

Supplementary information for

Gemini Surfactant Assisted Synthesis of Two-Dimensional Metal Nanoparticle/Graphene Composites

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Experimental details:

Preparation of RGO/surfactant/MNPs

GO was prepared from natural graphite flakes by using a modified Hummers method,¹ and the Gem was synthesized according to the literature.² The aqueous dispersion of GO (0.3 mg/mL) was added dropwise to the water solution of CTAB or Gem (1 mM) with ultrasonication, which yielded a light-yellow homogenous suspension. Afterwards, 2.7 mL of GO/Gem or GO/CTAB suspension was added into 20 mL aqueous solution of H₂AuCl₄ (or H₂PtCl₆, K₂PdCl₄) (1 mM) and the mixture was stirred at 80 °C for 30 min. Finally, 4.5 mg sodium borohydride (NaBH₄) was added and the mixture was stirred for another 120 min at the same temperature.

Characterizations

Zeta potential measurement of GO/CTAB and GO/Gem:

Zeta potential measurements were performed using Zetasizer ZS90 (Malvern

Instruments Ltd, UK). The aqueous dispersion of GO (0.3 mg/mL) was added dropwise to the water solution of CTAB or Gem of different concentration (from 0 mM to 5 mM) with ultrasonication and light-yellow homogenous suspensions were prepared accordingly. Then the suspensions were subject to the Zeta potential characterization.

FTIR characterization of GO/CTAB and GO/Gem:

FTIR spectra were recorded using Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer. The aqueous dispersion of GO (0.3 mg/mL) was added dropwise to the water solution of CTAB or Gem (1 mM) with ultrasonication, which yielded a light-yellow homogenous suspension. Then the suspension was dried and 1 mg of the resultant powder was dispersed in about 100 mg potassium bromide, which was finally pressed into a pellet for the FTIR characterization.

AFM characterization of GO/CTAB and GO/Gem:

AFM measurements were conducted with a Nanonavi scanner (SII Nanotechnology Inc., Japan) operated in tapping mode at room temperature. The aqueous dispersion of GO (0.3 mg/mL) was added dropwise to the water solution of CTAB or Gem (1 mM) with ultrasonication, which yielded a light-yellow homogenous suspension. Then the dispersion was spin coated on silica wafer and dried before study.

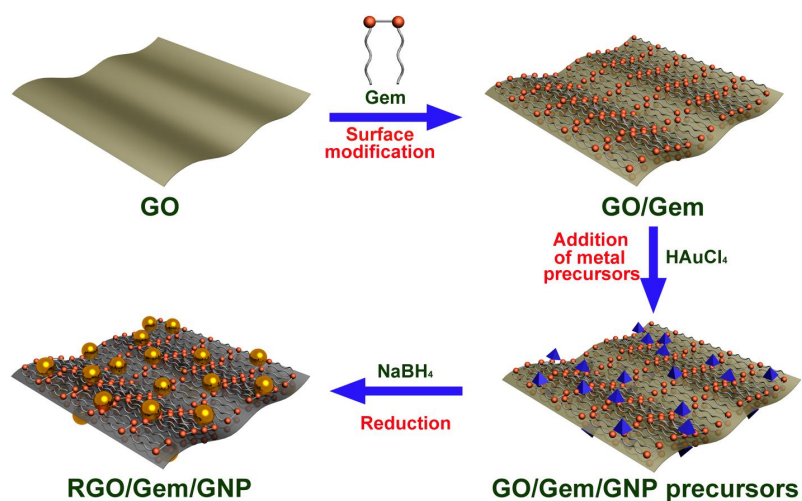
Other characterizations:

XRD measurements were carried out on a D/max-2200/PC (Rigaku Corporation, Japan) using Cu (40kV, 30mA) radiation. XPS experiments were carried out on a

AXIS Ultra DLD system from Kratos with Al K α radiation as X-ray source for radiation. TEM characterizations were conducted using a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200KV.

