

Supplementary Information

Chemicals-free growth of metal nanoparticles on graphene oxide sheets under visible light irradiation

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Experimental Section

Synthesis of GO and Ag/GO: Graphite oxide was prepared by the oxidation of graphite (SP-1 grade 200 mesh, Bay carbon Inc.) using modified Hummers method.¹ Graphite oxide (6 mg) in purified water (20 mL) was exfoliated by ultrasonication (JAC 4020, 400 W, Sonic) for 30 minutes, which was stored as a stock solution.² Four milliliter of graphene oxide (GO) solution (0.3 mg/mL) was diluted by 46 mL of purified water and then the metal precursor of silver nitrate (AgNO_3 , 0.1 mmol) or gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 0.025 mmol) was added. Before irradiation, the solution was purged with argon for 30 minutes. Then, the reactor was irradiated with a 300-W Xe arc lamp (Oriel) for 8 h under continuously slow stirring. Light was passed through a 10-cm IR water filter to minimize thermal heating and a cut-off filter ($\lambda > 420$ nm), which was focused onto a 50-mL Pyrex reactor with a quartz window.

Characterization: Absorbance was measured using a UV/visible spectrophotometer (Agilent 8453). Infrared spectra were measured by standard KBr method over a range of 600–2500 cm^{-1} with a Fourier transform infrared spectrophotometer (FT-IR, MB104, Bomen). The Raman spectra for graphite oxide and the films of GO and Ag/GO were obtained by using a Bruker Senterra Raman microscope (Bruker Optics, Inc) with 532 nm laser excitation. Photoluminescence (PL) of liquid samples was excited by Xe lamp and the emission was collected at 90° to the excitation source. To avoid Raman scattering and to enhance the peak intensity, the slit width of the excitation and emission source was changed and samples were excited at 300 nm in the presence of a cut-off filter ($\lambda \geq 390$ nm) in the front of the excitation source. To estimate the buffering capacity of the acidic functional groups on GO, GO suspension (25 mL) was titrated by NaOH solution (0.01 N) under argon purging. NaOH solution (10 μL) was continuously added per a minute with measuring pH (Orion 720A pH meter). X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800 pci) analysis for films of graphite oxide, GO, and Ag/GO was carried out by using the Mg $\text{K}\alpha$ line (1253.6 eV) as the excitation source. To identify the crystalline phase, powder X-ray diffraction (XRD) patterns were measured using a PANalytical X'Pert diffractometer with an X'Celerator detector using Cu $\text{K}\alpha$ radiation. The thickness of GO and Ag/GO, spin-coated on freshly cleaved mica, was measured by a tapping mode Veeco Dimension 3100 Nanoscope V scanning probe microscope (SPM). Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) measurement of Ag/GO film was obtained. Transmission electron microscopy (TEM), electron energy loss spectrum (EELS) mapping, and high resolution TEM (HRTEM) analysis were performed using a JEM-2200FS microscope with Cs correction.

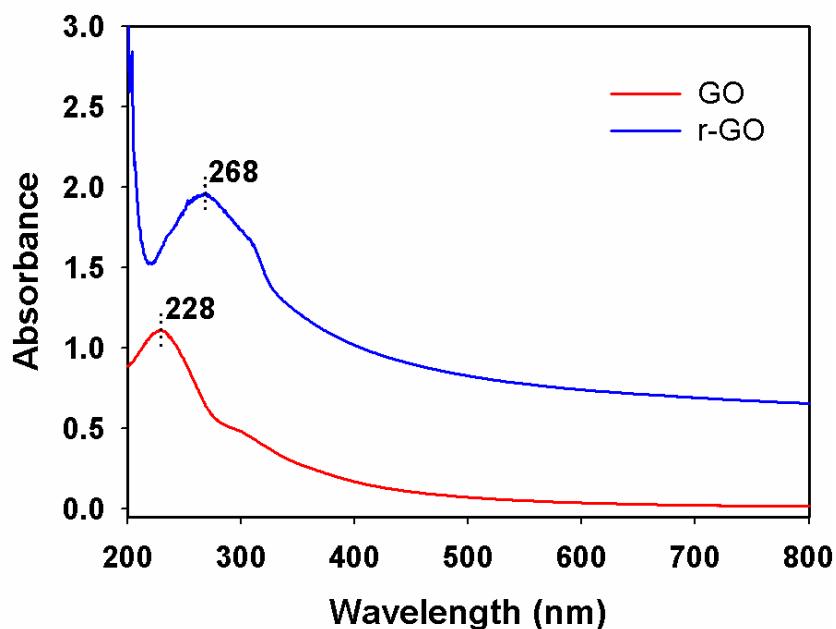


Fig. S1 UV/Visible absorption spectra of the aqueous suspension of GO and r-GO that was obtained by chemical reduction using hydrazine.

