Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2020

Supporting Information

Gold Nanoparticles Standing on PEG/PAMAM/Thiol-Functionalized Nanographene Oxide as Aqueous Catalysts

Bingjie Hao,[a,b] *Guolin Lu*,[a] *Sen Zhang*,[a] *Yongjun Li*,[a,c,*]

Aishun Ding,[a] *Xiaoyu Huang*[a,b,*]

[a] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[b] School of Physical Science & Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, People's Republic of China

[c] State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, 2005 Songhu Road, Shanghai 200438, People's Republic of China

* To whom correspondence should be addressed, E-mail: xyhuang@sioc.ac.cn (Tel: +86-21-54925310, Fax: +86-21-64166128), liyongjun78@sioc.ac.cn (Tel: +86-21-54925606, Fax: +86-21-64166128).

Experimental Section

Materials

Graphite powder (Aldrich, 99.99+%), potassium permanganate ($KMnO_4$, Aldrich, 99%), sulfuric acid (H_2SO_4, Aldrich,95~98%), sodium nitrate ($NaNO_3$, Aldrich, 99%), 2-aminoethanethio (Aladdin, 98%), $HAuCl_4 \cdot H_2O$ (Aldrich, 99%), citric sodium (Aldrich, 99%), 4-nitrophenol (4-NP, Aldrich, 99%), 4-nitroaniline (4-NA, Aldrich, 99%), sodium borohydride ($NaBH_4$, Aldrich, 99%) and Congo red (CR, Aldrich, 99%) were used as received. Six-armed PEG with six amino end groups (6-armed PEG-NH_2, M_n = 10,000 g/mol) was purchased from Ponsure Biotech. Inc. (Shanghai, China). *N*-(3-(dimethylamino)propyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl, Aldrich, 99%), *N*-hydroxysuccinimide (NHS, Aldrich, 99%), 3-mercaptopropionic acid (MPA, Aldrich, 99%), sodium triacetoxyborohydride ($(CH_3COO)_3BHNa$, Aldrich, 99%) and polyamidamine dendrimer with amino terminal groups (G1, PAMAM-NH_2) were purchased from J&K Scientific.

Measurements

FT-IR spectra are recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a 4 cm^{-1} resolution. UV/vis absorption spectra were acquired by a Hitachi U-2910 spectrophotometer. Elemental analysis was carried out on a Vario EL III system. X-ray photoelectron spectroscopy (XPS) was recorded on an EscaLab 250Xi photoelectron spectrometer. Thermogravimetric analysis (TGA) was conducted on a TA Discovery TGA 55 thermal analysis system in N_2 with a heating rate of 10°C/min.

X-ray diffraction (XRD) measurements were run by a Philips X'Pert PRO X-ray powder diffractometer with CuKα (1.541Å) radiation (40 kV, 40 mA), the samples were exposed at a scan rate of $2\theta = 0.04244^{o}$/s in the range from 5^{o} to 80^{o}. Unpolarized Raman scatterings were recorded performed on a Thermo Scientific DXR spectrometer (532 nm line from a semiconductor laser, scan number: 3, power at the sample: ~6.8 mW). Hydrodynamic diameter (D_h) was measured by dynamic light scattering (DLS) with a Malvern Nano-ZS90 Zetasizer at room temperature. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a PerkinElmer Elan 9000 instrument operating under normal Ar plasma conditions (1400 W forward plasma power, 17 L/ min Ar plasma gas flow, 1.2 L/min auxiliary Ar flow and 0.95 L/min nebulizer Ar flow). Atomic force microscope (AFM) images were taken by a JPK Nano Wizard Sense system in the AC mode of dropping the sample solution onto the freshly exfoliated mica substrate. Scanning electron microscope (SEM) images were taken by a FEI Nova NanoSEM 450 instrument. Transmission electron microscopy (TEM) images were taken by a JEOL JEM-1230 instrument operated at 80 kV.

