Electronic Supplementary Information (ESI) for Gold Nanoparticle Supported on Ionic Liquid-modified Graphene Oxide as an Efficient and Recyclable Catalyst for One-Pot Oxidative A³-coupling reaction of benzyl alcohols

Siyavash Kazemi Movahed, Noushin Farajinia Lehi, and Minoo Dabiri*

Shahid Beheshti University, Tehran, Islamic Republic of Iran.

TABLE OF CONTENTS

Contents	Page
Synthesis Preparation of Graphene Oxide (GO)	S3
Preparation of IL	S3
Preparation of GO-IL nanocomposite	S4
Preparation of Au@GO-IL nanocomposite	S4
General procedure for the Oxidative A ³ -coupling reaction	S4
Characterization	S4
Fig. S1. FT-IR spectra GO, GO-IL and Au@GO-IL nanocomposites.	S6
Fig. S2. XRD patterns GO and Au@GO-IL nanocomposites	S7
Fig. S3. TGA plots of GO, GO-IL and Au@GO-IL nanocomposites.	S8
Fig. S4. Scanning electron micrograph of a) Au@GO-IL nanocomposite and corresponding quantitative EDS element mapping of b) Au, c) N and d) Si.	S 9
Fig. S5. TEM micrographs of a) GO, b) GO-IL nanocomposites.	S10
Fig. S6. ¹ H NMR spectrum of IL	S11
¹ H NMR spectra of Products	S13-S16
Reference	S17

Preparation of GO

The graphite powder (2.5 g) was first treated with a mixture of 12.5 ml of concentrated H₂SO₄ with 2.5 g K₂S₂O₈ and 2.5 g P₂O₅. The mixture was kept at 80 °C for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 °C) concentrated H₂SO₄ (125 ml). Then KMnO₄ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H₂O₂ was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and then was dialyzed against DI water. The resulting GO solid was dried in air.^{s1}

Preparation of IL

In a well-dried 25 mL Schlenk flask, (3-chloropropyl)trimethoxy silane (10 mmol) was added to 1-methylimidazole (10 mmol), and then the system was evacuated and purged with argon five times. After being stirred at 90 °C for 48 h under argon atmosphere, the resulting mixture was allowed to cool down to room temperature, was washed with dry ethyl acetate four times and dried under vacuum for 24 h at room temperature. The finally obtained ionic liquid was a kind of yellowish sticky liquids.^{s2} The ¹H NMR (300 MHz) spectral data for the ionic liquid is as follows: $\delta = 0.43$ (m, 2H), 1.81(m, 2H), 3.39 (s, 9H), 3.9 (m, 2H), 4.1 (m, 2H), 7.3 (s, 1H), 7.6 (s, 1H), 10.3 (s, 1H).

Preparation of GO-IL nanocomposite

The GO (0.20 g) was ultrasonically dispersed in 100 mL of ethanol. Then, IL (2 mmol) was added to the GO suspension under stirring, and refluxed for 12 h. The yielded suspension

was filtered and washed with ethanol for several times to get a purified GO-IL. The loading of imidazolium was determined to be 2.70 mmol.g⁻¹ by means of the nitrogen content obtained from elementary analysis (CHN).

Preparation of Au@GO-IL nanocomposite

The GO-IL (0.4 g) was ultrasonically dispersed in 40 mL of DI water. Then, 17.2 mg of HAuCl₄ was added to the GO-IL suspension under stirring. The mixture was kept at room temperature for 3 h with constant stirring. The resulted precipitation was collected and repeated washing with DI water and Ethanol, and dried at room temperature. The ICP analysis gave the actual Au contents as 2.07 wt.% for Au@GO-IL nanocomposite.

General procedure for the Oxidative A³-coupling reaction

A mixture of benzylalcohol (1.0 mmol), amine (1.2 mmol), phenylacetylene (1.3 mmol) in H₂O (3 mL) under bubbling of air was refluxed at 100 °C for 24 h. After completion of the reaction (TLC), the heterogeneous mixture was cooled to room temperature and filtered through a pad of celite. The filtrate was concentrated and then residue was purified by thin layer chromatography (SiO₂, Ethyl acetate and *n*-Hexane (1:3)) to yield pure product. The catalysts were recovered by simple filtration and washed extensively with ethylacetate and deionized water and drying in the air.

