

Dual role of Zn/acid medium for one-step rapid synthesis of M@rGO (M= Au, Pt, Pd and Ag) hybrid nanostructures at room temperature

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Experimental Details:

Graphene oxide (GO) was synthesized according to the Hummers' method. Then 25 mg of graphene oxide was taken in 50 ml of water solution and dispersed in the solution by ultrasonication for about 1 h. Then deep brown colour solution was collected by centrifugation. In order to synthesize Au@rGO (reduced graphene oxide), 10 ml of GO solution was taken in a glass vial for experiments with 1g of metallic Zn powder and then make a homogeneous solution by around 2-5 minutes sonication. Then we added 10 ml of 1M, 5M and 10M of H₂SO₄ solution along with the 2 ml of 0.01 M HAuCl₄, 3H₂O solution. Then we allow the experiments up to 1h. The excess Zn was removed by adding corresponding acid solution. Then, the products were collected by centrifuges, washing with the DI water several times. All the reaction was carried out in room temperature and ambient pressure. We used K₂PtCl₄, Na₂PdCl₄ and AgNO₃ for the source of Pt²⁺, Pd²⁺ and Ag⁺ for synthesis of Pt@rGO, Pd@rGO and Ag@rGO hybrids nanostructures. rGO is obtained by reducing GO without Mⁿ⁺ ions.

Characterizations:

The presence of Au in the rGO was characterized by X-ray diffraction (XRD) using PANalytical X'Pert Pro equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The Raman scattering measurements of all the sample were performed on a Raman system (WITec) with confocal microscopy at room temperature. A Nd:YAG laser (532 nm) was used as an excitation source. UV-vis and catalysis properties of the Au@rGO was carried out on a Hitachi UV-vis spectrophotometer. The microstructures of the sample were characterized with field emission scanning electron

microscopy (FE-SEM, FEI-INSPECTF50). The layer structure and crystalline nature of the hybrid sample were characterized by using transmission electron microscopy (TEM, JEOL-JEM-2100F) and cross sectional high resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) pattern operated at a 200kV accelerating voltage. The TEM sample was prepared by dispersing the sample in DMF solution by ultrasonic bath and drop-casted on carbon coated copper grid, and then dried for TEM analysis. The X-ray photoelectron spectroscopy was performed for the elemental analysis as well as the reduction of the functional groups of the GO.

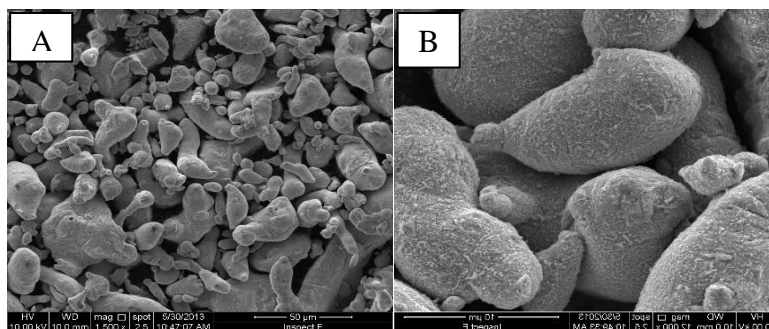
Catalytic Performance test:

The tests for the catalytic reduction of 4-Nitrophenol (4-NP) were carried out at room temperature in batch mode. With the addition of NaBH₄ solution to 4-NP, the color of the solution changes from pale yellow to deep yellow green due to the formation of 4-nitrophenolate ions and the reactant shows a strong absorption peak at 400 nm. An aqueous solution of 0.5 ml 1mM 4-NP was taken in a quartz cuvette with 0.1 ml of freshly prepared 1M NaBH₄ solution, then the UV-vis absorbance spectra were measured every 5 minutes interval without any catalyst. For the catalytic performance test, we took 5 ml of 1mM 4-NP solution in a 15 ml glass vial, added 0.1 ml (250 µg) of hybrid catalyst, and sonicated the solution for dispersion of catalyst material. We then added 1 ml of 1M freshly prepared NaBH₄ solution in the glass vial and shake vigorously. The reaction progress was recorded by UV-absorbance spectrophotometer with regular time interval (2 minutes) in the range of 200-500 nm and the scan speed was 800nm/minute.