Preparation of nanographene oxide

Graphene oxide (GO) was prepared from graphite powder through a modified Hummer's method.[1] Graphite powder was oxidized by concentrated H_2SO_4, $NaNO_3$ and $KMnO_4$ in low-temperature (0°C), and room-temperature (35°C) followed by adding H_2O_2 (30%) slowly while the color of solution changed from black to yellow, then the resultant suspension was extensively washed with distilled water by filtration and finally subjected to dialysis to remove residual salts and acids. The preparation of nanographene oxide (NGO) was based on the breakage of GO by ultra-sonication process. The as-prepared GO suspension was subjected to ultra-sonication by a SONICS VCX750 instrument operated at 20 KHz for 1 hour in ice bath.[2]

Preparation of NGO-PEG

NGO aqueous dispersion was pre-treated with NaOH followed by adding 6-armed PEG-NH_2 and EDC·HCl for sonication at room temperature for 1 h, ultimately the mixed solution was kept stirring vigorously at room temperature for 24 h. The final product, GO-PEG, was obtained by purifying the crude product by dialysis (MW_{cutoff} = 14 kDa) against the double-distilled water for 1 week to remove unbound 6-armed PEG-NH_2.[3]

Preparation of SH-NGO-PEG

NGO-PEG aqueous dispersion (20 mL, 0.05 wt%) was mixed with cysteamine (10 mg) and KOH (5 mg), the homogeneous dispersion was vigorously stirred at 80°C for 24 h. Finally, the resulting product was dialyzed (MW_{cutoff} = 3.5 kDa) against the double-distilled water for several days to remove residual salts and basics.[4]

Preparation of SH-PAMAM-NGO-PEG

NGO-PEG aqueous dispersion (30 mL, 0.05 wt%) was mixed with PAMAM-NH_2

(100 mg) and KOH (6 mg), the homogeneous dispersion was vigorously stirred at 80°C for 12 h. The resultant dispersion was dialyzed ($MW_{cutoff} = 14$ kDa) against the double-distilled water, providing PAMAM-NGO-PEG. MPA (63 mg) was activated by EDC/NHS (molar ratio of MPA:EDC:NHS = 1:4:4) in aqueous solution at room temperature for 5 h. PAMAM-NGO-PEG dispersion (45 mL) was treated with activated MPA at 30°C for at least 12 h, affording SH-PAMAM-NGO-PEG. Finally, the resulting product was dialyzed ($MW_{cutoff} = 14$ kDa) against the double-distilled water for several days to remove residual salts and basics.[5]

Preparation of AuNP@SH-NGO-PEG

SH-NGO-PEG aqueous dispersion (25 mL, 0.01 wt%) was mixed with $HAuCl_4 \cdot H_2O$ (0.26 mL, 0.24 mM) followed by vigorous stirring at room temperature for 30 min. Citric sodium (0.92 mL, 0.17 mM) was then added into the solution quickly followed by stirring at 80°C for 1 h. The final product, AuNP@SH-NGO-PEG dispersion (0.05 mg/mL), was obtained after dialysis ($MW_{cutoff} = 14$ kDa) against the double-distilled water. The concentration of Au in AuNP@SH-NGO-PEG dispersion was determined to be ~28.3 mg/L by ICP-MS.[6]

Preparation of AuNP@SH-PAMAM-NGO-PEG

SH-PAMAM-NGO-PEG aqueous dispersion (2 mL, 0.04 wt%) was mixed with $HAuCl_4 \cdot H_2O$ (0.05 mL, 0.24 mM) followed by vigorous stirring at room temperature for 10 min. $(CH_3COO)_3BHNa$ (0.05 mL, 1.0 mM) was then added into the solution quickly followed by stirring at room temperature for 8 h. The final product, AuNP@SH-PAMAM-NGO-PEG dispersion (2.0 mg/mL), was obtained after dialysis (MW_{cutoff} = 14 kDa) against the double-distilled water.

AuNP@SH-NGO-PEG catalyzed reduction of 4-NP, 4-NA and CR

The reduction of 4-NP by $NaBH_4$ was selected as a model reaction to test the catalytic activity of AuNP@SH-NGO-PEG. 4-NP aqueous solution (0.14 mL, 2 mM) and $NaBH_4$ (0.2 mL, 0.1 M) were added to deionized water (1.3 mL) in a cuvette under stirring. After adding AuNP@SH-NGO-PEG dispersion (1.4 mL, 0.05 mg/mL), the bright yellow solution gradually faded as the reaction proceeded. UV/vis measurements were run to determine the conversion of 4-NP at different intervals. Similar procedure was employed for examining the performance on catalytic reduction of 4-NA and CR.

