

Supplemental Data

Photolysis of graphene oxide in the presence of nitrate: implications for graphene oxide integrity in water and wastewater treatment

Lin Duan[†], *Tong Zhang*[†], *Weihua Song*[‡], *Chuanjia Jiang*[†], *Yan Hou*[†], *Weilu Zhao*[†], *Wei Chen*^{*†},
Pedro J.J. Alvarez[§]

[†] College of Environmental Science and Engineering, Ministry of Education Key Laboratory of
Pollution Processes and Environmental Criteria, Tianjin Key Laboratory of Environmental
Remediation and Pollution Control, Nankai University, 38 Tongyan Road, Tianjin 300350,
China

[‡] Department of Environmental Science & Engineering, Fudan University, 220 Handan Road,
Shanghai 200433, China

[§] Department of Civil and Environmental Engineering, Rice University, 6100 Main Street,
Houston, Texas 77005, United States

Submitted to *Environmental Science: Nano*

Number of pages: 14

Number of figures: 13

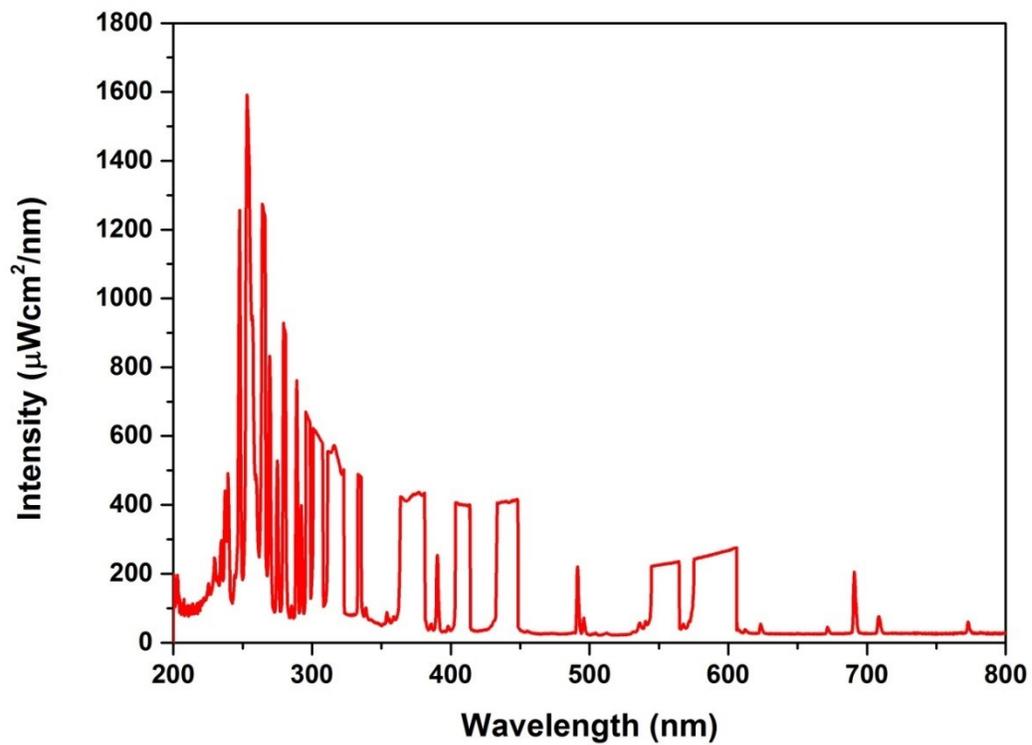


Fig. S1 The spectrum of light emitted from medium-pressure Hg lamp, measured with a radiometer.