Electrochemical experiments:

Electrochemical experiments were performed using a CHI660c electrochemical analyzer (CH instruments,Chenhua Co., China), with GCE as working electrode, a platinum sheet as counter electrode and Saturated calomel electrode(SCE) as reference electrode. Glass carbon electrode (GCE) (3 mm in diameter) was first polished with 0.05 μm aluminium powder carefully, and rinsed with de-ionized water, followed by ultrasonication in water and ethanol for 5 minutes. The electrode was then dried under nitrogen. For the CV test, 6 μL of samples (RGO, GNPs and RGO/Gem/GNPs) was dropped on the surface of GCE and dried in air under ambient temperature.



Scheme S1. Schematic illustration of the synthesis of 2D RGO/Gem/GNPs composites.

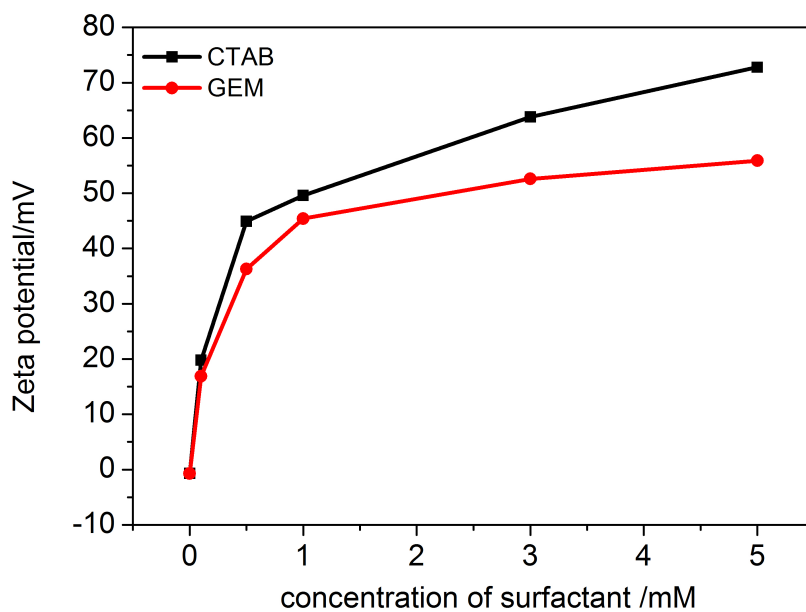


Fig. S1 Zeta potential of CTAB (black) and Gem (red) aqueous solution of different concentrations.

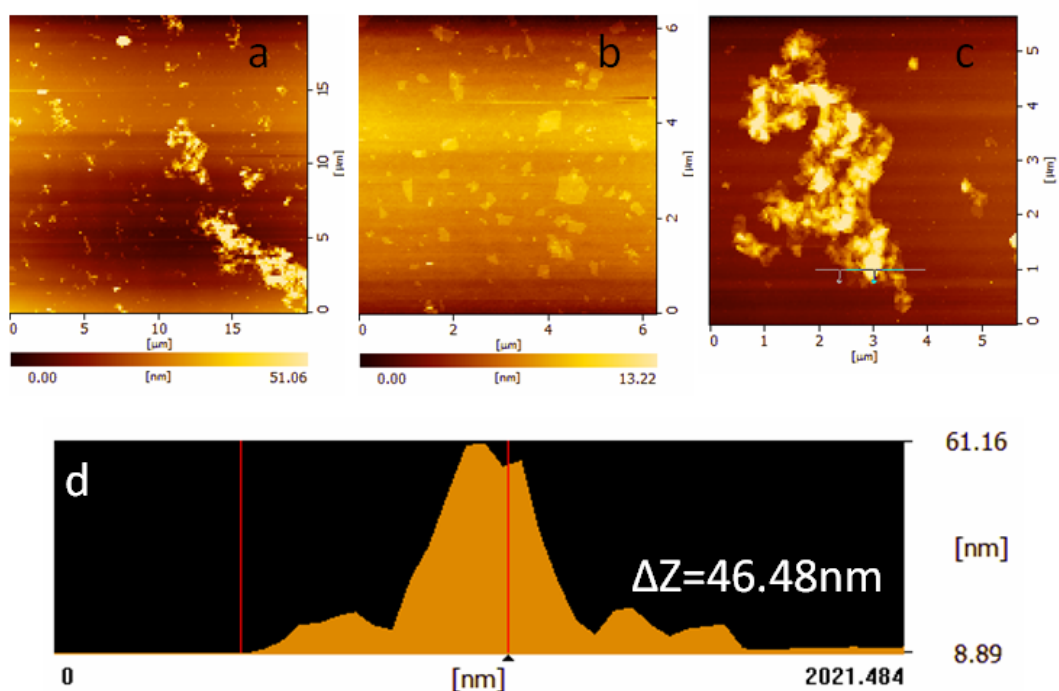


Fig. S2 (a) AFM image of GO/CTAB reveals the aggregation of GO. (b) AFM image of GO/Gem shows that GO/Gem is evenly distributed on the silica surface. (c) AFM image of GO/CTAB. (d) The cross section identified by the line in Fig. S2c shows the heights of individual GO.