AuNP@SH-PAMAM-NGO-PEG catalyzed reduction of 4-NP

The reduction of 4-NP by $NaBH_4$ was selected as a model reaction to test the catalytic activity of AuNP@SH-PAMAM-NGO-PEG. 4-NP solution (0.04 mL, 20 mM) and $NaBH_4$ (0.04 mL, 1.0 M) were added to deionized water (1.0 mL) in a cuvette under stirring. After adding AuNP@SH-PAMAM-NGO-PEG dispersion (2.0 mL, 2.0 mg/mL), the bright yellow solution gradually faded as the reaction proceeded. UV/vis measurements were run to determine the conversion of 4-NP at different intervals.

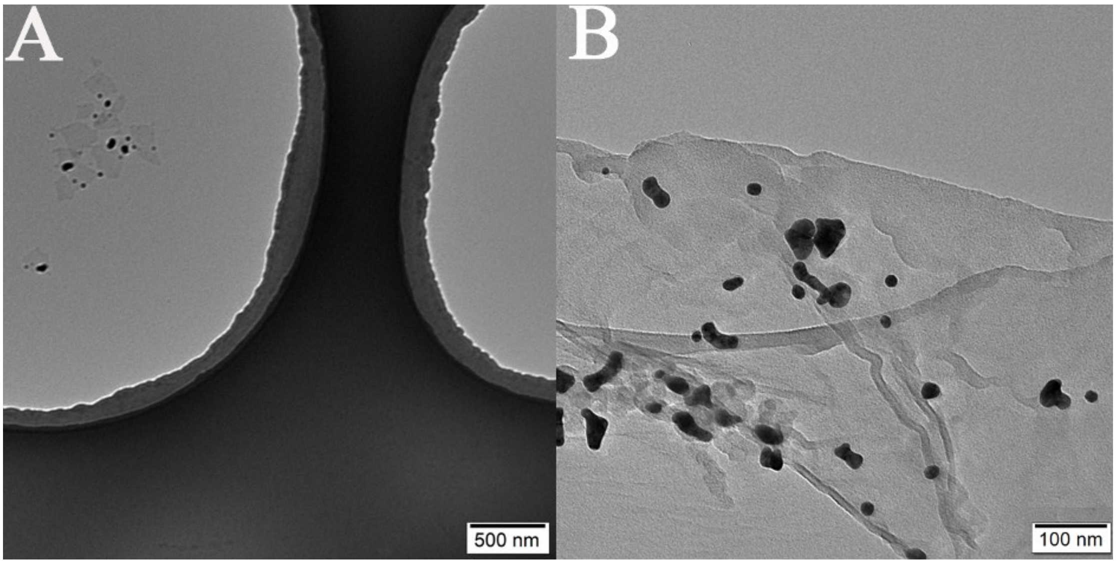

Figure S1. TEM images of AuNP@SH-NGO-PEG.