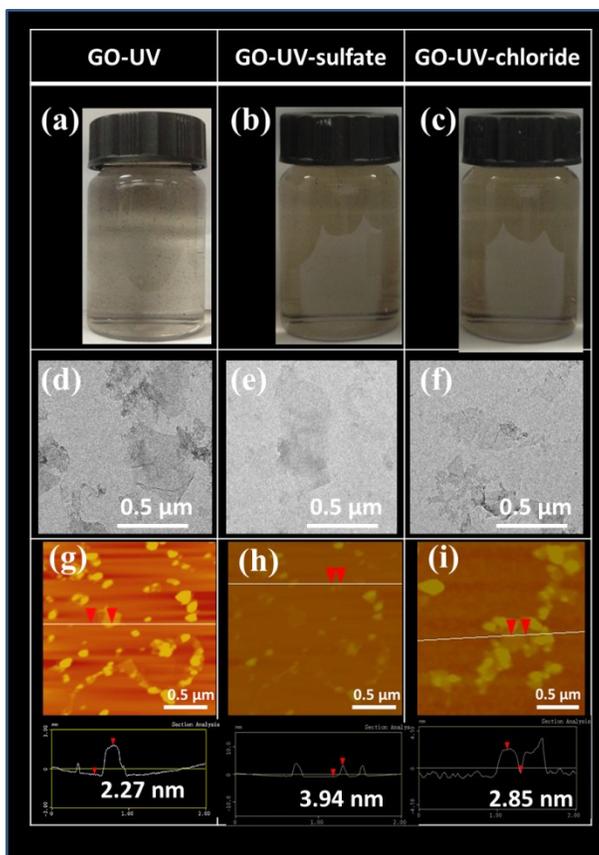


Fig. S2 Changes of GO suspension (10 mg/L) appearance and GO morphology after 9 h of UV irradiation, showing the addition of sulfate (1 mM) or chloride (1 mM) has no distinguishable effect on the transformation of GO, as evidenced by the color changes of GO suspensions (a-c: photographs), morphology (d-f: TEM images) and size (g-i: AFM images) of GO samples.

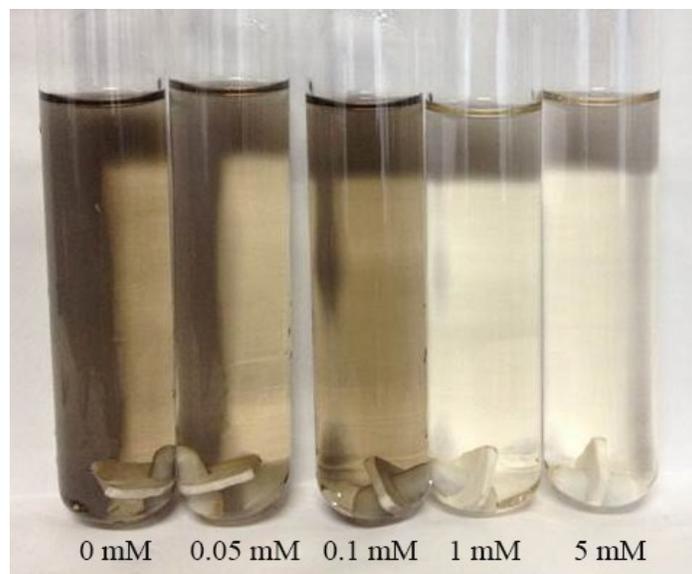


Fig. S3 Color changes of GO suspensions (10 mg/L) after 9 h UV irradiation in the presence of different nitrate concentrations (0, 0.05, 0.1, 1 and 5 mM), showing that the nitrate effect on GO photolysis was concentration-dependent. The nearly transparent color was only observed at nitrate concentration of 1 mM and above.