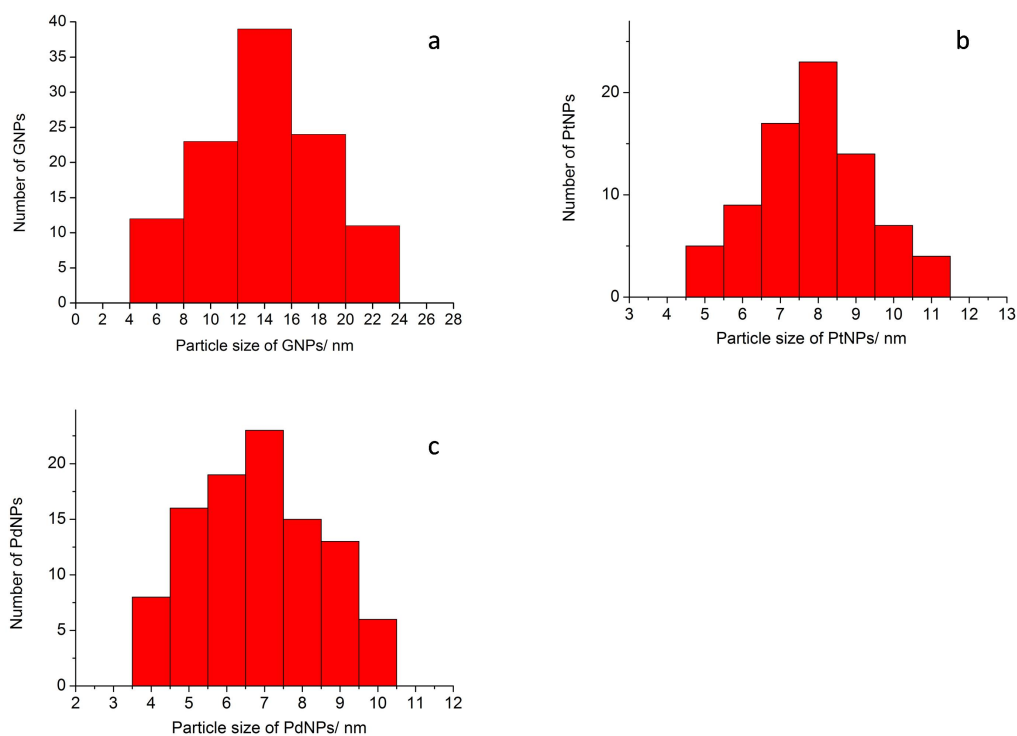


Fig. S3 The particle size distribution analysis of GNPs (a), PtNPs (b) and PdNPs (c) deposited on the RGO substrate.