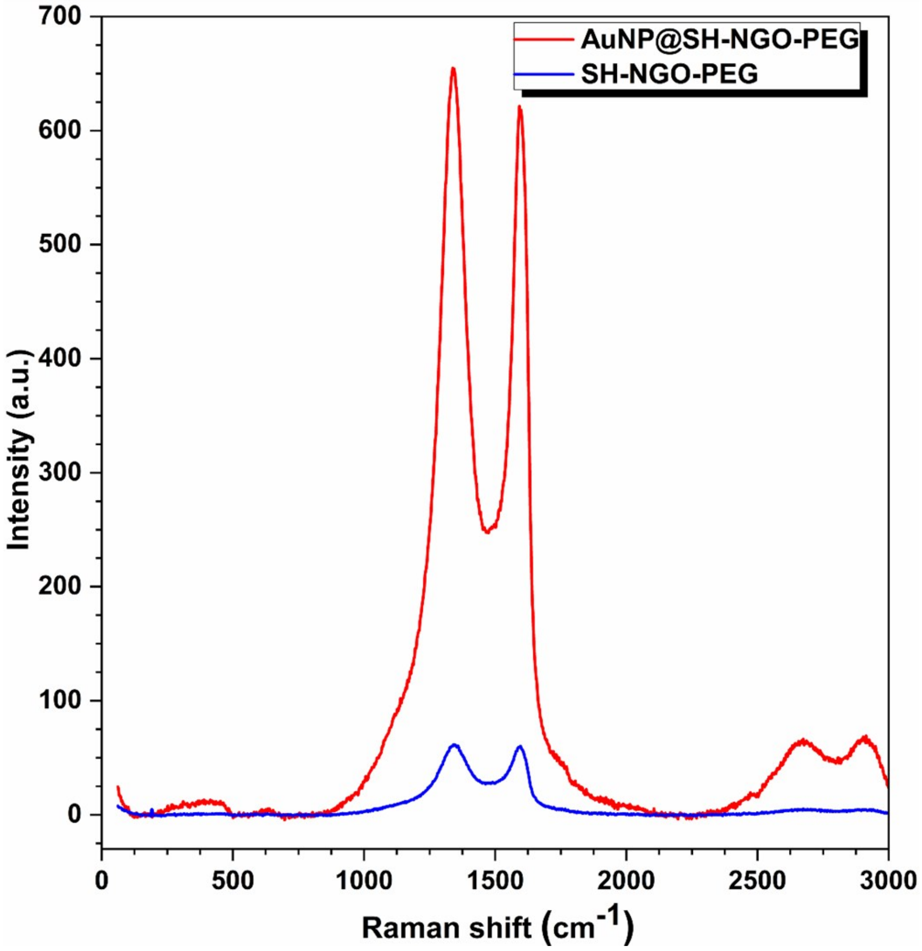

Figure S2. Raman spectra of SH-NGO-PEG and AuNP@SH-NGO-PEG (the spectra consist of D, G, 2D and D+D´ bands located at 1347, 1585, 1739, 2718 and 2930 cm^{-1}).

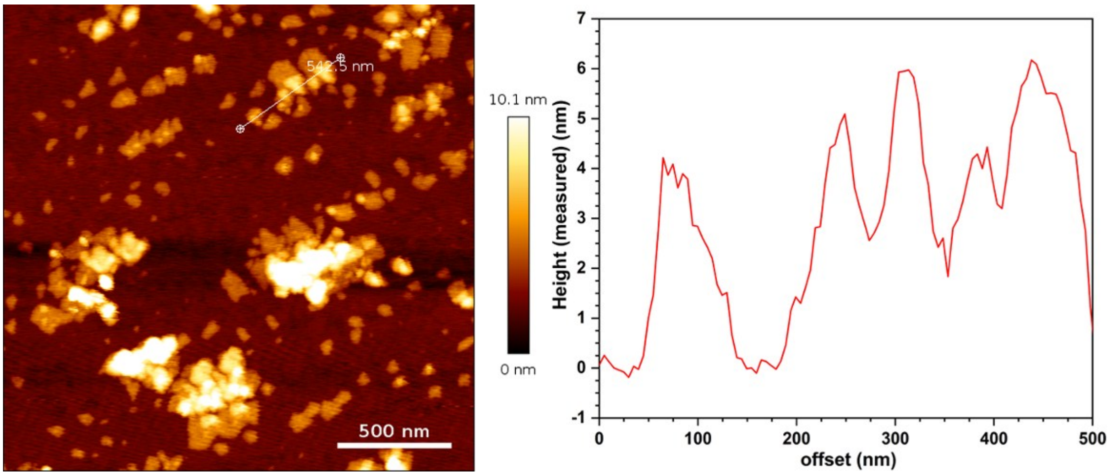

Figure S3. AFM image of SH-PAMAM-NGO-PEG.

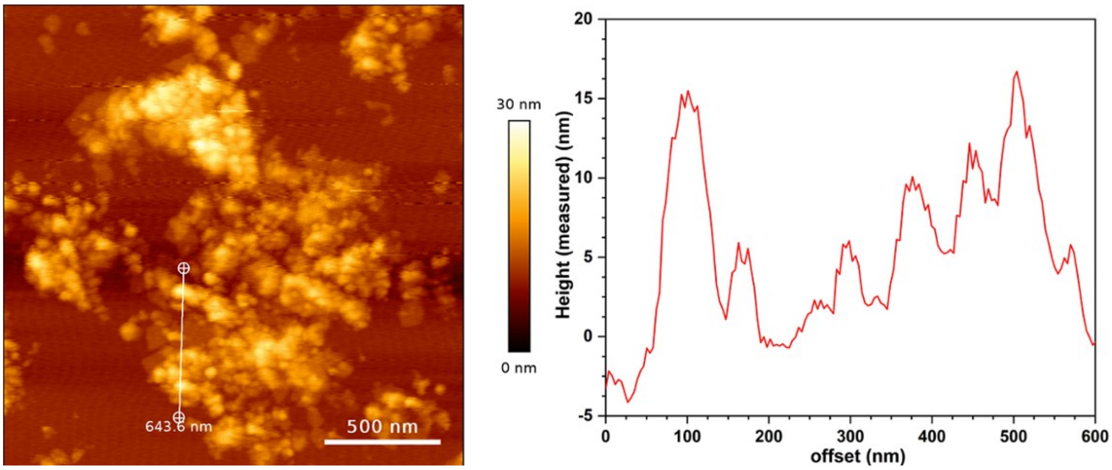

Figure S4. AFM image of AuNP@SH-PAMAM-NGO-PEG.

