

Supporting Information

Bi-functional ZnO/RGO/Au substrate : photocatalysts for degrading pollutant and SERS substrates for real-time monitoring

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1. Experimental section

Chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. GO was supplied by Nanjing Xinfang NANO Inc. (China).

Fabrication of ZnO nanorod arrays. The ZnO nanorod arrays were prepared in a typical two-step method [S1]. The Si wafers were cut to square pieces (1 cm × 1 cm), which were then cleaned by acetone, ethanol, and ultra-violet ozone, successively. The seeding process was carried out by spin coating with zinc acetate ethanol solution (5 mM) and thermal decomposition at 573 K for 20 min. The seeded wafer was placed aslant in an aqueous solution of zinc nitrate (0.021 M) and methenamine (0.021 M) at 363 K for 90 min. Then, the Si pieces were washed by deionized water and dried in air to get ZnO nanorod arrays.

Fabrication of ZnO/RGO composite. The above pieces were immersed into 0.05 mg/ml GO aqueous solution and lift up horizontally, then put under UV light for 30 min to obtain ZnO/RGO composites [S2].

Fabrication of ZnO/RGO/Au substrate. Firstly, the HAuCl_4 aqueous solution was prepared freshly by adding HAuCl_4 (0.1 ml, 10 g/l) and hexadecyl trimethyl ammonium bromide (CTAB, 0.2 ml, 0.01 M) into 9.7 ml deionized water, and then stirred for 5 min. Secondly, the ZnO/RGO composite was immersed in freshly HAuCl_4 aqueous solution. They were irradiated under UV light for 5 min. Then the composite was taken out and rinsed slightly with deionized water. After repeated the process of irradiation and rinsing for 5 times, the ZnO/RGO/Au composite was dried in air. Thirdly, the composite was annealed at 350 °C for 20 minutes in the presence of N_2 atmosphere in order to remove CTAB.

SERS monitoring and degradation of R6G. The SERS monitoring and photodegradation were processed in a liquid system. The ZnO/RGO/Au substrate was put into a square groove (1.5 cm × 1.5 cm × 0.2 cm) made of Teflon, then the R6G aqueous solution (200 μl , 1×10^{-5} M) was added into the groove and covered with a quartz coverslip. The groove was placed on sample stage of the Raman spectroscope and irradiated simultaneously under UV light. And the SERS signals of the R6G were collected at one minute interval using a 633 laser as excited source.

Recyclable SERS detection. After SERS detection of R6G with 633 nm laser, the substrate was taken out from the square groove and then washed with deionized water and irradiated with a 100W high-intensity ultraviolet lamp (365 nm) at room temperature for 30 min. Then the substrate was rinsed slightly with deionized water several times, and dried at 80 °C under vacuum. There are only the signals of Si wafer and RGO after the self-cleaning process. The recycled substrate was used as SERS

substrate to detect Raman signal of R6G (10^{-5} M), showing strong Raman signal. Repeating the process of self-cleaning and detection for three times.

Controlled experiments of photocatalytic performance. 0.1 ml 10 mg/ml catalysts aqueous solution was mixed with 2.9 ml 1×10^{-5} M R6G aqueous solution, and then the mixture was stirring under dark condition for 30 min. Subsequently, the mixture was irradiated with UV light for different time and the results were recorded using UV-vis spectra.

Characterization. Morphologies and structures of the samples were characterized with FESEM (FEI Co., model Quanta-200), TEM (Tecnai G2 F20), XRD (Philips X'Pert XRD with Cu $K\alpha$ radiation). Spectroscopic properties were recorded by UV-vis absorption spectra (PerkinElmer Lambda 750 spectrophotometer) and Raman spectroscopy (Laser Confocal Raman Microspectroscopy, LabRAM HR 800, laser wavelength 633 nm, laser size 2 μm , accumulation time 2 s and microscopic objective 50X). The photocatalytic reaction was conducted under UV lamp irradiation (SB-100P/FA, 365 nm, 100 W, USA).