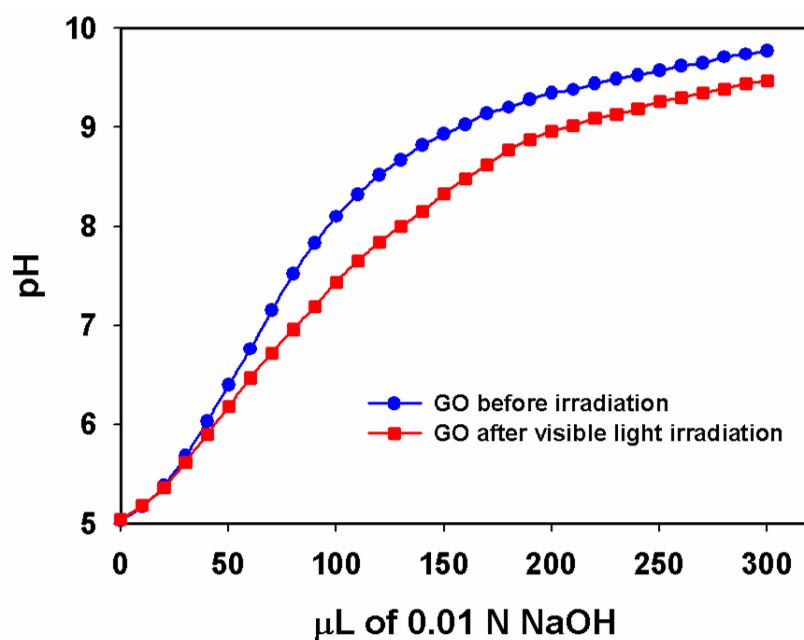


Fig. S2 pH change in GO suspension upon titrating with base. Ten microliter of 0.01 N NaOH solution is continuously added to 25 mL of GO aqueous suspension per a minute.

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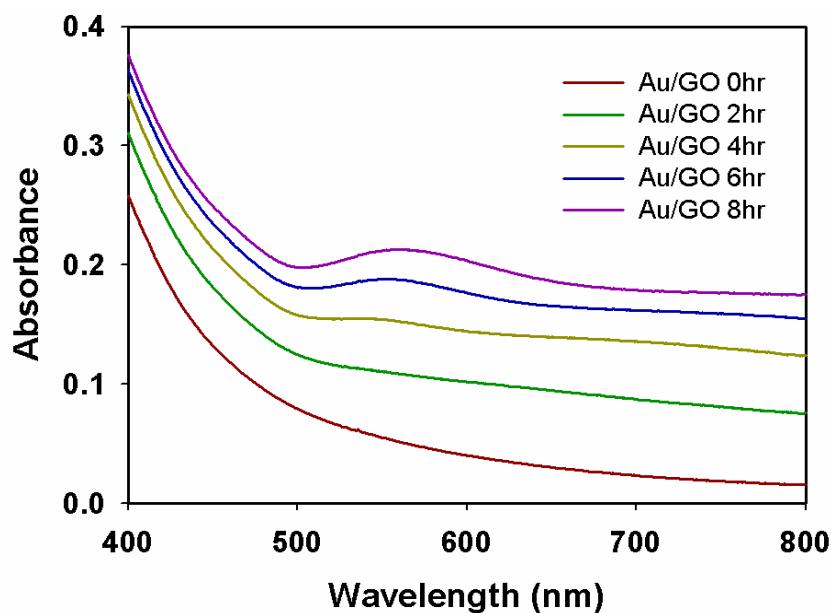


Fig. S3 Time-dependent UV/Visible absorption spectra of Au/GO under visible light irradiation in the absence of any chemical reducing agents.

