Supporting Information

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Covalent Decoration of Graphene Oxide with Dendrimer-Encapsulated Nanoparticles for Universal Attachment of Multiple Nanoparticles on Chemically Converted Graphene

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Experimental Section

Chemicals and materials Amine-terminated sixth-generation polyamidoamine dendrimers (G6-NH_2 PAMAM dendrimers), $HAuCl_4•3H_2O$, K_2PtCl_4, $NaBH_4$, cellulose dialysis sacks (MW cutoff of 12,000), graphite powder, P_2O_5, $K_2S_2O_8$, KOH, and hydrazine (35 wt%) were purchased from Sigma-Aldrich, Inc. (USA). $KMnO_4$, H_2O_2, HCl, H_2SO_4, NaOH, and NH_4OH were obtained from Daejung, Inc. (South Korea). 18 MΩ•cm deionized water was used in the preparation of aqueous solutions (Ultra370, Younglin Co., Korea).

Synthesis of dendrimer-encapsulated nanoparticles (DENs) Au and Pt DENs were synthesized as previously reported with some modification.[1] Briefly, 147 or 200 mol equivalent of an aqueous 10 mM $HAuCl_4$ or 40 mol equivalent of an aqueous 10 mM K_2PtCl_4 was added to an aqueous 10 μM G6-NH_2 PAMAM dendrimer solution for complexation of the metal ions with the interior amines of the dendrimers. Especially, the mixture solution (pH 5) of Pt ions and dendrimers was stirred for 76 h to ensure the binding of the Pt ions to the intradendrimer tertiary amines. A stoichiometric excess of aqueous $NaBH_4$ was then added slowly to the mixture under vigorous stirring. Specifically, a 10 fold excess of $NaBH_4$ in 0.3 M NaOH was added to the Au ion-dendrimer complex solution, which resulted in color change of the solution from pale yellow to brown. This color change indicates reduction of the complexed Au ions to zerovalent Au nanoparticles inside the dendrimers. Similarly, a 20 fold excess of an aqueous $NaBH_4$ solution was added to the Pt ion-dendrimer complex solution. The mixture solution (pH 7 ~ 8) was kept in a closed vial overnight to ensure complete reduction of the Pt. Finally, the prepared DEN solutions were dialyzed overnight using a cellulose dialysis sack to remove impurities.

Synthesis of graphene oxide (GO) GO was prepared according to a modified Hummer's method.[2] Briefly, graphite powder (3 g) was added into an 80 °C mixture solution of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). The mixture was kept at 80 °C for 5 h and then cooled down to room temperature. The resulting solution was carefully diluted with 500 mL of deionized (DI) water and left overnight. The diluted solution was filtered using a 0.45 micron Nylon Millipore filter and washed with copious amounts of DI water to remove acid residues. The pre-oxidized graphite, after being air-dried, was put into cold concentrated H_2SO_4 (120 mL) in an ice bath under continuous stirring. $KMnO_4$ (15 g) was gradually added into the solution maintained below 20 °C. The mixture was stirred at 35 °C for 2 h and then carefully diluted with DI water (250 mL) in an ice bath to keep the temperature below 50 °C as the dilution of concentrated H_2SO_4 medium released a large amount of heat. After additional stirring for 2 h, the reaction was stopped by adding 700 mL of DI water and 20 mL of H_2O_2 (30 %). The resulting bright yellow product was filtered and washed with 1:10 aqueous HCl and DI water. The GO product was air-dried and suspended in DI water. The resulting GO dispersion (*ca.* 0.5 mg/ml) was further purified by dialysis for 2 days. Exfoliation was carried out by sonicating the *ca.* 0.5 mg/mL GO dispersion for 5 h. Unexfoliated GO was removed by centrifugation. The resulting homogeneous GO solution had a concentration of *ca.* 0.2 mg/mL.

Preparation of DEN-GO and DEN-RGO composites DEN-GO composites were prepared as following. Briefly, 2 mL of DEN solution (10 μM) was added to 2 mL of GO solution (*ca.* 0.1 mg/mL) containing KOH (20 mM). The mixture was stirred at 40 °C for 12 h. 160 μL of 0.5 M H_2SO_4 solution was then added and the mixture was further stirred for 30 min. The resulting DEN-GO composites were collected, purified by centrifugation, and washed with

DI water several times. The DEN-GO was chemically reduced by mixing 1 mL of the DEN-GO (*ca.* 0.03 mg/mL), 3 μL of hydrazine (35 wt% in DI water), and 21 μL of ammonia (28 wt% in DI water); reduction occurred at 80 °C for 90 min.