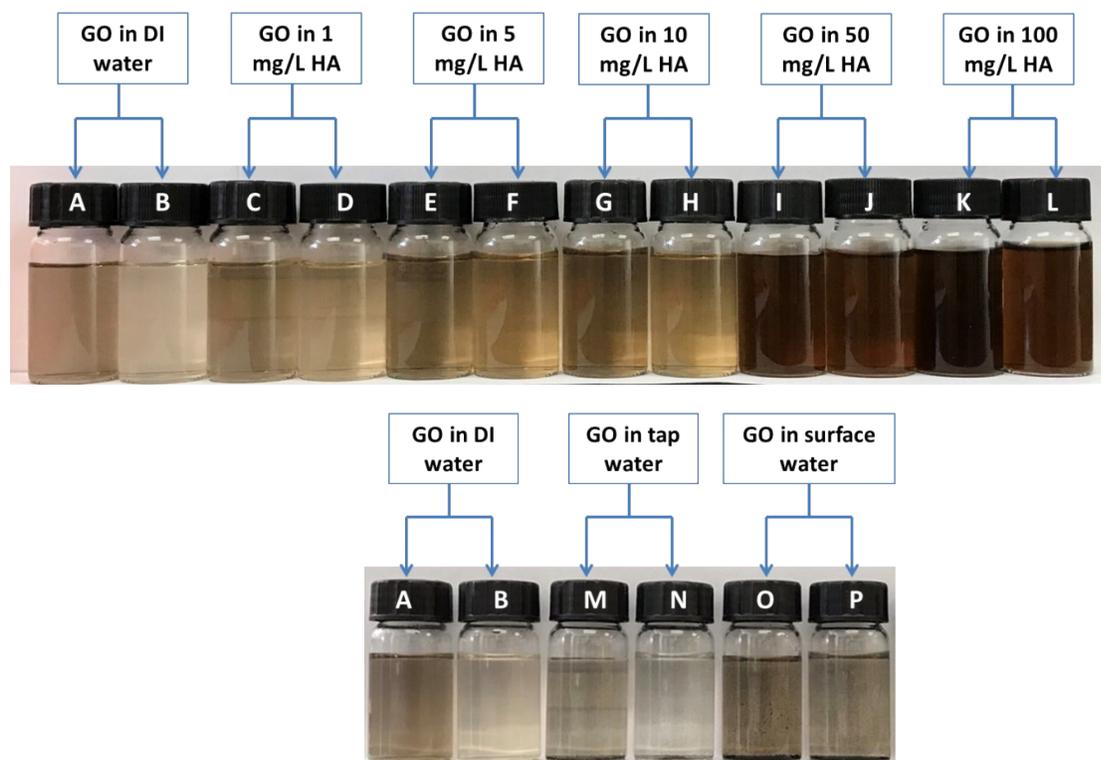


Fig. S4 Color changes of GO suspensions (10 mg/L) in the presence of different concentrations (1, 5, 10, 50 or 100 mg/L) of humic acid, and GO suspensions in tap water or pond water, after 9 h of UV irradiation in the absence and presence of nitrate, showing that the significant effects of nitrate on GO transformation were also observed under more complex solution chemistry conditions. A, C, E, G, I, K, M, and N represent GO suspensions in the absence of nitrate; B, D, F, H, J, L, N, and P represent GO suspensions in the presence of nitrate.