Characterization

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation ($\lambda =1.5406$ Å). XPS analysis was performed using a Gammadata-scienta ESCA 200 hemispherical analyzer equipped with an A1 Ka (1486.6 eV) X-ray source. Raman spectra of GO, GO-IL and Au@GO-IL nanocompositeS were recorded on a Bruker SENTERR (2009) with an excitation beam wavelength at 785 nm. Scanning electron microscopy and EDX mapping characterizations of Au@GO-IL nanocomposite were performed using an electron microscopy Philips XL-30 ESEM. Transmission electron microscopy characterization of GO-IL and Au@GO-IL fresh and reused nanocomposites were performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 kV. HNMR spectra were recorded on a BRUKERDRX-300AVANCEspectrometer. NMR spectra were obtained in DMSO- d_6 using TMS as internal standard. The concentration of gold was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The thermal stability of the GO, GO-IL and Au@GO-IL nanocomposites were determined using a thermogravimetric analyzer (TGA/DTA BAHR: STA 503) under air and a heating rate of 5 °C min⁻¹. Elemental analysis of GO-IL nanocomposite was performed using an Elementar Analysensysteme GmbH VarioEL CHNS. FT-IR spectra of GO and Au@GO-IL nanocopmosite were studied (Fig. S1, ESI[†]). In the spectrum of GO, the characteristic bands at 1049, 1235, 1402, 1623 and 1732 cm⁻¹ correspond to the C–O–C stretching vibrations, the C–OH stretching peak, the O–H deformation of the C–OH groups, the C=C stretching mode and the C=O stretching vibrations of the –COOH group, respectively.^{S3} The FT-IR spectrum of GO-IL, exhibited new three peaks around 1566, 1084 and 744 cm⁻¹, compared with the FT-IR spectroscopy of GO. These peaks corresponded to the ring vibration of the imidazole,^{S2} and stretching vibrations of Si–O–C, respectively, and provide direct evidences for the successful silylanization of GO.^{S4}



Fig. S1. FT-IR spectra GO, GO-IL and Au@GO-IL nanocomposites.

X-ray Diffraction (XRD) patterns of GO and Au@GO-IL are displayed in Fig. S2. It can be seen that GO shows a strong diffraction peak centered at 2θ =10.8° corresponding to the (001) interlayer spacing of 0.81 nm. In the XRD patterns of Au@GO-IL where the peaks at 2θ = 38.0°, 44.1°, 64.5° and 77.5° can be assigned to the (111), (200), (220) and (311) crystal face of Au that indicates the nanoparticles are the pure metallic fcc gold (JCPDS No: 4-0784). Also, the intensity of the peak at 10.9° significantly decreased, and a broad diffraction peak at 2θ = 20-30° appeared, indicating that IL was conjugated onto the surface of GO.



Fig. S2. XRD patterns GO and Au@GO-IL nanocomposites

TGA plots of GO, GO-IL and Au@GO-IL nanocomposites are shown in Fig. S2. In the GO, the weight lost was about 58% at temperatures below 154°C, due to pyrolysis of the labile oxygen-containing functional groups. In contrast, the GO-IL and Au@GO-IL nanocomposites showed good thermal stability. The total weight lost for GO-IL and Au@GO-IL nanocomposites were only 16.5% and 4.2% at temperatures below 153 °C, respectively.



Fig. S3. TGA plots of GO, GO-IL and Au@GO-IL nanocomposites.

A scanning electron microscopy (SEM) image of the Au@GO-IL displayed twodimensional structures with crumpling feature (Fig. S3a). The density and distribution of the Au and IL group on the Au@GO-IL nanocomposite are evaluated by quantitative energy dispersive X-ray spectroscopy (EDS) mapping. As can be seen in Fig. S4b-d, rather than only located at the edges of graphene sheets, the elements Au, N and Si are found to be uniformly dispersed on the whole surface of Au@GO-IL nanocompiste indicating the homogeneous distribution of the Au and IL group.



Fig. S4. Scanning electron micrograph of a) Au@GO-IL nanocomposite and corresponding quantitative EDS element mapping of b) Au, c) N and d) Si.



Fig. S5. TEM micrographs of a) GO, b) GO-IL nanocomposites.



Fig. S6. ¹H NMR spectrum of IL

All of products are known compounds and were reported previously.

The peaks for *n*-Hexane and Ethyl acetate residue as solvents in thin layer chromatography high filed in spectra were previously observed (H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512 (Table 1)).

 δ (ppm) 0.87 and 1.30 for *n*-Hexane.

 δ (ppm) 1.27, 2.05 and 4.12 for Ethyl acetate.

 δ (ppm) 1.61 for H₂O.









References

- S1-W.S. Hummers and R.E. Offeman J. Am. Chem. Soc., 1958, 80, 1339; N.I. Kovtyukhova, P.J. Olliver, B.R. Martin, T.E. Mallouk, S.A.Chizhik, E.V. Buzaneva and A.D. Gorchinsky Chem. Mater., 1999, 11, 771.
- S2-H. Yang, X. Han, G. Li, and Y. Wang, Green Chem., 2009, 11, 1184.
- S3-H. T. Hu, X. B. Wang, F. M. Liu, J. C. Wang and C. H. Xu, Synth. Met., 2011, 161, 404.
- S4-S. Hou, S. Su, M. L. Kasner, P. Shah, K. Patel and C. J. Madarang, *Chem. Phys. Lett.*, 2010, **501**, 68.