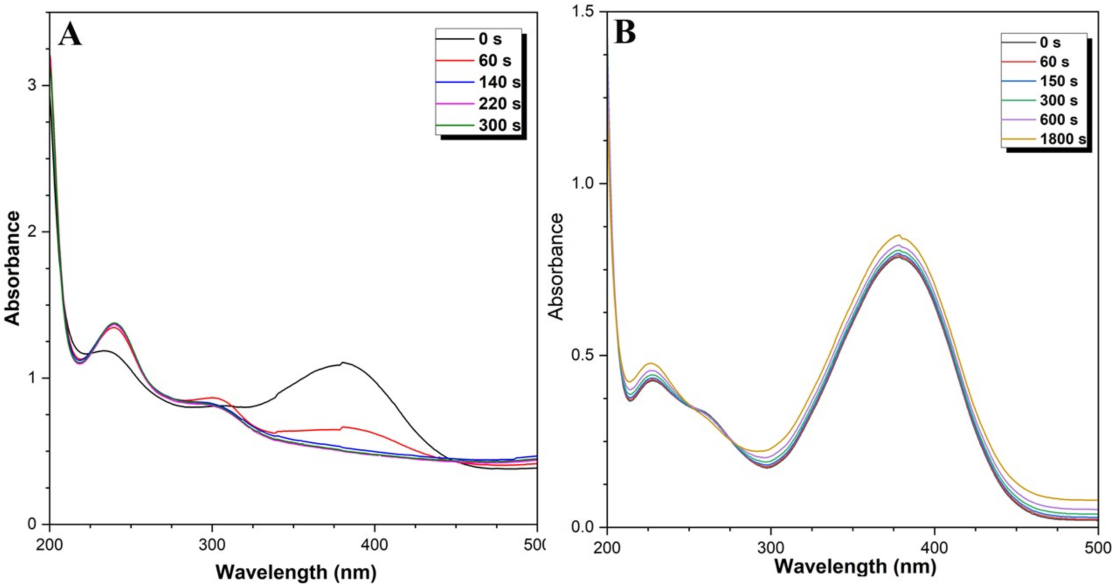

Figure S5. (A) Successive UV/vis absorption spectra of the reduction of 4-nitroaniline aqueous solution (0.2 mM) in the presence of AuNP@SH-NGO-PEG; (B) Successive UV/vis absorption spectra of the reduction of 4-nitroaniline aqueous solution (0.2 mM) without AuNP@SH-NGO-PEG.