Characterization TEM images were collected using a Tecnai G2 F30 instrument (FEI Co., USA) operating at 200 kV. TEM samples were prepared by evaporating a drop of aqueous sample solution on a 200 mesh carbon-coated copper grid (Ted Pella Inc., USA). UV-vis absorption spectra were obtained using an Agilent 8453 UV-vis spectrometer (Agilent Tech., USA) with 2 mm optical path length, and DI water or an aqueous mixture of hydrazine and ammonia solutions used as blanks. XPS measurements were performed with a PHI 5000 spectrometer (Physical Electronics Inc., USA) using an Al Kα radiation (hν = 1486.6 eV). XPS samples were prepared by dropping the sample solutions on Si wafers and allowing them to dry. All obtained spectra were deconvoluted with a mixed Gaussian-Lorentzian function. AFM images were acquired in tapping mode in air using a Multimode Nanoscope IV (Veeco Instruments Inc., USA). AFM samples were prepared by depositing dilute aqueous samples on freshly cleaved Si surfaces. Electrochemical measurements were carried out in a conventional three-electrode cell with a Model 440 electrochemical analyzer (CH Instruments, USA). A Pt wire and a Ag/AgCl (3M NaCl) electrode were used as a counter and a reference electrode, respectively. Glassy carbon electrodes modified with DEN-RGO or RGO were used as a working electrode. The working electrodes were prepared by drop-casting the aqueous dispersion (*ca.* 0.1 mg/mL) of the DEN-RGO or RGO on glassy carbon electrodes followed by drying at room temperature overnight.

References

1 (a) Y.-G. Kim, S.-K. Oh and R. M. Crooks, *Chem. Mater.*, 2004, **16**, 167-172; (b) T. H. Kim, H. S. Choi, B. R. Go and J. Kim, *Electrochem. Commun.*, 2010, **12**, 788-791; (c) M. Zhao and R. M. Crooks, *Adv. Mater.*, 1999, **11**, 217-220; (d) H. Ju, C. M. Koo and J. Kim, *Chem. Commun.*, 2011, **47**, 12322-12324.

2 (a) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339; (b) N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771-778.

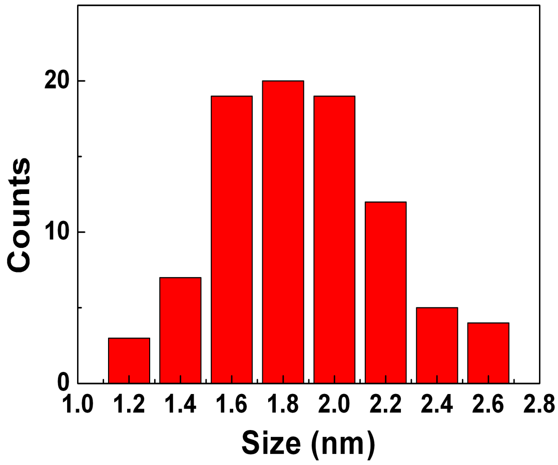


Figure S1. Particle size distribution of as-prepared G6-NH_2(Au_{147}) DENs.

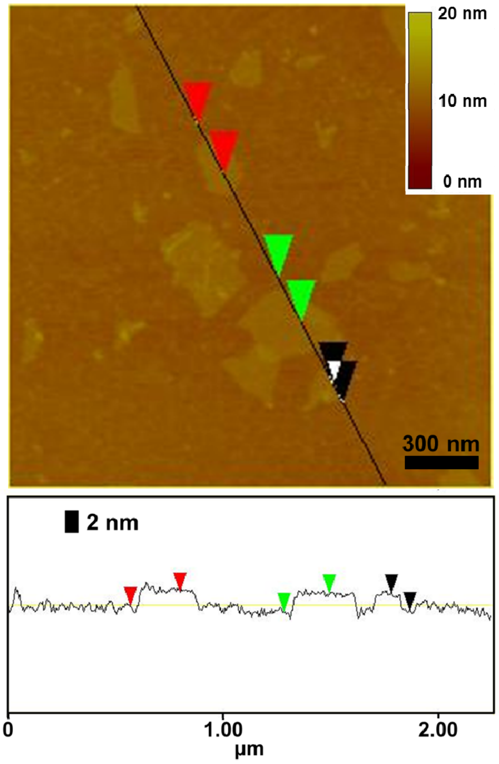


Figure S2. A typical AFM image of GO sheets. The cross section analysis shows the thickness of GO sheets (average thickness: ~1.5 nm).

