Electronic Supplementary Material (ESI) for RSC Advances.

Novel synthesis of Silver/Reduced Graphene Oxide nanocomposite and its high catalytic activity towards hydrogenation of 4-nitrophenol

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Supporting Information (SI)

Preparation of Graphene Oxide (GO).

All the chemical reagents used in the experiment were analytical grade without further purification. Yellow power of Graphene oxide (GO) was fabricated from nature graphite as the same as our recently reported method.[1]

Preparation of RGO aerogel

A 20 mL portion of 2 mg/mL GO aqueous dispersion was sealed in a 35 mL Teflon-lined autoclave and maintained at 180 ^oC for 12 h. Then, cylindrical and black graphene hydrogel was formed when the autoclave was cooled naturally. RGO aerogel was obtained after the freezing-drying of graphene hydrogel.

Catalytic property of Ag/RGO:

1 mL 4-NP or MB or RhB or MO (10 ppm) was mixed with 0.6 mL $NaBH_4$ (0.03 mol/L). Then, 0.2 mL Ag/RGO (2 mg/mL) was injected and shacked homogeneously. The evolution of the conversion of 4-NP was measured at a fixed time interval in a standard quartz cell. For comparison, a series of contrast experiments were also detected.

Characters

X-ray diffraction patterns (XRD) of the samples were recorded on a PERSEE XD-3 diffractometer using Cu Kα (λ= 0.154178 nm) at a scanning rate of 4 ^{o}/min and step scan 0.02°. The accelerating voltage and the applied current were 36 kV and 20 mA, respectively. UV-1800 (SHIMADZU) with wavelength resolution of 1 nm was employed to detect the UV-Visible spectrophotometer of samples using quartz cuvettes. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 870 spectrometer. The morphology and microstructure were observed with a Hitachi S-4800 scanning electron microscope (SEM), a Hitachi JEM-2100 transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM). The Raman characterization of samples was charactered by inVia-Reflex (Renishaw) instrument with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) (VG Microtech2000 ESCA) was performed using a monochromatized Al Kα X-ray source (1486.6 eV). The mass of Ag in sample was determined by an IRIS Intrepid II ICP-OES ICP (Thermo Electron Corporation)