Electrochemical Measurements:

For fabrication of the working electrodes of Au/rGO hybrids, 25µL of catalyst ink was loaded onto a glass carbon electrode of 3 mm in diameter and then a drop of Nafion solution (5 wt %) was drop-casted on the electrode. Then the electrode was dried at 60 °C. Cyclic voltammetry was performed in a three-electrode electrochemical cell using Pt foil and an Ag/AgCl electrode as counter-electrode and reference electrode, respectively. For all the electrochemical measurements were performed in 0.1M KOH aqueous solution act as an electrolyte. N₂/O₂ was used to purge the

solution about 30 minutes to achieve an O₂ free or O₂ saturated condition. All the experiments were carried out at room temperature



SEM images of Zn granules, used in all the experiments.

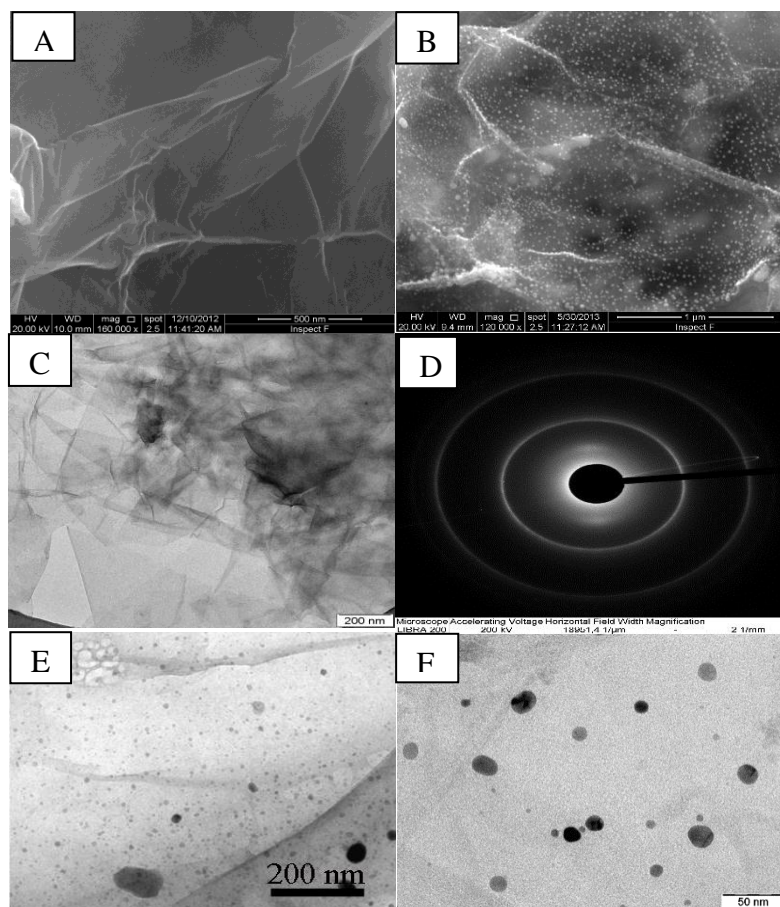


Fig. (A and B) SEM images of GO and Au@rGO hybrids structures. (C and D) TEM images and SAED pattern of GO and (E and F) low and high magnification TEM images of Au@rGO.

ESI-1

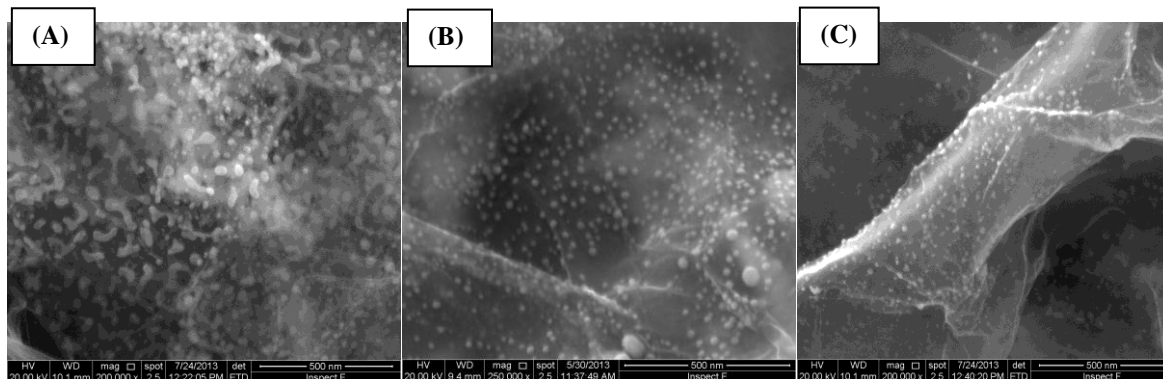


Fig.1 (A-C) SEM images of Au@rGO prepared with 1M, 5M and 10M different molarity of H_2SO_4 acid solution in the reaction mixtures. The gradual decrease of the Au nanoparticles is clearly visible.

