

Electronic Supplementary Information

Nonlinear optical performances of graphene oxide ternary nanohybrids functionalized by axially-coordinated gallium porphyrins

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Experimental Section

Instruments and measurements

Fourier transform infrared (FTIR) spectra were used to determine the characteristic vibration of all samples, which were measured by a MB154S-FTIR spectrometer (Canada) between 400 and 4000 cm^{-1} using KBr disks. The optical characterization was performed by the ultraviolet/visible (UV/Vis) absorption spectra with a JASCO V-570 spectrophotometer using 1 cm path length quartz cuvettes. Raman spectra were taken at room temperature on a Renishaw Invia Raman Microscope operating at the wavelength of 532 nm-line of a Ar^+ ion laser as the excitation source provided in backscattering geometry. The chemical nature and elemental composition of GO and its nanocomposites were characterized by X-ray photoelectron spectroscopy (XPS), which was performed on a RBD upgraded PHI-5000C ESCA (PerkinElmer) electron spectrometer with a Mg $K\alpha$ line at 280 eV. Scanning electron microscopy (SEM) images were acquired using a Hitachi S4800 instrument to investigate the morphology of the samples.

The photoelectrochemical measurements including the transient photocurrent and impedance spectroscopy were carried out in an electrochemical workstation (CHI

614E, CH Instrument) with a three-electrode quartz using PBS (PH = 7.4) electrolyte solution. Pt wire ($1 \times 1 \text{ cm}^2$) was used as the counter electrode and silver/ silver chloride (Ag/AgCl) electrode was used as the reference electrode. The samples was dropped onto the fluorine-doped indium tin oxide (ITO) substrate with an area of 0.7854 cm^2 and used as the working electrode. A xenon lamp (350 W) was employed as the light source and the incident intensity of illumination was adjusted to 100 mW cm^{-2} before every experiment. The transient photocurrent-time dependent measurements and electrochemical impedance spectroscopy (EIS) experiments were performed at an open circuit potential.

For open Z-scan measurement, the linearly polarized 4 ns pulsed laser radiation at 532 nm was used for excitation. For measurements of the nonlinear optical properties, all samples were placed in quartz cells of 2 mm, and adjusted to have the same transmittance. The incident laser intensity is $9 \text{ }\mu\text{J}$ for nanosecond Z-scan experiments. The incident energy and transmittance were monitored by two energy detectors (Rjp-765 energy probes), which were linked to an energy meter (Rj-7620 Energy Ratiometer, Laserprobe). Investigation of the optical limiting performances of all samples was carried out by the Z-scan technique with the laser system as in the nonlinear optical experiments, where the intensity of the incident energy is varied continuously by using a polarizer-analyzer combination and the total output energy is captured by a large aperture photodetector kept at a distance of 10 cm from the optical limiting materials; curves of transmittance versus incident energy were obtained in this experiment. The beam waist at the focal plane is estimated to be $30 \text{ }\mu\text{m}$ for all experiments. To avoid cumulative thermal effects interfering with experiments directed at identifying the major optical limiting mechanism, the laser pulses were delivered at a low frequency of 2 Hz; each pulse of light was thus ensured to encounter fresh sample.

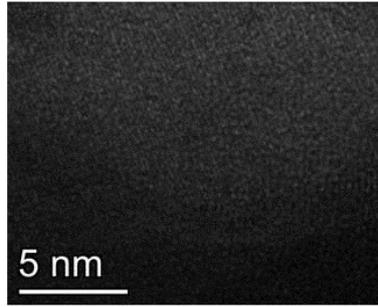


Figure S1. HRTEM spectrum of GaTPP-GO-GaTTP.

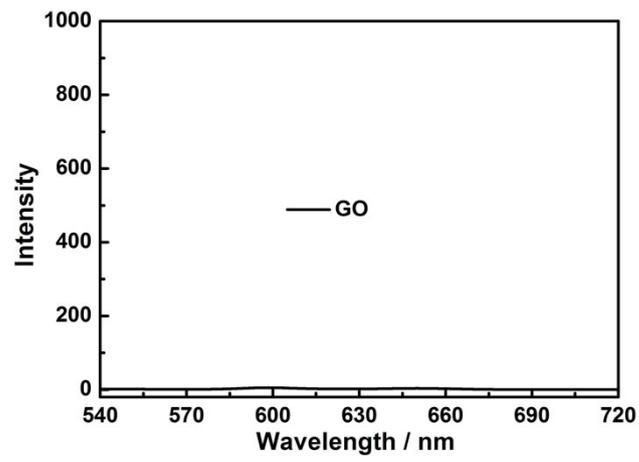


Figure S2. Fluorescence spectrum of GO.