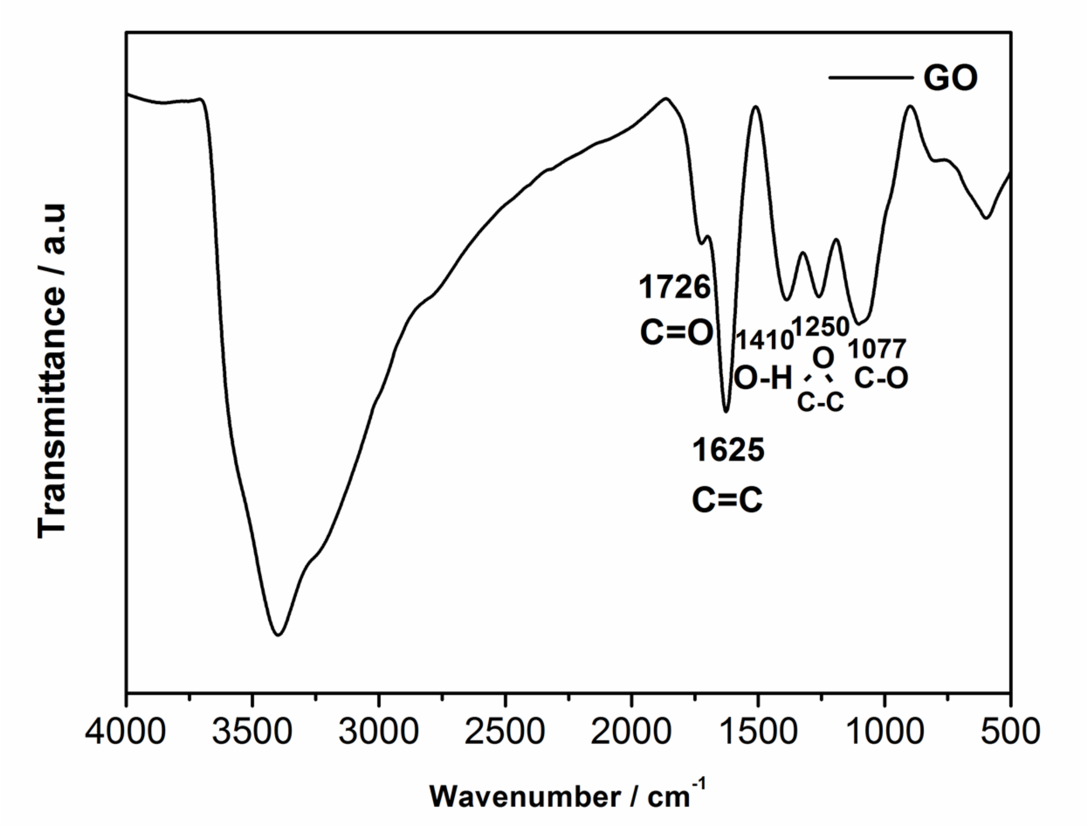
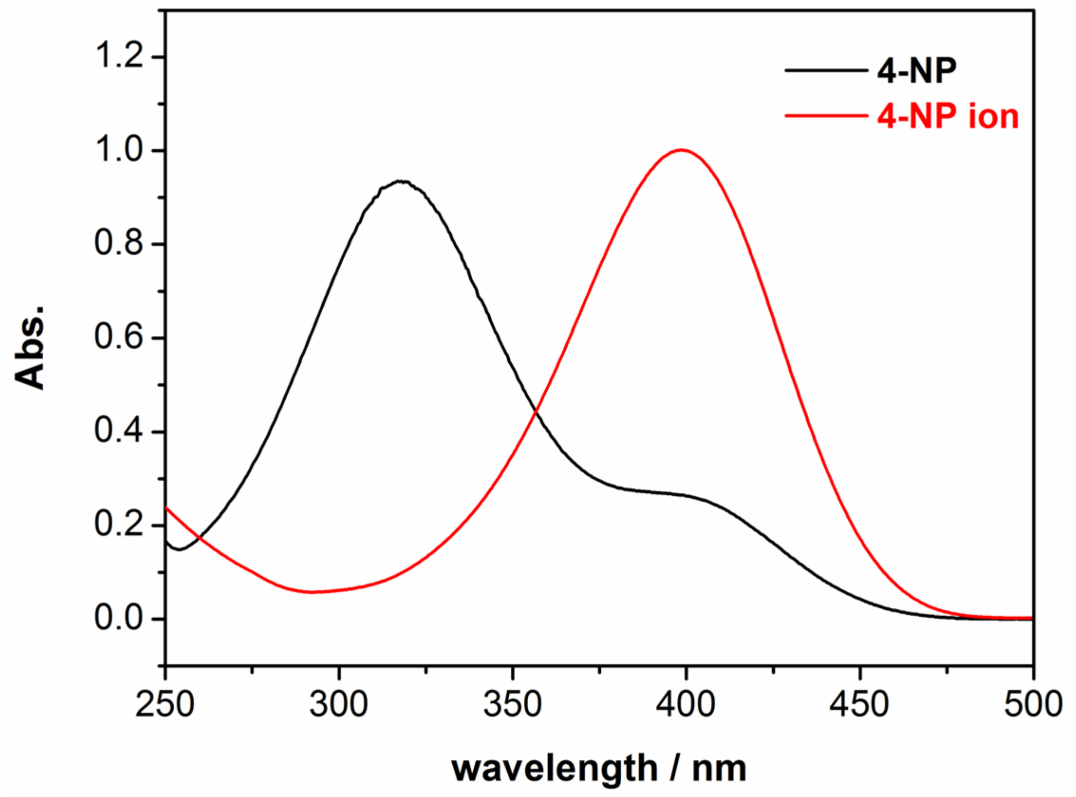


Fig. S1. FT-IR spectrum of GO[2]

The FT-IR peaks of GO corresponding to the oxygen functionalities including the C=O stretching vibration peak at 1726 cm^{-1}, the vibration and deformation peaks of O-H groups at 3395 cm^{-1} and 1410 cm^{-1}, respectively, the C-O (epoxy) stretching vibration peak at 1250 cm^{-1}, and the C-O (alkoxy) stretching peak at 1077 cm^{-1} and 1625 cm^{-1} attributed to C=C bond were observed.