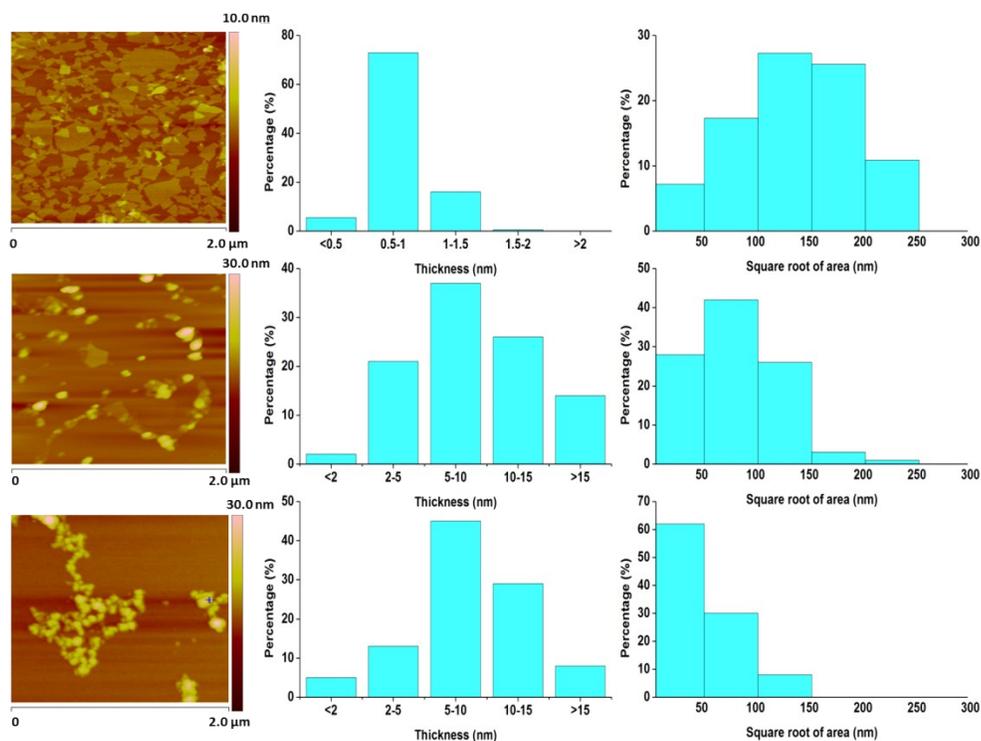


Fig. S5 AFM images of GO-dark (top), GO-UV (middle) and GO-UV-nitrate (bottom), showing the changes of the thickness and lateral size of GO nanosheets upon UV irradiation in the absence or presence of nitrate. The thickness and lateral size were determined based on more than 100 pieces of GO nanoflakes in each AFM image.

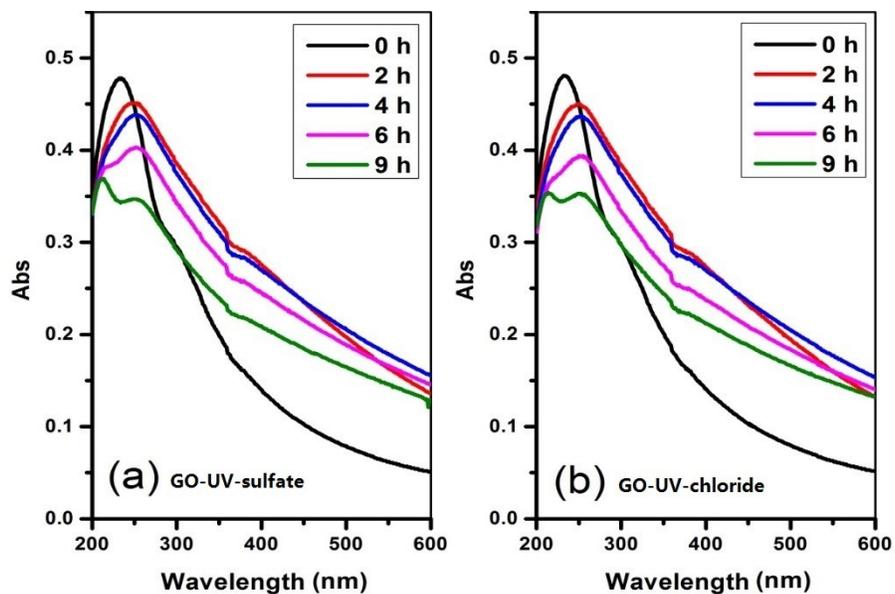


Fig. S6 UV-vis spectra of GO suspensions (10 mg/L) before and after UV irradiation in the presence of 1 mM sulfate (a) and 1 mM chloride (b). For both GO samples, red shift of λ_{\max} , indicating the restoration of π -conjugated structures, was observed.