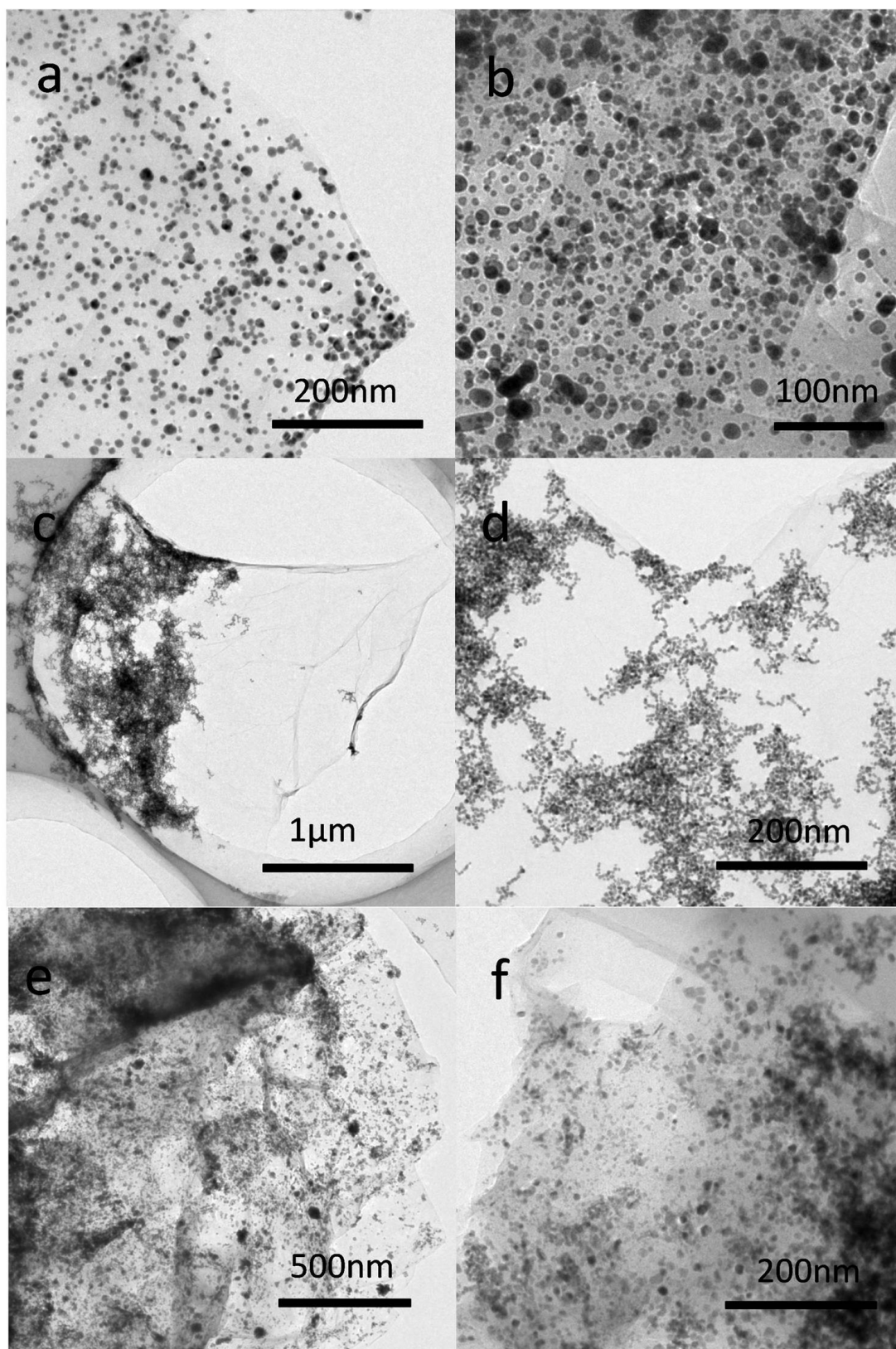


Fig. S4 TEM image of RGO/Gem/GNPs(a), RGO/CTAB/GNPs (b), RGO/GNPs at different magnifications (c-d), RGO/CTAB/PtNPs(e) and RGO/CTAB/PdNPs(f).

The morphology of the RGO supported MNPs depends strongly on the selection of

surfactant. RGO/Gem/GNPs, RGO/CTAB/GNPs, RGO/CTAB/PtNPs, RGO/CTAB/PdNPs and RGO/GNPs without using surfactant were prepared and characterized by TEM (Fig. S4). It can be clearly recognized that the GNPs underwent serious stacking on RGO once CTAB was used. In the contrast, for RGO/Gem/GNPs (Fig. S4a), the GNPs were uniformly distributed with average particle diameter of about 7 nm. As to RGO/GNPs (Fig. S4 c-d), the nanoparticles had irregular shape and were mainly stacked on certain parts of RGO. Meanwhile, for RGO/CTAB/GNPs, RGO/CTAB/PtNPs and RGO/CTAB/PdNPs (Fig. S4 b, e and f), severe aggregation of MNPs took place. All these results suggest that the use of Gem is crucial for the uniform distribution of MNPs on the RGO surface.