ESI-2

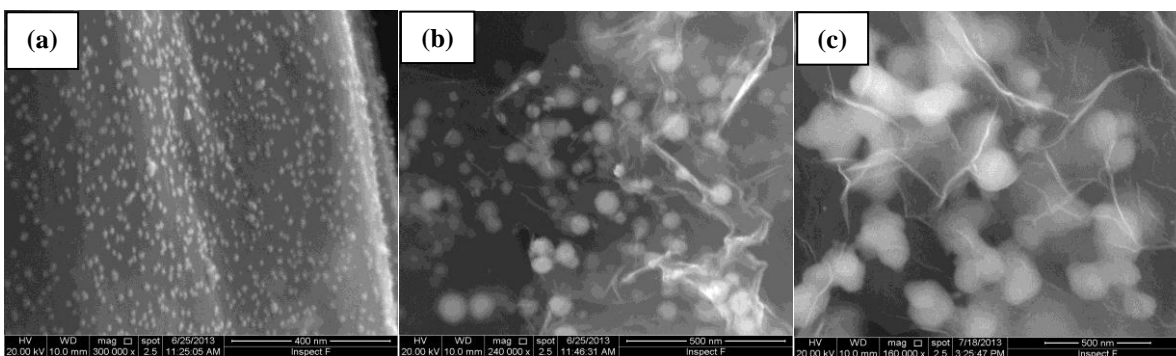


Fig.2 SEM images of (a) Pd@rGO (b) Pt@rGO and (c) Ag@rGO hybrid nanostructures.

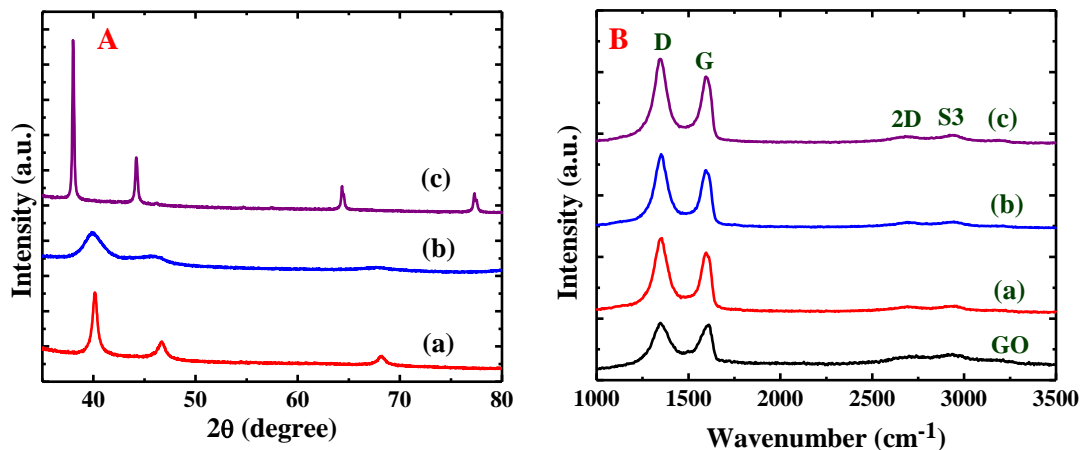


Fig.3 (A) and (B) shows the XRD and Raman spectra of (a) Pd@rGO (JCPDS card No. 87-0643) (b) Pt@rGO (JCPDS card No. 87-0646) and (c) Ag@rGO ((JCPDS card No. 87-0720) hybrid nanostructures.

ESI-3

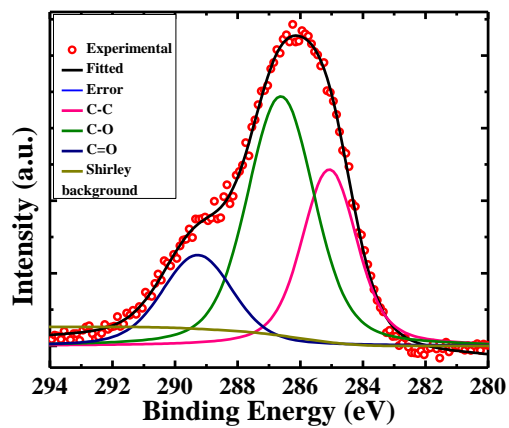


Fig.4 XPS spectra of C1s of the GO, which shows the C-C, C-O and C=O bonding energy corresponding to the 284.4, 286.54 and 286.3 eV, respectively.