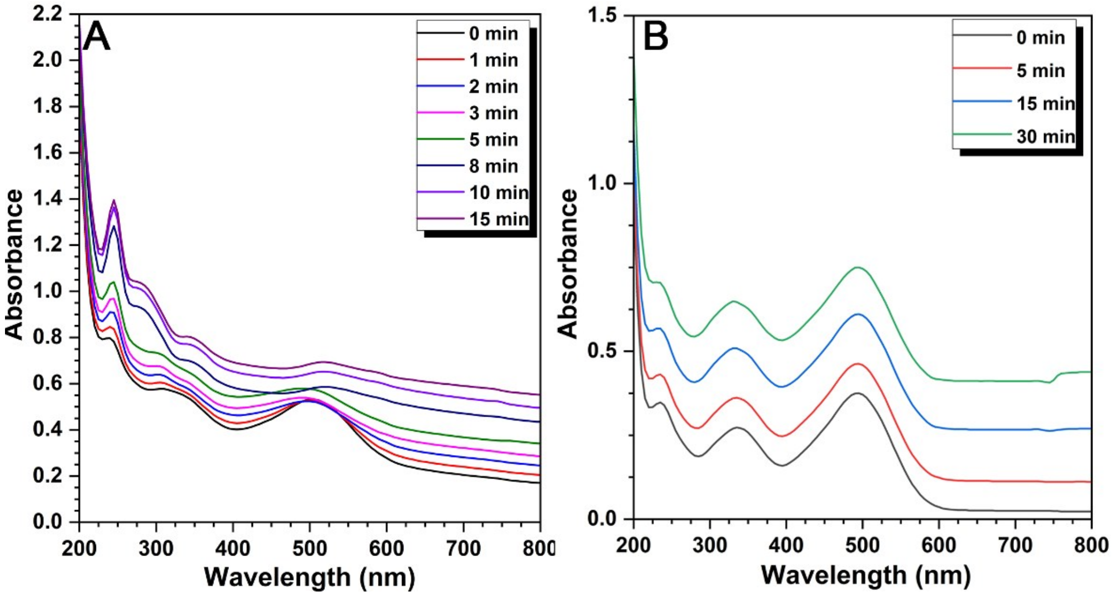

Figure S6. (A) Successive UV/vis absorption spectra of the reduction of Congo red aqueous solution (0.2 mM) in the presence of AuNP@SH-NGO-PEG; (B) Successive UV/vis absorption spectra of the reduction of Congo red aqueous solution (0.2 mM) without AuNP@SH-NGO-PEG.

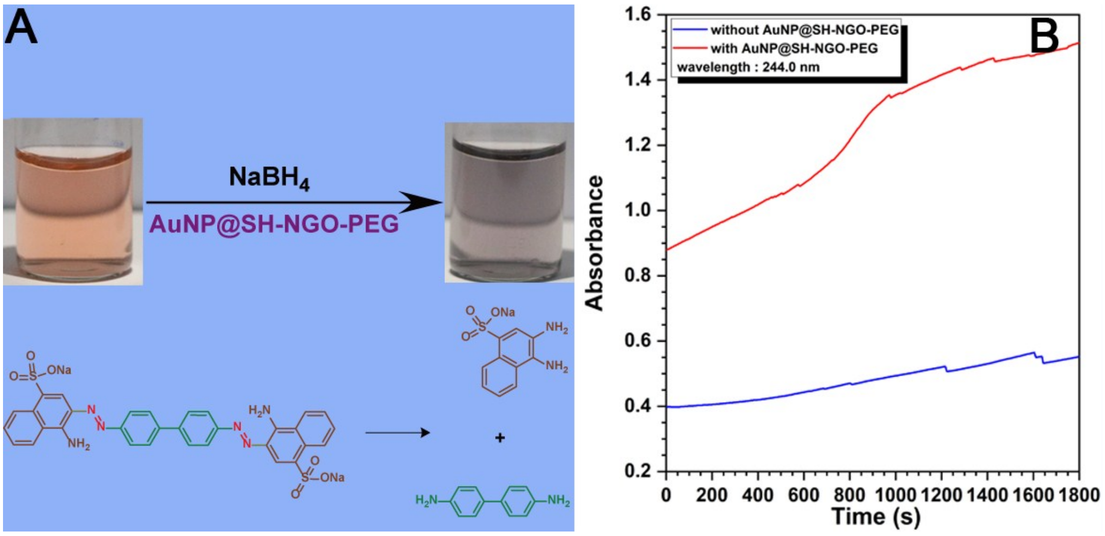

Figure S7. (A) Reaction scheme of the reduction of Congo red catalyzed by AuNP@SH-NGO-PEG and the color comparison of Congo red aqueous solution (0.2 mM) before and after the reduction; (B) Time scan curves at 244 nm for the reduction of Congo red aqueous solution (0.2 mM) in the presence of AuNP@SH-NGO-PEG (red line) or without AuNP@SH-NGO-PEG (blue line) via UV/vis spectroscopy.