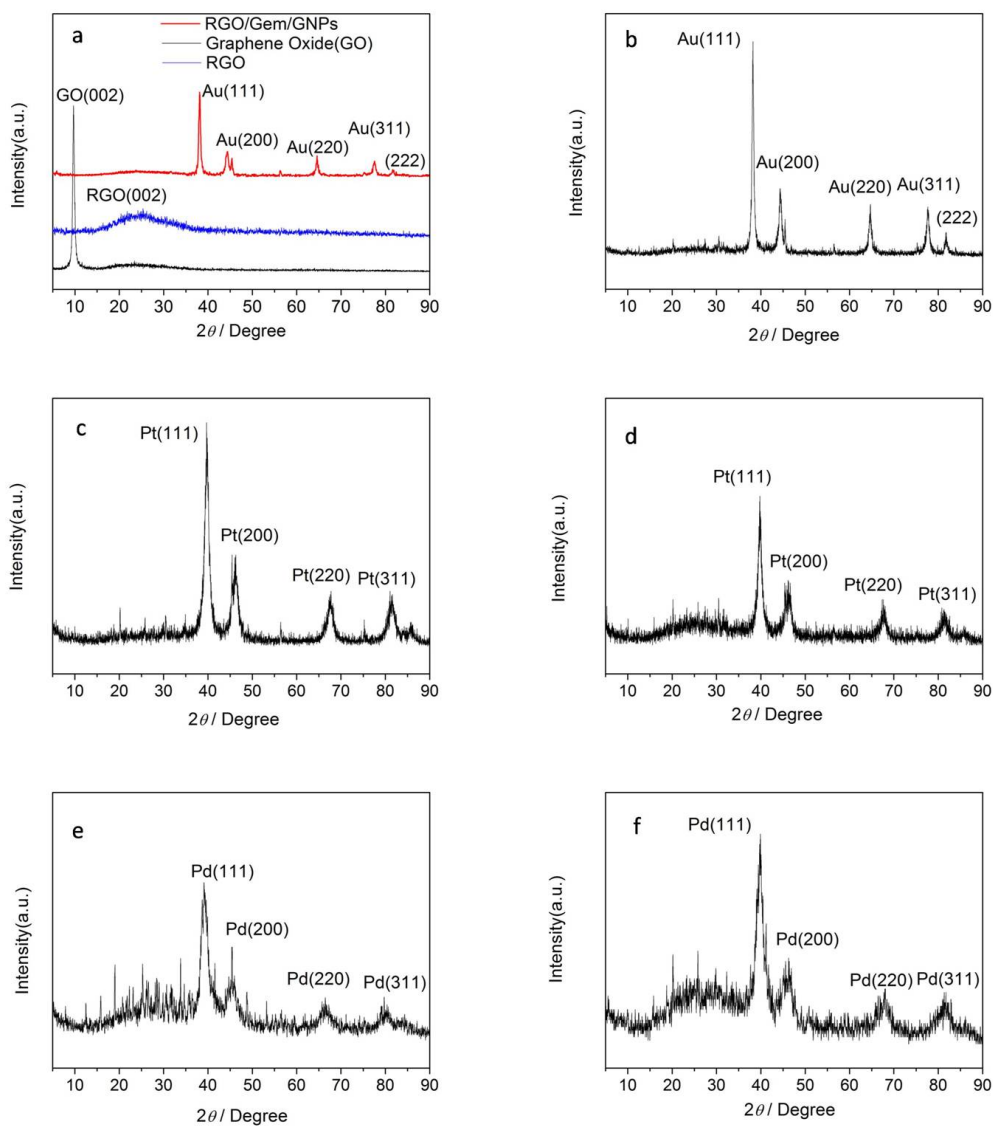


Fig. S5 (a) XRD pattern of GO, RGO via NaBH₄ reduction and RGO/Gem/GNPs composites, (b-f) XRD pattern of RGO/CTAB/GNPs, RGO/Gem/PtNPs, RGO/CTAB/PtNPs, RGO/Gem/PdNPs and RGO/CTAB/PdNPs, respectively.

Crystallite size of MNPs can be calculated based on the Scherrer formula³: $D = K\lambda / \beta \cos\theta$, where K represents for the Scherrer constant (normally $K=0.89$), λ is the wavelength of X-ray (0.15406 nm for Cu $K\alpha$), β is the full width at half maximum (FWHM, rad) of the peak and θ stands for Bragg diffraction angle. As shown in Table S1, the crystallite size calculated from XRD measurement is in good

accordance with TEM results.