ESI-4

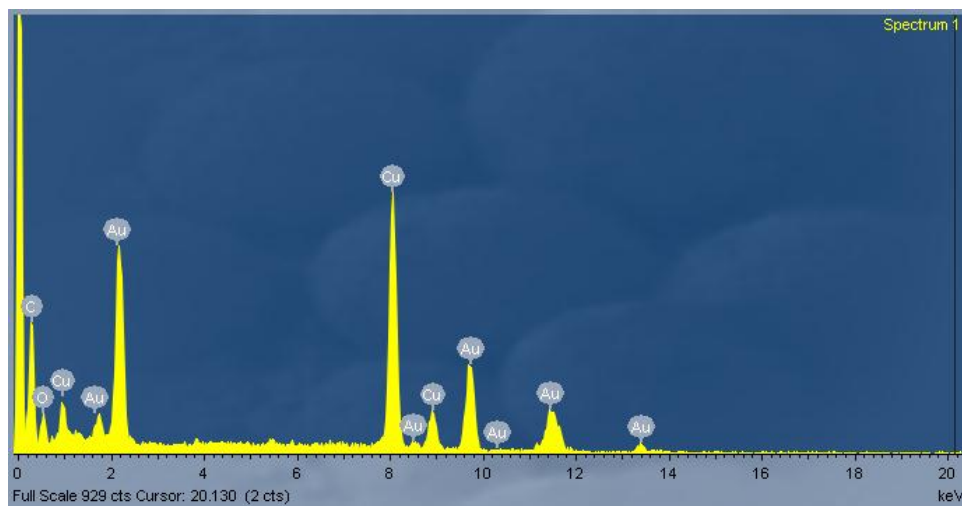


Fig.5 Energy dispersive x-ray spectroscopy (EDS) of Au@rGO hybrid nanostructures.

ESI-5

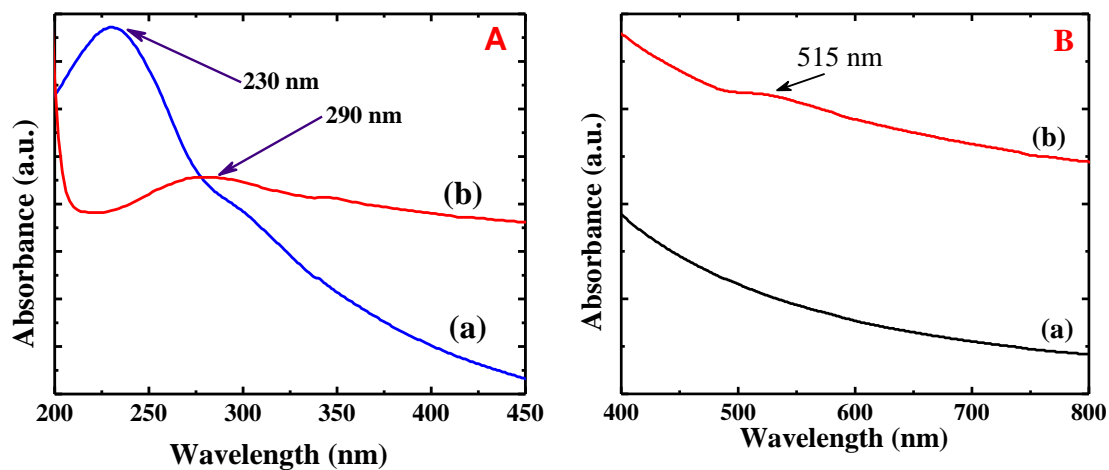


Fig.6 (A, B) shows the UV-visible spectroscopy of the (a) GO and (b) Au@rGO hybrid nanostructures at different wavelength ranges.

ESI-6

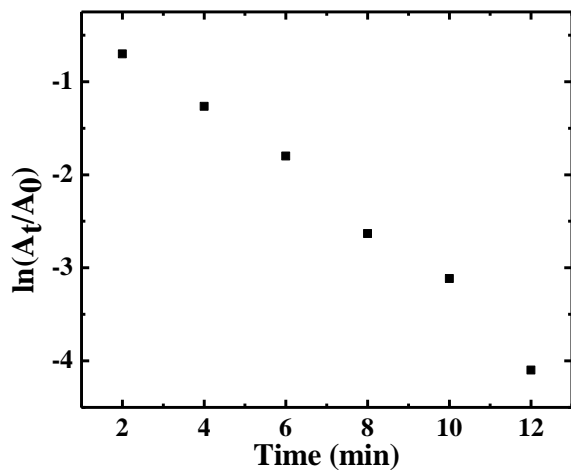


Fig.7 $\ln(A_t/A_0)$ vs time for the reduction of 4-NP by NaBH_4 in the presence of Au@rGO.