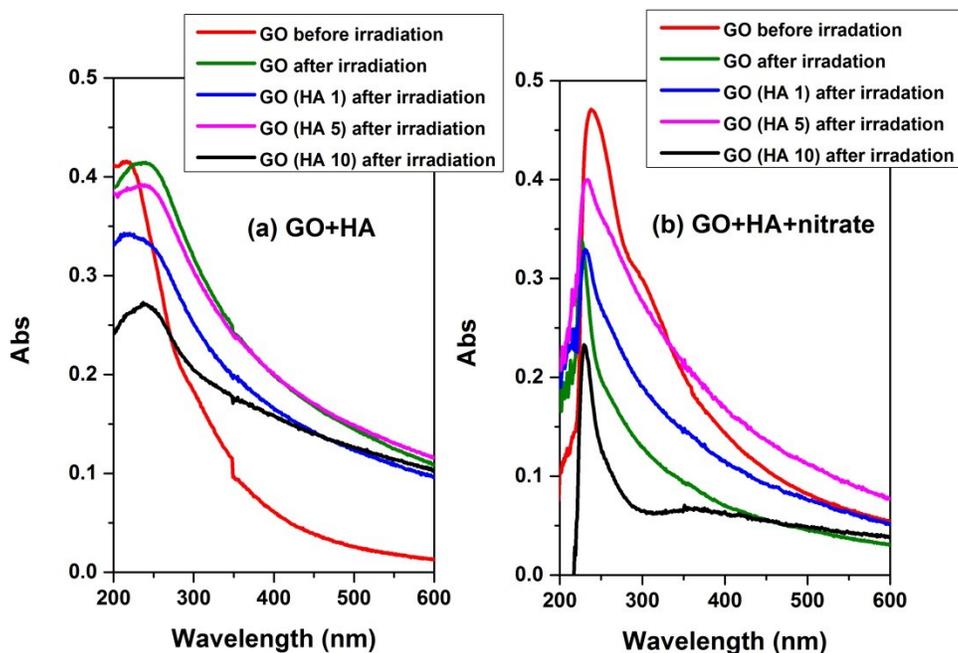


Fig. S7 UV-vis spectra of GO suspensions (10 mg/L) with nitrate (a) or without nitrate (b) before and after 9 h of UV irradiation. For GO samples without nitrate (regardless whether humic acid (HA) was present), red shift of λ_{\max} , indicating the restoration of π -conjugated structures, was observed; for GO samples with nitrate (regardless whether HA was present), blue shift of λ_{\max} , indicating the damage of the local π -conjugated structures of GO sheets, was observed. GO represents GO in DI water; GO(HA 1) represents GO in 1 mg/L HA; GO(HA 5) represents GO in 5 mg/L HA; GO(HA 10) represents GO in 10 mg/L HA.

