

Recyclable Non-metal Surface Enhanced Raman Scattering Substrate based on Graphene Oxide/ZIF-67 nanocomposites

Shuang Wang, Xiaoya Zhang, Qun Xiang, Sijie Zhou, Jun Zheng,

Ruiwen Yan* and Guiqi Gao*

*Institute of Physical Science and Information Technology, Anhui University, Hefei,
230601, China*

Experimental section

Materials and general methods

CoCl₂ and 2-methylimidazole were analytical grade and purchased from sigma-aldrich Shanghai trading company and Aladdin industrial corporation (Shanghai, China), respectively. All reagents used in this work were of analytical grade and were used directly without further processing. Graphite Oxide (GO) powder was provided by Shanghai Ashine Technology Development Co., Ltd (99%). All chemicals were used without further purification, and Mil-li-Q water was used throughout this study.

Typically, 284 mg of Co(Cl)₂·6H₂O (0.012 mol) were dissolved in 20 mL of water under stirring to obtain a clear pink solution . 11.76 g of 2-methylimidazole (0.5 mmol) was dissolved in 20mL of water to form a transparent homogeneous solution . After 1 h sonication and the mixture was continuously stirred for 4 h, and the above MOF dispersions were mixed with 20 mL of the aqueous solution of GO (0.3 mg·mL⁻¹). After stirring at room temperature for 12 hours, the products were collected by centrifugation, washed with a large amount of deionized water, and finally dried at 80 °C for 6 h.

For the preparation of SERS substrates, firstly, the SiO₂/Si substrate was washed clean by ultrasonication in acetone, ethanol, and water. ZIF-67, GO and GO/ZIF-67 were then deposited on the surface of the SiO₂/Si substrate (300 nm thick oxide) by simple drop-casting. To ensure comparable substrates with the same target molecules, 10 μL of R6G solutions with the same concentration (10⁻⁶ M) were dropped onto the substrates respectively and dried by vacuum evaporation to collect the whole substrate

for the Raman spectra each sample.

The Raman spectra of the samples were measured by a Renishaw inVia microspectrometer using an excitation wavelength of 532 nm. A 50× objective was used to focus the laser beam and to collect the Raman signal. The lateral resolution of the instrument was about 1 μm , and the laser power on the sample was about 1 mW to avoid laser-induced heating. Before every data acquisition, the intensity of the Raman peak at 520 cm^{-1} from silicon was normalized, and the Raman spectra were recorded in the range of 550-1800 cm^{-1} during a 10 s acquisition.

Recycling is performed by an annealing process, 10 μL of R6G solutions with the same concentration (10^{-6} M) were dropped onto the substrates respectively, which were heated at 300 $^{\circ}\text{C}$ for 30 min in air to clean off the adsorbed R6G molecules, repeated four times on the same sample.

Raman mapping measurements were performed under the 532 nm excitation line on an inVia Raman microscope in a standard backscattering configuration. A computer-controlled XY translation stage was used to acquire a total of 121 SERS spectra within the scan area of 30 $\mu\text{m} \times 30 \mu\text{m}$ divided into an acquisition grid by 3 μm step size in both dimensions. All spectra in this work were obtained with an exposure time of 1 s and at 0.5 mW laser power before the objective. The SERS intensity maps of R6G vibration mode (613 cm^{-1}) was derived using the signal intensity map generation algorithm of WiRE 3.4 software.

The signal stability was tested by using a time evolution method in which the Raman signals of the R6G coated SERS substrate were collected at the same position for 10 min at 1 min intervals.

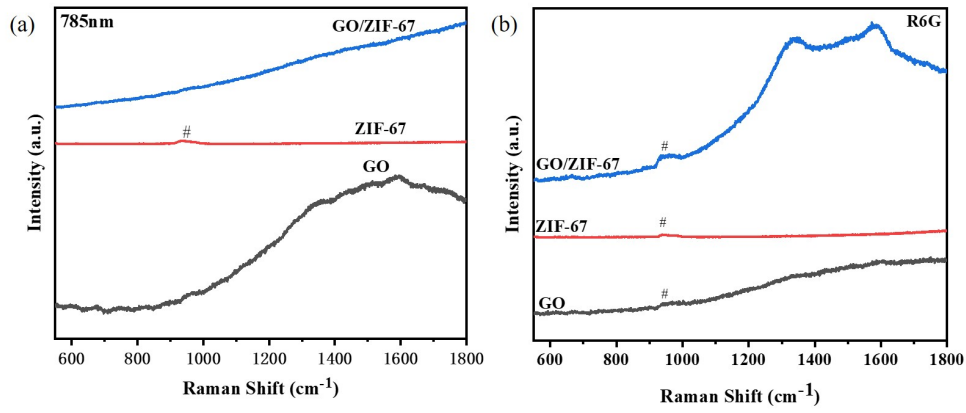


Figure S1. Raman spectra of GO, ZIF-67 and GO/ZIF-67 at 785nm laser lines (a); Raman spectra of the R6G molecules (10⁻⁶M) on the GO, ZIF-67 and GO/ZIF-67 substrates at 785nm laser lines.