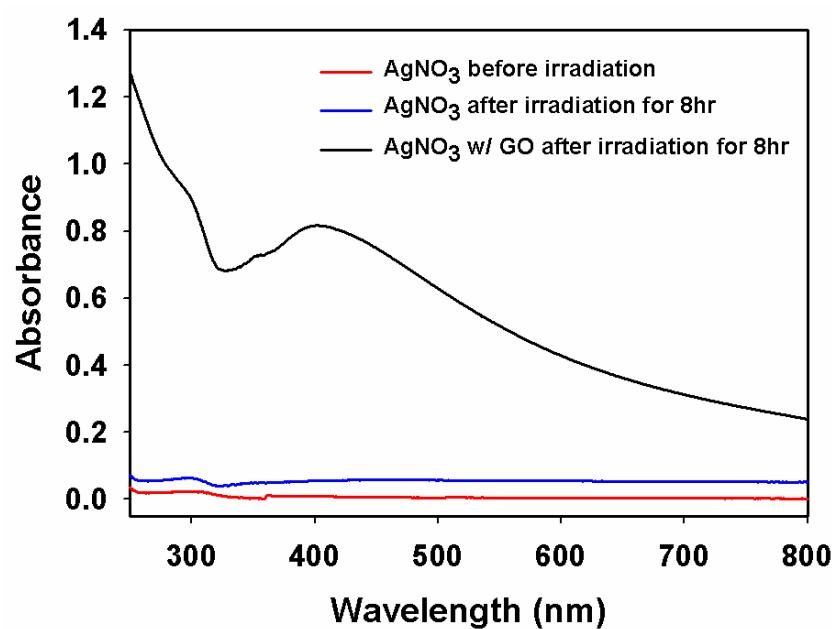


Fig. S4 UV/Visible absorption spectra of AgNO₃ solution with and without GO under visible light irradiation for 8 h.

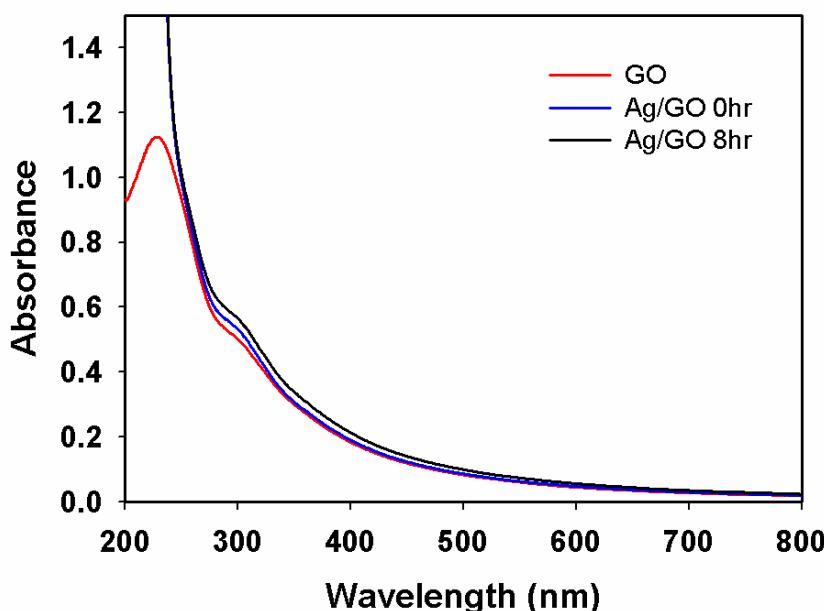


Fig. S5 UV/Visible absorption spectra of Ag/GO solution heated up to 50 °C for 8 h.