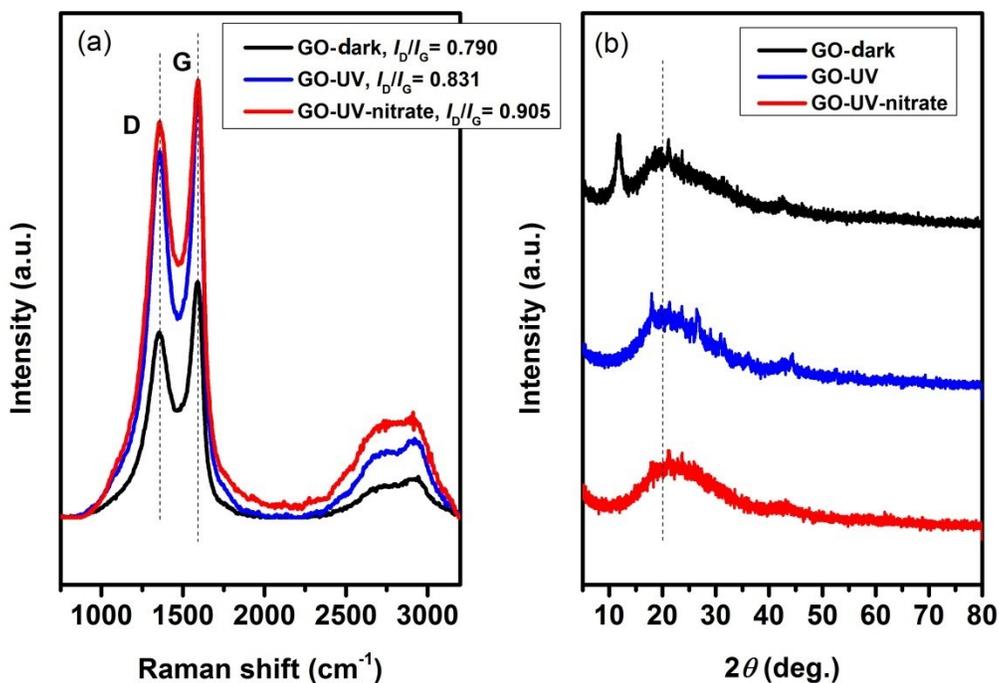


Fig. S8 Raman spectra (a) and XRD patterns (b) of GO, GO-UV and GO-UV-nitrate, showing the nitrate effects on the structural changes of GO. A larger increase of I_D/I_G value was observed for GO-UV-nitrate, indicating an increase in the abundance of GO edges or defects. The peak at 2θ of 10.4° (the characteristic peak of GO in XRD patterns) was not observed for both GO-UV and GO-UV-nitrate, indicating that GO was reduced after UV irradiation.