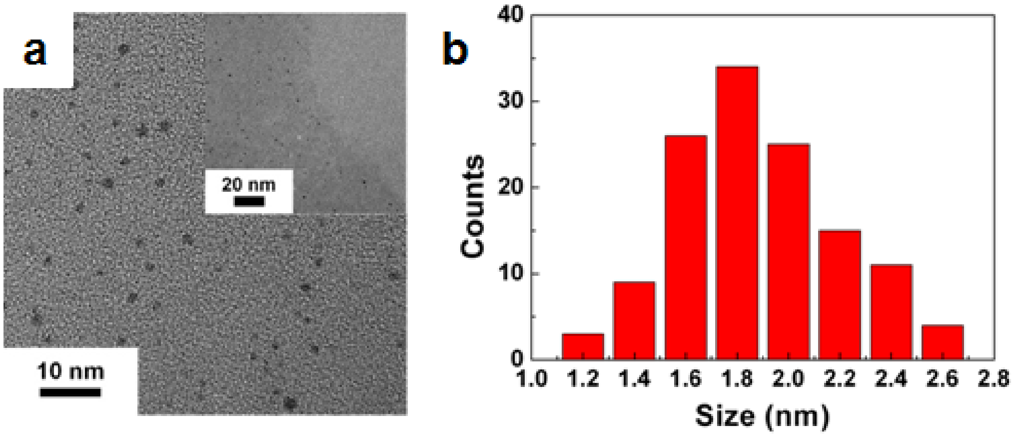


Figure S3. (a) TEM images and (b) particle size distribution of the Au DENs immobilized on Au DEN-GO composites, *i.e.* G6-$NH_2(Au_{147})$ DEN-GO.

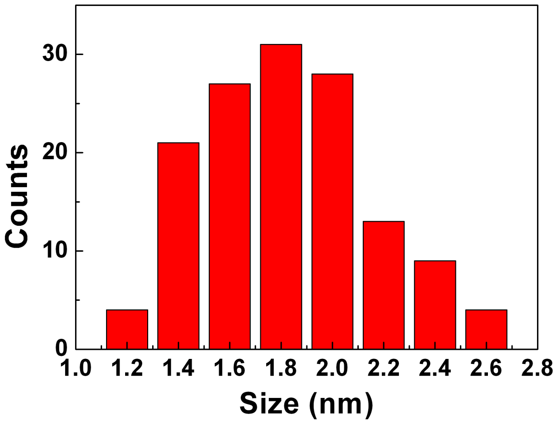


Figure S4. Particle size distribution of the Au DENs immobilized on Au DEN-RGO composites, *i.e.* G6-$NH_2(Au_{147})$ DEN-RGO.

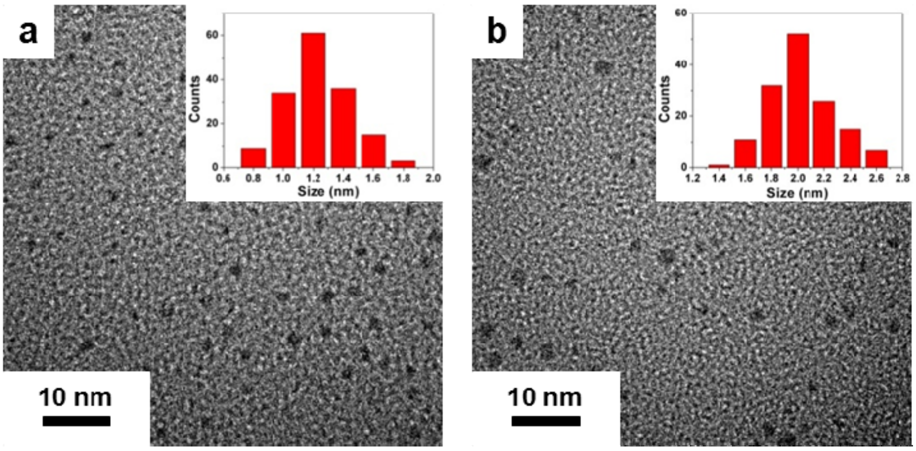


Figure S5. TEM images and particle size distributions of (a) as-prepared Pt DENs and (b) as-prepared Au DENs. The Pt DEN and Au DEN are G6-$NH_2(Pt_{40})$ and G6-$NH_2(Au_{200})$, respectively.