UV-Vis absorption spectra of 4-NP before (black line) and after (red line) adding fresh $NaBH_4$[3]

An aqueous solution of 4-NP has a maximum absorption at 317 nm. After immediate addition of $NaBH_4$, the peak of 4-NP was red shifted from 317 to 400 nm (4-NP ions).[3] The 4-NP ions showed a strong absorbance peak at 400 nm, but their reduced counterparts, 4-AP, has no absorbance at this wavelength, enabling the rate of 4-NP reduction to be readily monitored by the UV-Visible absorption spectroscopy.[4]

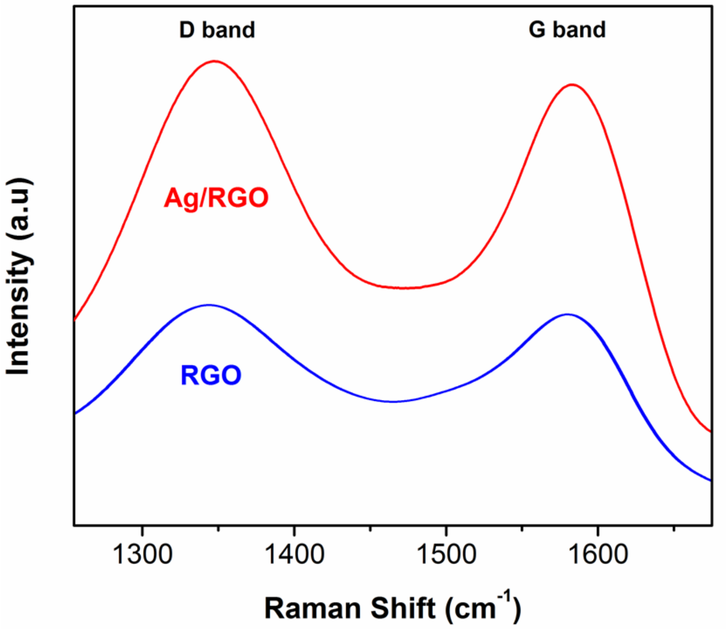


Fig. S2. The Raman spectra of Ag/RGO and RGO

The intensity ratio of D to G of Ag/RGO (1.26) is higher than that of RGO aerogel (1.02), suggesting that the reduction degree of RGO in Ag/RGO composite is higher than RGO aerogel due to $NaBH_4$ can further reduce the GO during the impregnation process.[5]

Table. S1 Comparison of reaction rate constant of current Ag/RGO composite with those of other catalysts reported in literatures.

Species	k* ($min^{-1}g^{-1}$)	References
TOC-Ag-1.0	77.6	J Phys Chem C. 2007, 111, 16750-16760
11.3 nm Ag	88.9	J Phys Chem C. 2009, 114, 977-982
PtAu-nanoflowers/rGO	826.7	J Mater Chem. A. 2015, 3, 5321-5327
AgNP-PG-5K	1375	Nanoscale. 2015, 7, 1201-1208
Au-Fe3O4@MIL-100(Fe)	1638	Nanoscale. 2012, 4, 6298, 6306
PtAu nanocubes	1998	CrystEngComm. 2014, 16, 1606-1610
$Au_{180}(SC_6H_{13})_{100}$	3000	Chem Commun. 2013, 49, 276-278
Ag@Au	3216	Acs Appl Mater Interfaces. 2013, 5, 5072-5079
$Au25(SC_8H_9)_{18}$	5100	Chem Commun. 2013, 49, 276-278
Ag/RGO	2939.3	Current Work

*: k = K/m, where K and m are apparent rate constant and the mass of metal catalyst, repectively.