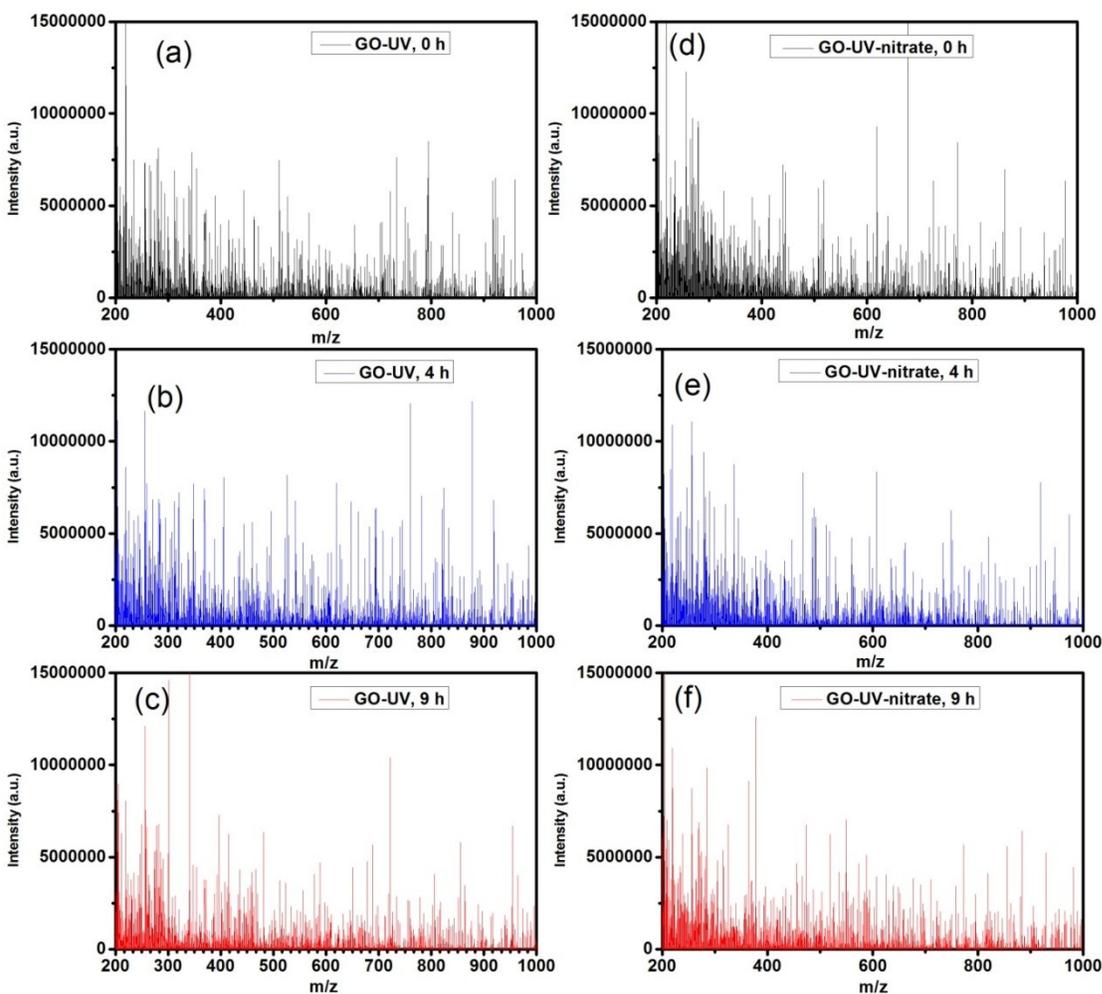


Fig. S9 Mass spectra of the photo-transformation products for GO-UV and GO-UV-nitrate, after receiving UV irradiation for increasing durations (0, 4 and 9 h). All spectra are plotted on the same scale. A variety of low molecular-weight chemical species were observed in the presence of nitrate. After prolonged UV irradiation (9 h), the abundance of the chemical species with higher m/z (i.e., 700–1000) was significantly lower in the GO suspension with nitrate (f), compared to that without nitrate (c).

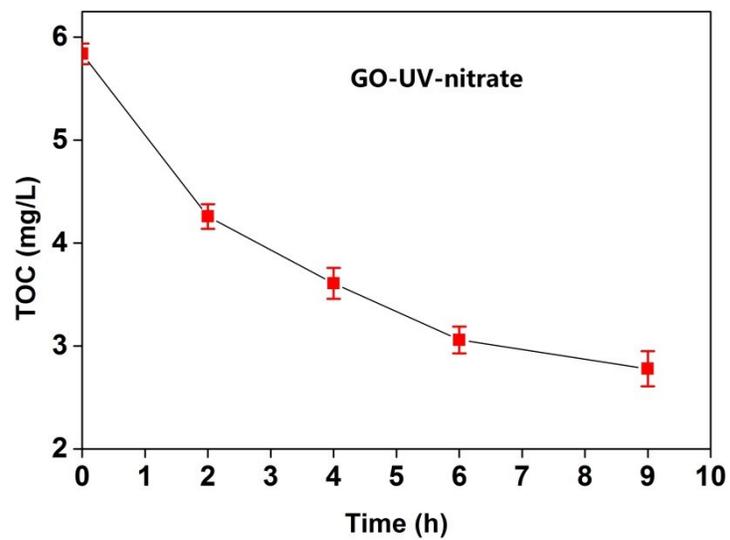


Fig. S10 Change of total organic carbon (TOC) concentration of 10 mg/L GO suspension with irradiation time in the presence of 1 mM nitrate.

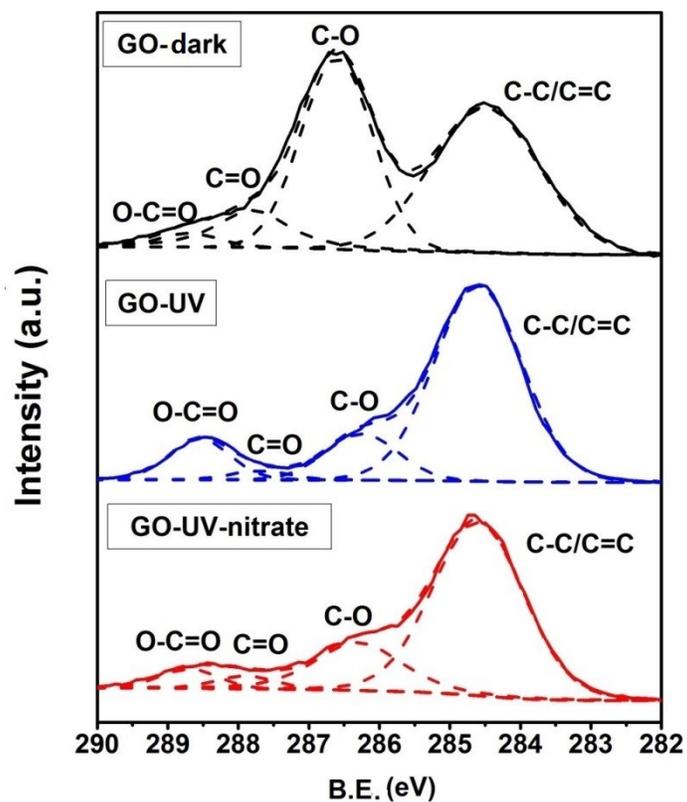


Fig. S11 C 1s XPS spectra showing the changes in the distributions of GO surface functional groups: (a) GO-dark; (b) GO-UV; (c) GO-UV-nitrate. Increased intensity of C–C/C=C peak but decreased intensity of C–O peak were observed for both GO-UV and GO-UV-nitrate. Higher intensity of C–O peak was observed for GO-UV-nitrate than that for GO-UV.