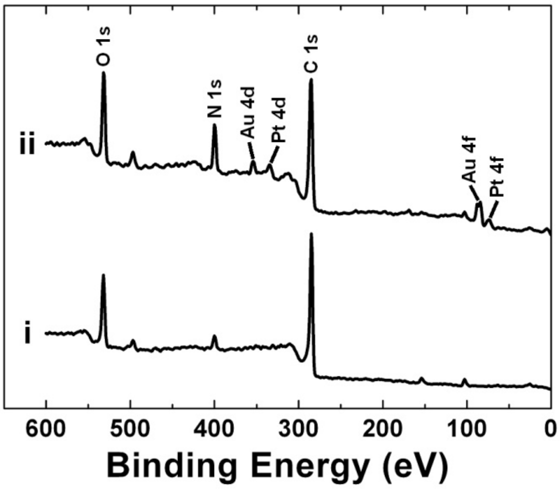
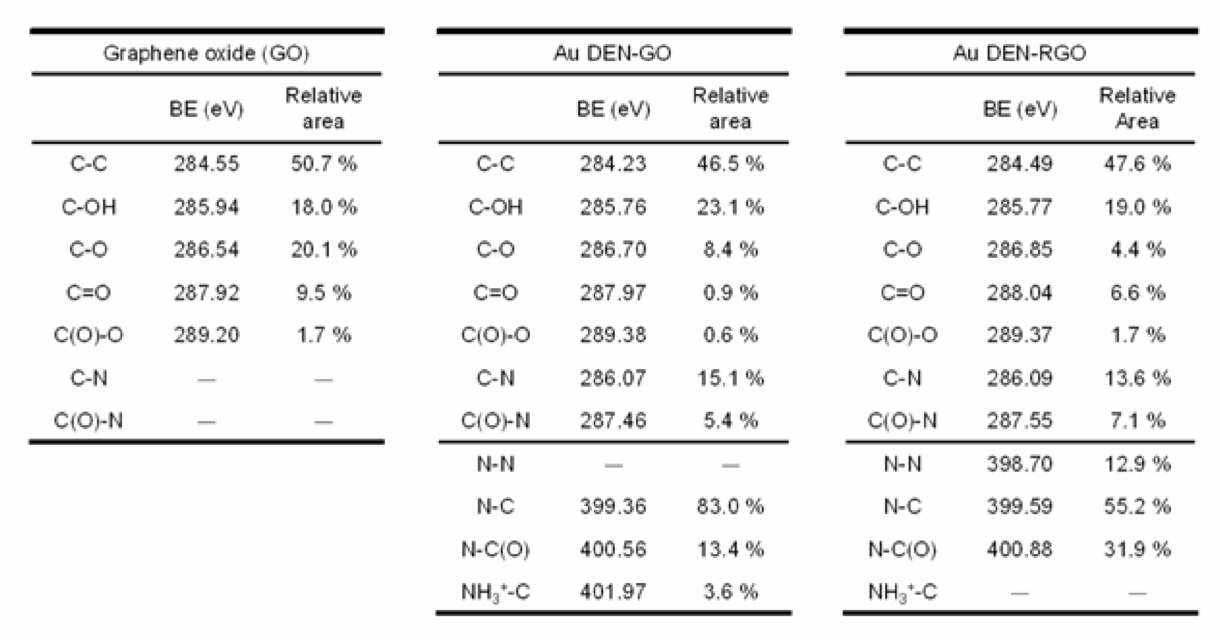


Figure S6. XPS spectra of (i) a bare RGO and (ii) a Pt DEN/Au DEN-RGO composite, *i.e.* G6-$NH_2(Pt_{40})$ DEN/G6-$NH_2(Au_{200})$ DEN-RGO.

Table S1. Tabulated XPS peak locations for GO, Au DEN-GO, and Au DEN-RGO. The Au DEN is G6-NH_2(Au_{147}).



Graphene oxide (GO)	BE (eV)	Relative area
C-C	284.55	50.7 %
C-OH	285.94	18.0 %
C-O	286.54	20.1 %
C=O	287.92	9.5 %
C(O)-O	289.20	1.7 %
C-N	—	—
C(O)-N	—	—

Au DEN-GO	BE (eV)	Relative area
C-C	284.23	46.5 %
C-OH	285.76	23.1 %
C-O	286.70	8.4 %
C=O	287.97	0.9 %
C(O)-O	289.38	0.6 %
C-N	286.07	15.1 %
C(O)-N	287.46	5.4 %
N-N	—	—
N-C	399.36	83.0 %
N-C(O)	400.56	13.4 %
NH_3^+-C	401.97	3.6 %

Au DEN-RGO	BE (eV)	Relative Area
C-C	284.49	47.6 %
C-OH	285.77	19.0 %
C-O	286.85	4.4 %
C=O	288.04	6.6 %
C(O)-O	289.37	1.7 %
C-N	286.09	13.6 %
C(O)-N	287.55	7.1 %
N-N	398.70	12.9 %
N-C	399.59	55.2 %
N-C(O)	400.88	31.9 %
NH_3^+-C	—	—