Table S1 Crystallite size of MNPs calculated from XRD measurement.

Sample	β(deg)	2θ(deg)	Size/nm(XRD)	Size/nm(TEM)
RGO/Gem/GNPs	0.659	44.356	12.87	14
GO/CTAB/GNPs	0.392	38.08	21.02	5-30
RGO/Gem/PtNPs	1.1	39.751	7.59	8
RGO/CTAB/PtNPs	0.33	39.806	25.31	~ 20
RGO/Gem/PdNPs	1.607	39.736	5.20	7
RGO/CTAB/PdNPs	0.685	39.113	12.17	~ 16

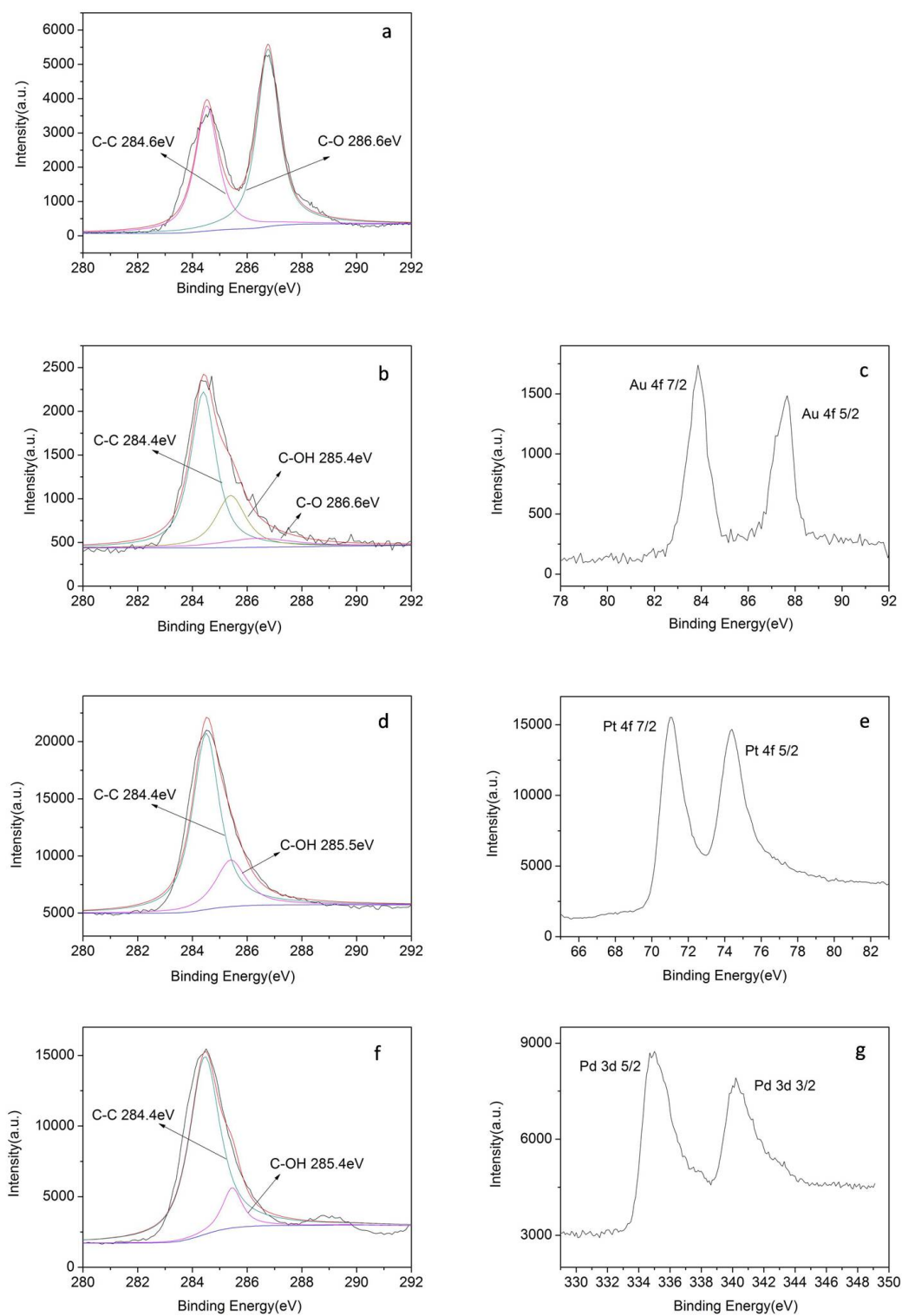


Fig. S6 C1s XPS spectra of GO(a); XPS spectra of RGO/Gem/GNPs: C1s (b) and Au4f (c); XPS spectra of RGO/Gem/PtNPs: C1s (d) and Pt4f (e); XPS spectra of RGO/Gem/PdNPs: C1s (f) and Pd3d (g).

Standard binding energy of Au 4f: 7/2 84 eV, 5/2 87.7 eV

Standard binding energy of Pt 4f: 7/2 71 eV, 5/2 74.4 eV

Standard binding energy of Pd 3d: 5/2 335 eV, 3/2 340.3 eV

C1s and Pt4f/Pd3d XPS spectra for GO/Gem/PtNPs and RGO/Gem/PdNPs were measured respectively. For C1s spectra of both RGO/Gem/PtNPs and RGO/Gem/PdNPs, the peaks associated with C-C (284.6 eV) become predominant and the intensity of