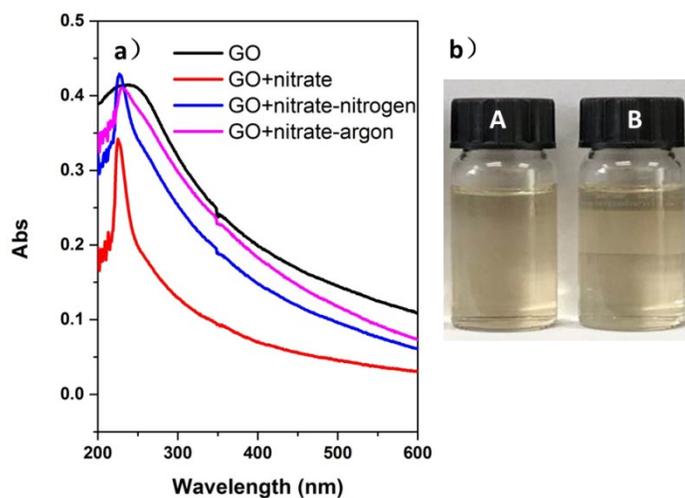


Fig. S12 UV-vis spectra (a) and photographs (b) of GO suspensions (10 mg/L) upon 9 h of UV irradiation. A and B represent the GO suspensions purged (1 h) with of 99.99% nitrogen and argon, respectively, to remove dissolved oxygen prior to UV irradiation. Essentially the same results of N₂-assisted and Ar-assisted experiments were observed.

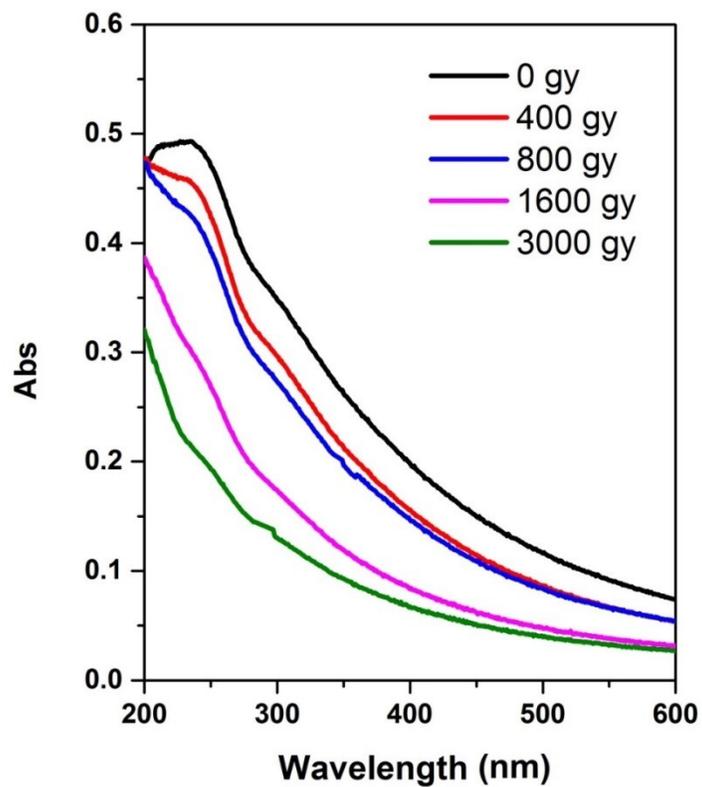


Fig. S13 UV-vis spectra of 10 mg/L GO suspensions after receiving increasing doses of steady-state γ -radiation under N_2O -saturated conditions. The characteristic peak of GO centered at 230 nm gradually disappeared during γ -radiolysis, indicating molecular alteration due to the reaction of GO with $\bullet OH$.