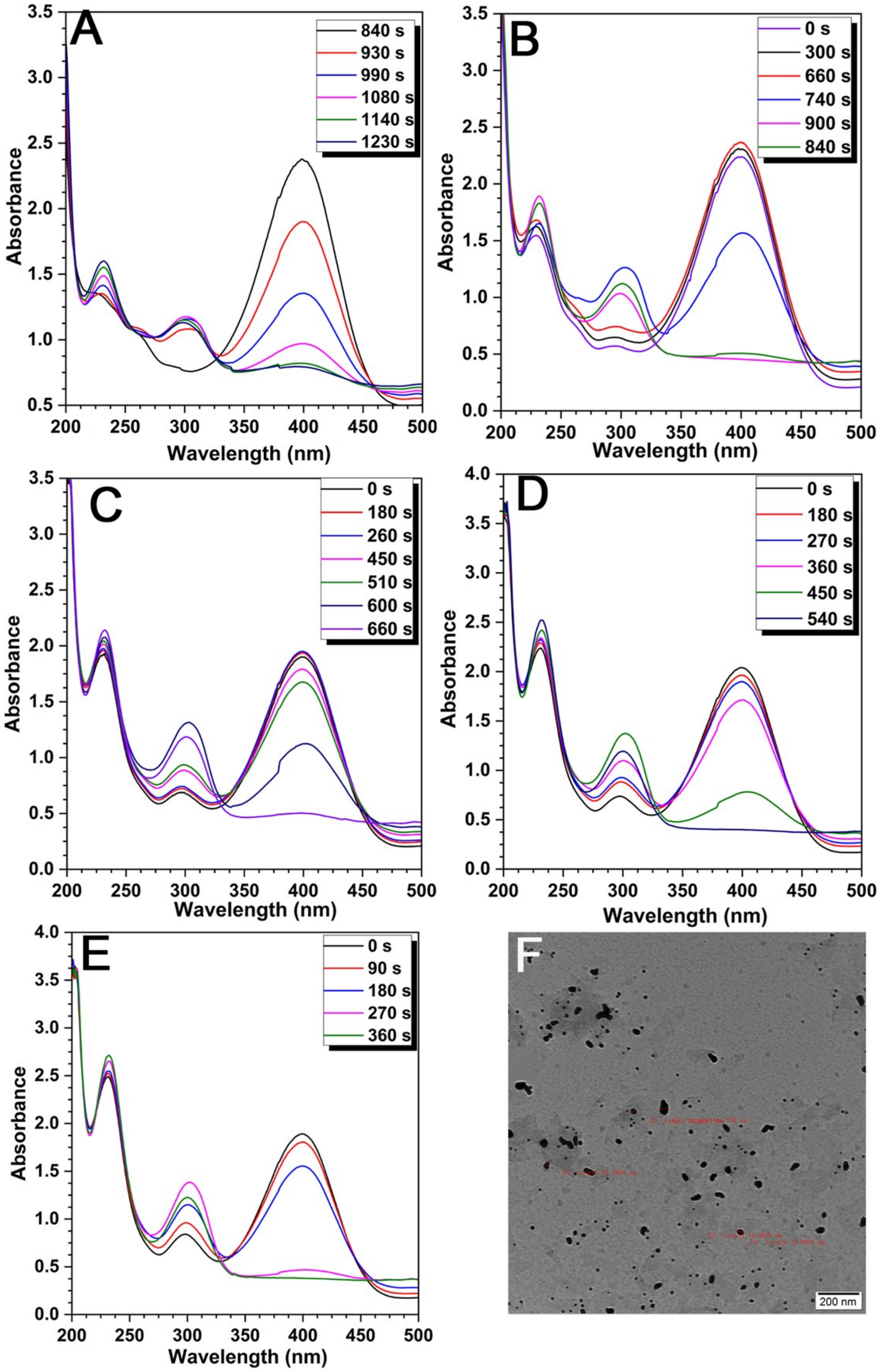

Figure S8. UV/vis absorption spectra of the reduction of 4-nitrophenol aqueous solution (0.2 mM) in the presence of AuNP@SH-NGO-PEG during 1st (A), 2nd (B), 3rd (C), 4th (D) and 5th (E) cycle; (F) TEM image of AuNP@SH-NGO-PEG after recyclable catalysis tests.