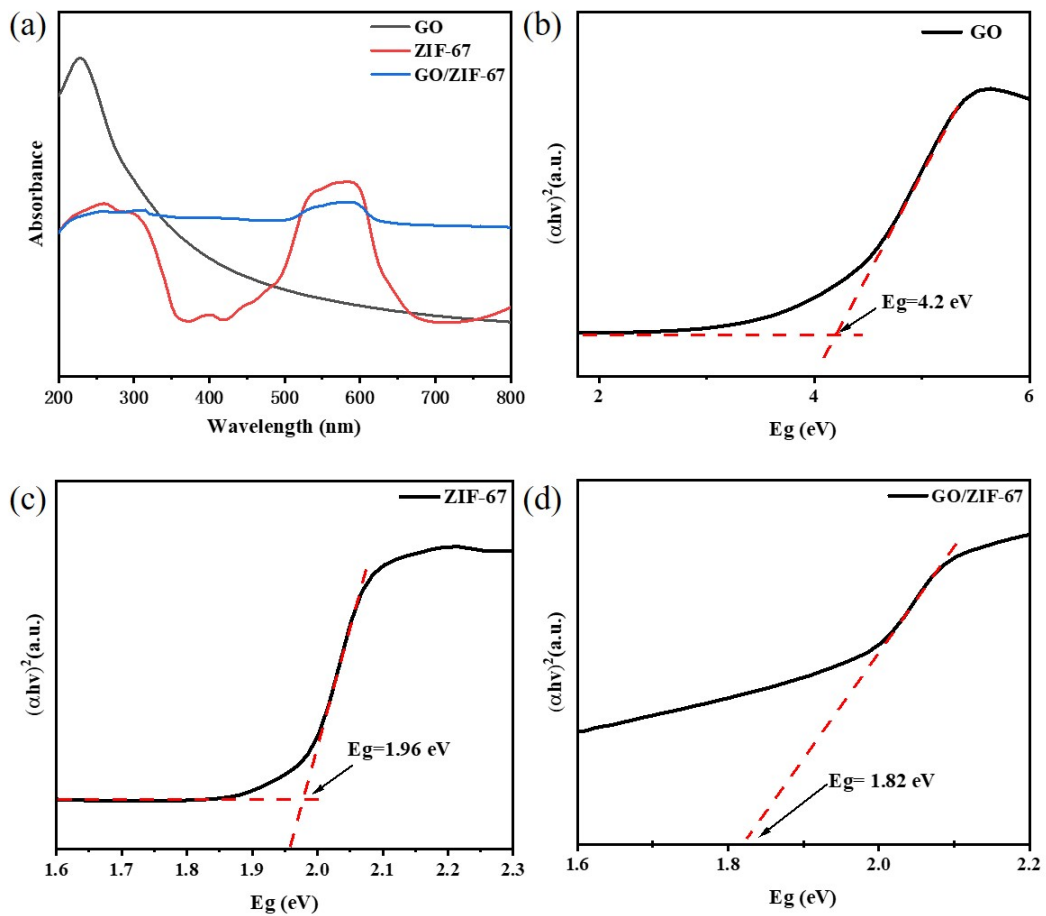


Figure S2. (a) UV-Vis absorbance spectra of ZIF-67, GO and GO/ZIF-67; (b-d) Band gap of GO (b), ZIF-67 (c) and GO/ZIF-67 (d);