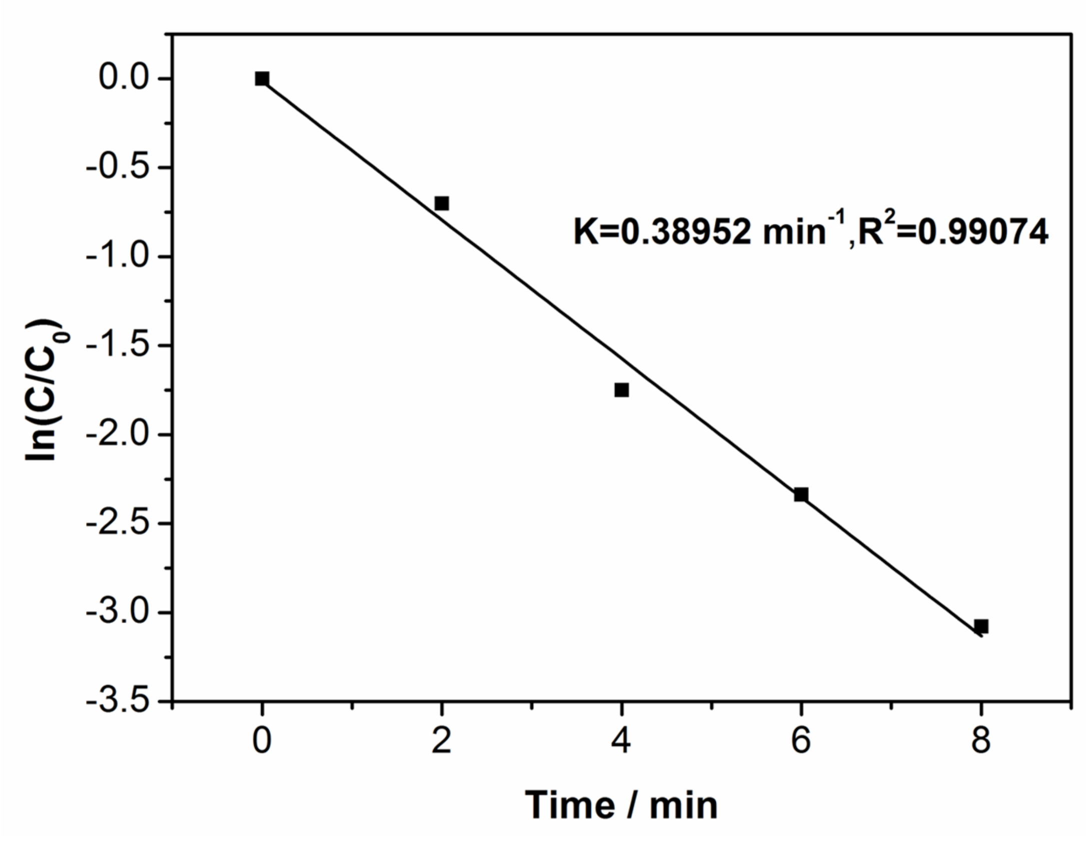


Fig. S3. Pseudo-first-order kinetic rate plots of Ag/RGO[6]

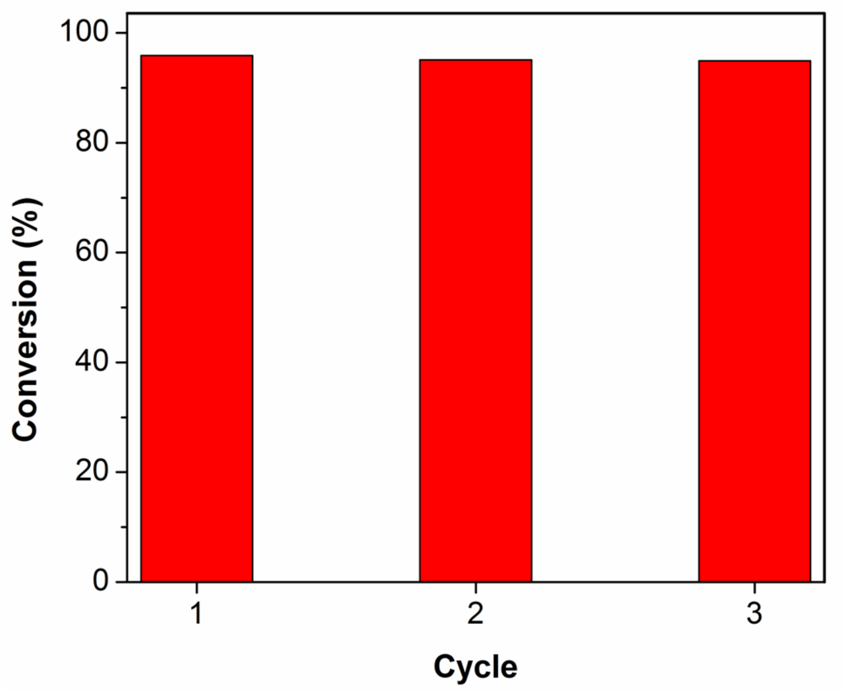


Fig .S4.The reusability of Ag/RGO composite as catalyst in the reduction of 4-NP

References

1. XY Liu, YF Zhou, WY Nie, LY Song, PP Chen. J Mater Sci. 2015, 50: 6113-6123.
2. JL Zhang, HJ Yang, GX Shen, P Cheng, JY Zhang, SW Guo. Chem Commun. 2010, 46: 1112-1114.
3. A Gangula, R Podila, M Ramakrishna, L Karanam, C Janardhana, AM Rao. Langmuir. 2011, 27: 15268-15274.
4. S Yang, C Nie, HR Liu, HM Liu. Mater Lett. 2013, 100: 296-298.
5. SD Perera, RG Mariano, K Vu, N Nour, O Seitz, Y Chabal, et al. Acs Catal. 2012, 2: 949-956.
6. P Zhang, CL Shao, ZY Zhang, MY Zhang, JB Mu, ZC Guo. Nanoscale. 2011, 3: 3357-3363.