ESI-7

The reduction reaction of 4- nitrophenolate ions is summarized by the following equation:

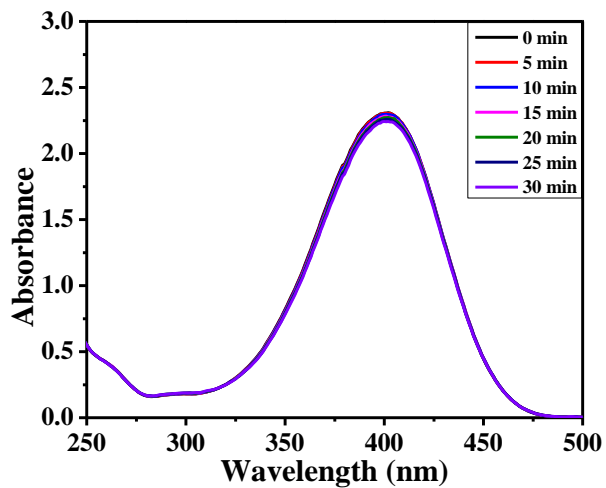
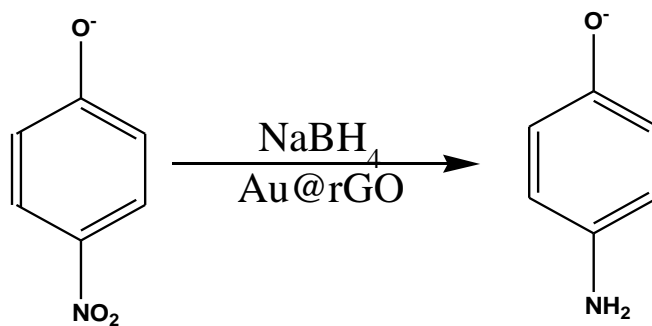


Fig.8 Absorbance spectra 4-nitrophenolate (4-NP) recorded at different time without catalyst.

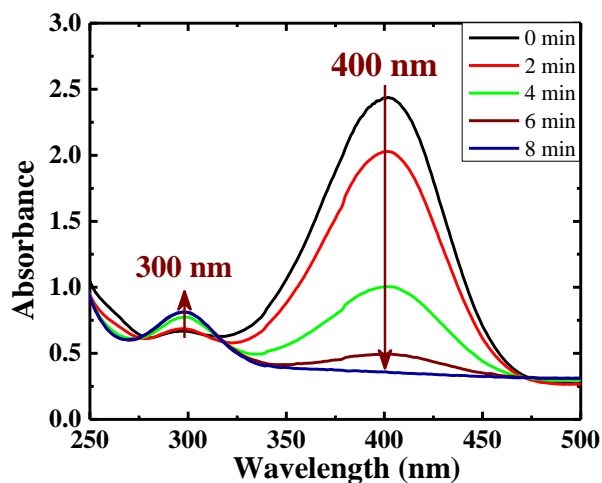


Fig. 9 The time dependent UV- vis absorbance spectroscopy of for the reduction of 1mM of 0.5 ml of 4- nitrophenolate ions with 1M of 0.1 ml NaBH_4 in presence of Au@rGO hybrid nanostructures. The reduction occurs at about 8 min.

ESI-8

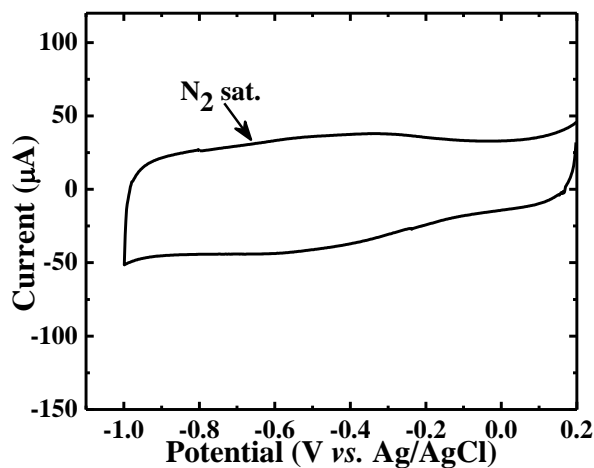


Fig.10 O_2 reduction peak was not observed in N_2 saturated 0.1M KOH electrolyte solution by the Au@rGO hybrid nanostructures.