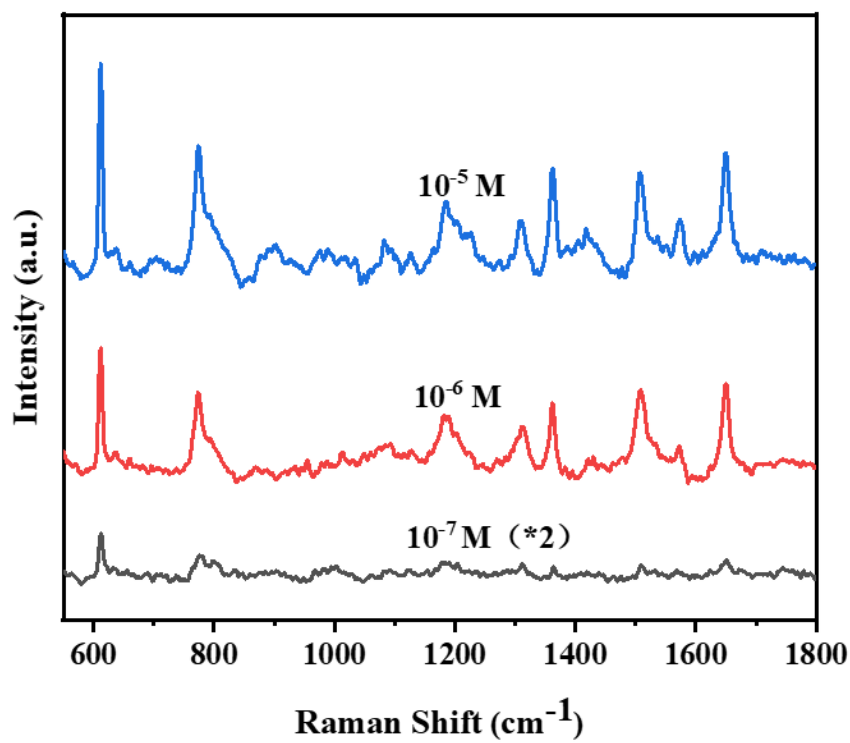


Figure S3. SERS spectra of R6G on the ZIF67 substrate at four different concentrations, 10⁻⁵, 10⁻⁶ and 10⁻⁷ M, suggesting that the detection limit is as low as 10⁻⁷ M.

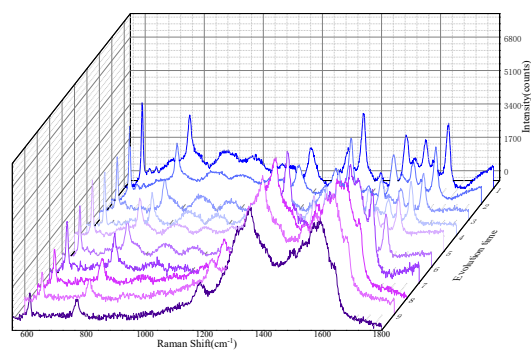


Figure S4. The signal stability of the GO/ZIF-67 substrates.

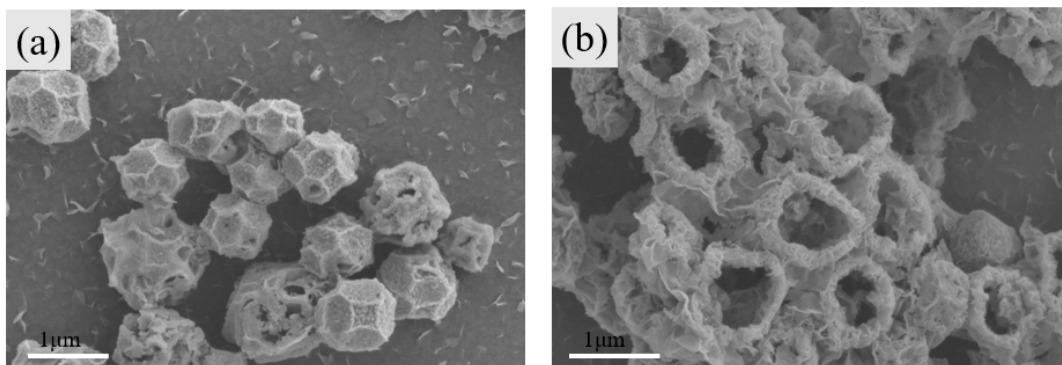


Figure S5. SEM images of bare ZIF67, after one cycle heat treatment, four cycles heat treatment, respectively.

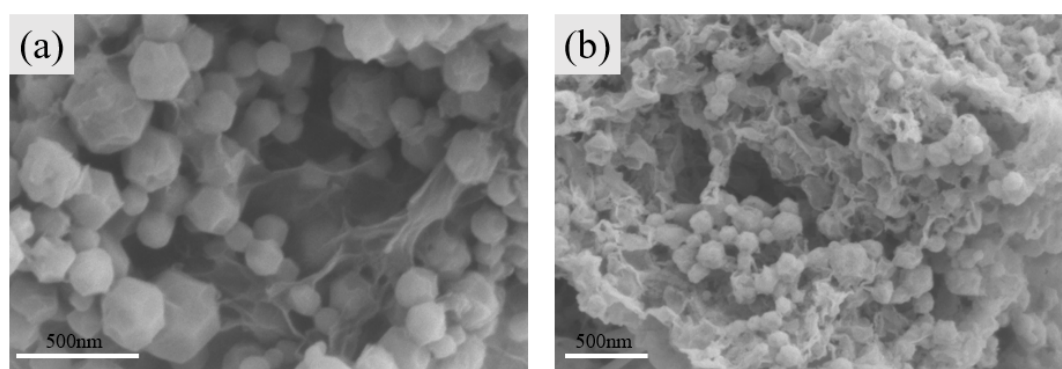


Figure S6. SEM images of GO/ZIF67, after one cycle heat treatment, four cycles heat treatment, respectively.