNO₃, HAuCl₄ and GO has been demonstrated. The GO nanosheets act as both a reducing agent and a support for the Au–Ag bimetallic nanoparticles. By modifying the concentration of the reactants, the reaction temperature and the reaction time, Au–Ag nanoparticles with different shapes including core–shell-like, flower-like, dendrimer-like and non-core–shell-like can be obtained. With no reducing or stabilizing agents added, the Au–Ag/GO shows superior catalytic performance for the reduction of 4-nitrophenol and the aerobic homocoupling of phenylboronic acid. The Au–Ag/GO could potentially be applied in catalyzing green chemical reactions.
Acknowledgments

This work was supported by the National Science Foundation of China (21074089, 21276181 and 51202158).

References


[41] Zhang P, Shao C L, Zhang Z Y, Zhang M Y, Mu J B, Guo Z C and Liu Y C 2011 In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol Nanoscale 3 3357–63


[43] Zhang Q B, Xie J P, Lee J Y, Zhang J X and Boothroyd C 2008 Synthesis of Ag@AgAu metal core/alloy shell bimetallic nanoparticles with tunable shell compositions by a galvanic replacement reaction Small 4 1067–71


[45] Zhang X and Su Z H 2012 Polyelectrolyte-multilayer-supported Au@Ag core–shell nanoparticles with high catalytic activity Adv. Mater. 24 4574–7

[46] Premkumar T, Lee K and Geckeler K E 2011 Shape-tailoring of gold nanostructures: can a detergent act as the reducing or protecting agent? Nanoscale 3 1482–4