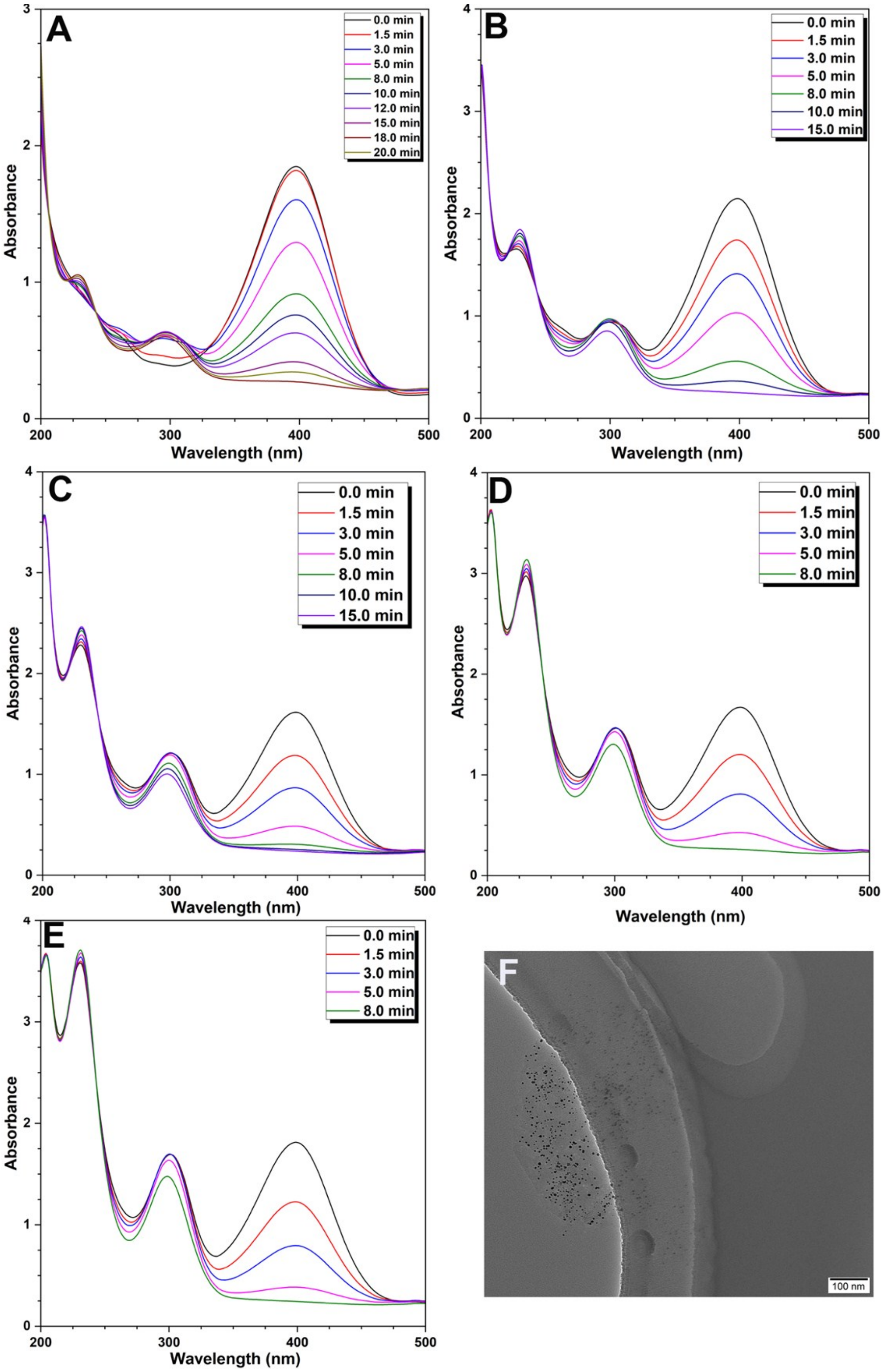

Figure S9. UV/vis absorption spectra of the reduction of 4-nitrophenol aqueous solution (0.2 mM) with AuNP@SH-PAMAM-NGO-PEG during 1st (A), 2nd (B), 3rd (C), 4th (D) and 5th (E) cycle; (F) TEM image of AuNP@SH-PAMAM-NGO-PEG after recyclable catalysis tests.

References

1. C. K. Chua, Z. Sofer and M. Pumera, *Chem. Eur. J.*, 2012, **18**, 13453-13459.
2. J. Ma, R. Liu, X. Wang, Q. Liu, Y. Chen, R. P. Valle, Y. Y. Zuo, T. Xia and S. Liu, *ACS Nano*, 2015, **9**, 10498-10515.
3. X. Sun, A. Zebibula, X. Dong, G. Zhang, D. Zhang, J. Qian and S. He, *ACS Appl. Mater. Interfaces*, 2018, **10**, 25037-25046.
4. H. Zhou, X. Wang, P. Yu, X. Chen and L. Mao, *Analyst*, 2012, **137**, 305-308.
5. N. Yan, X. Wang, L. Lin, T. Song, P. Sun, H. Tian, H. Liang and X. Chen, *Adv. Funct. Mater.*, 2018, **28**, 1800490
6. J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin and R. L. Letsinger, *J. Am. Chem. Soc.*, 1998, **120**, 1959-1964.