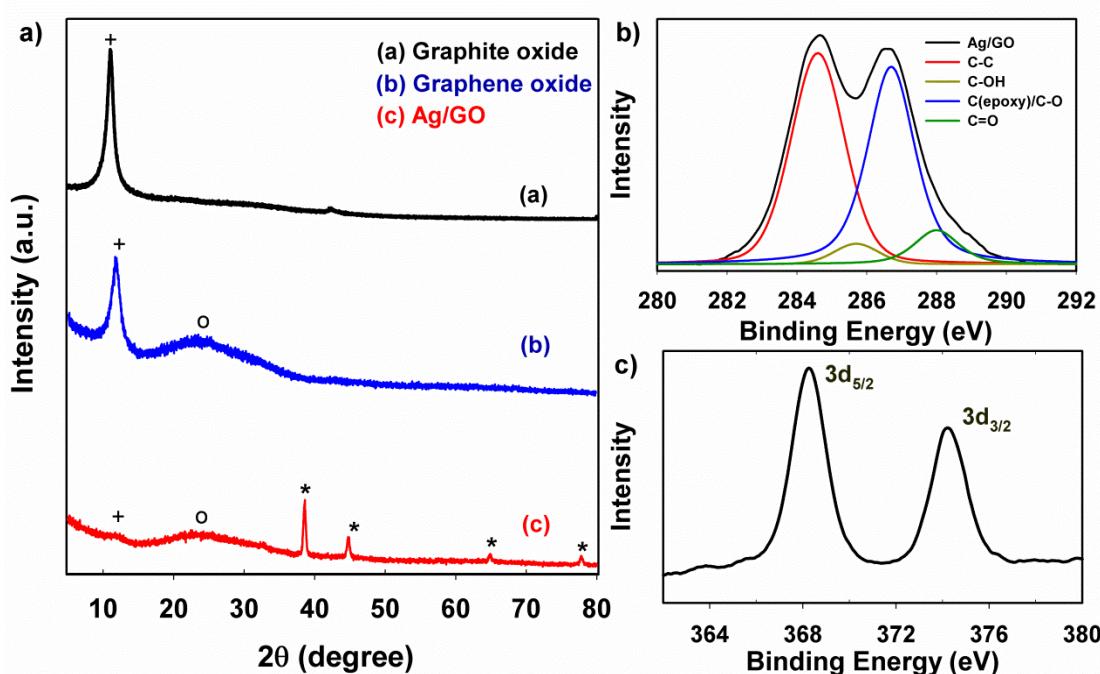


Fig. S6 (a) XRD patterns of graphite oxide, graphene oxide, and Ag/GO. (1) The (001) diffraction peak of graphite oxide is indicated by “+” mark around 11°. (2) After the exfoliation of graphite oxide and irradiation for 8 h, a weak and broad peak at 22.6° (indicated by “o” mark) appears after re-stacking of individual GO sheets. (3) The peaks at 38.5°, 44.5°, 65°, and 78° (indicated by “*” mark) appear after the loading of silver NPs on GO sheets, which correspond to (111), (200), (220), and (311) planes of metallic silver, respectively. (b) XPS C1s band analysis of Ag/GO film. (c) XPS Ag 3d band analysis of Ag/GO film.

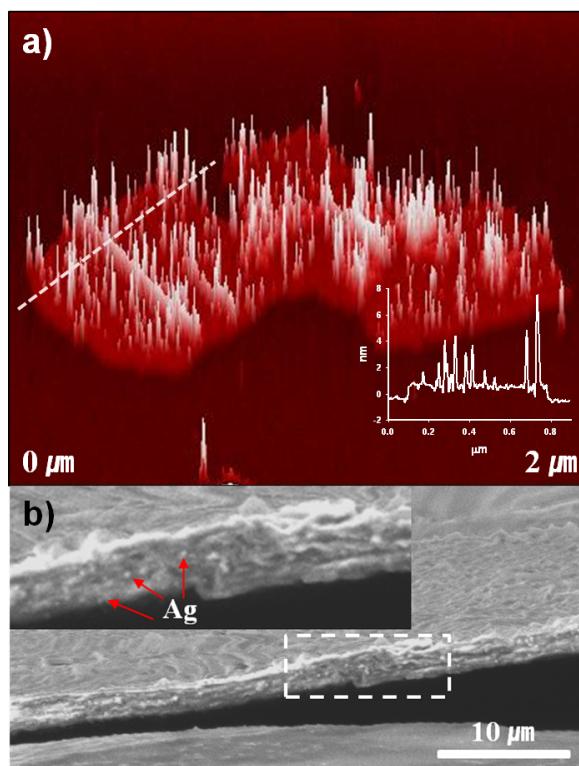


Fig. S7 (a) 3-dimensional AFM image and height profile of Ag/GO. The suspension of Ag/GO (0.24 mg/mL) was spin-coated on freshly cleaved mica substrate. (b) FE-SEM image of Ag/GO film. The inset is a magnified image and arrows point to silver NPs.

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