oxidized carbon species (C-O at 286.6 eV) is greatly weakened. These features are typical for an efficient reduction of GO to RGO. Meanwhile, the significant Pt4f signal (70.9 eV and 74.4 eV) (Fig. S6e) corresponding to the binding energy of Pt4f 7/2 and Pt4f 5/2 is shown for RGO/Gem/PtNPs. Similarly, signal (335 eV and 340.4 eV) (Fig. S6g) corresponding to the binding energy of Pd3d 5/2 and Pd3d 3/2 is shown for RGO/Gem/PdNPs.

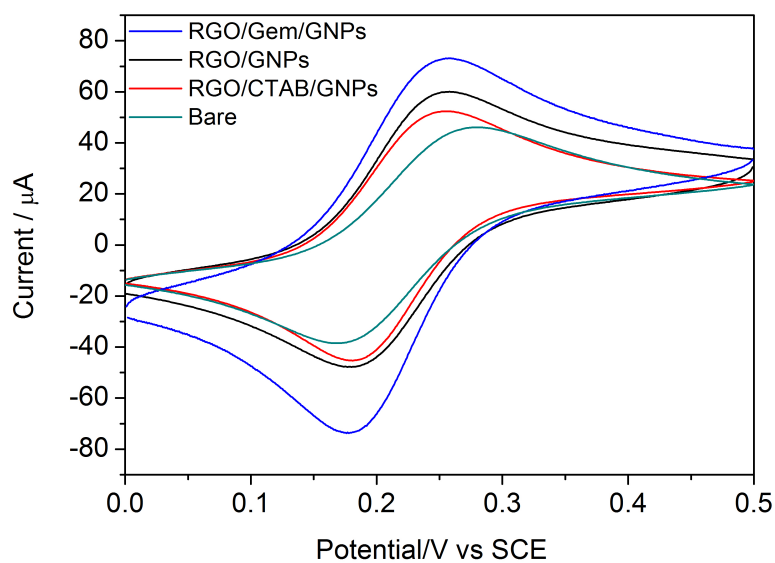


Fig. S7 Cyclic voltammograms of bare GCE and RGO/CTAB/GNPs, RGO/GNPs and RGO/Gem/GNPs modified GCE in the aqueous solution of 5mM $\text{Fe}(\text{CN})_6^{4-}$ and 1M KCl at a potential scan rate of 50 mV/s.

Notes and references

1. W. S. Hummers and R. E. Offerman, *J. Am. Chem. Soc.*, 1958, 80, 1339-1339.
2. R. Zana, M. Benraou and R. Rueff, *Langmuir*, 1991, 7, 1072-1075.
3. W. Z. Li, C. H. Liang, W. J. Zhou, J. S. Qiu, Z. H. Zhou, G. Q. Sun and Q. Xin, *J. Phys. Chem. B*, 2003, 107, 6292-6299.