2. Morphology of ZnO nanorod arrays at side view

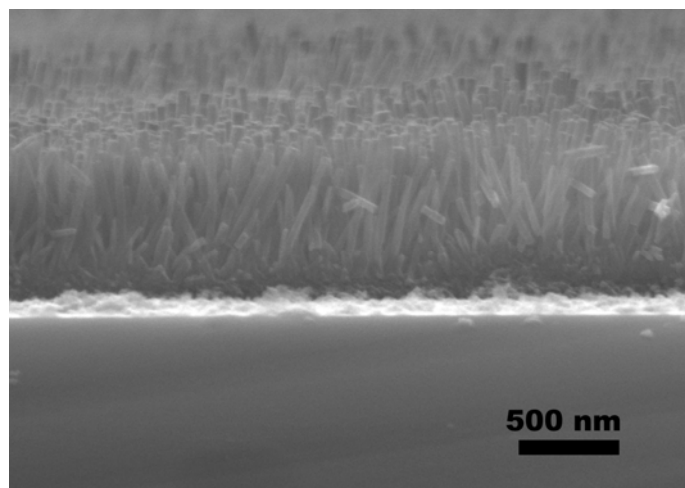


Figure S1. SEM image of ZnO nanorod arrays.

3. Controllability of density of Au NPs on the ZnO/RGO substrate

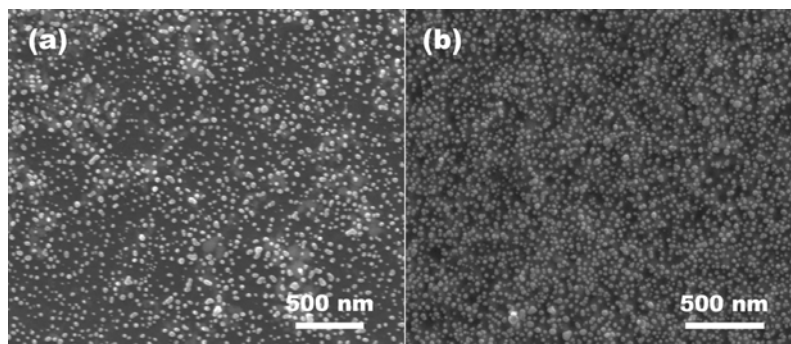


Figure S2. SEM images of ZnO/RGO/Au substrate for different growing time. (a) First cycle, 30 min; (b) second cycle, 60 min.

4. The XRD patterns and Raman spectrum

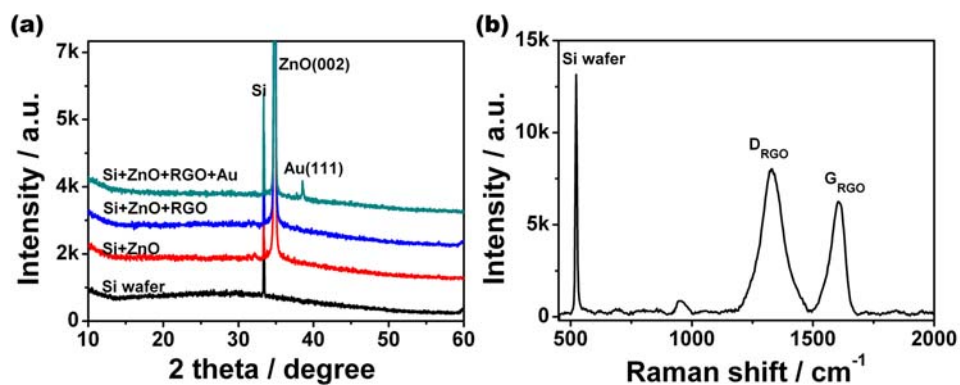


Figure S3. (a) The XRD patterns of Si wafer, Si/ZnO, Si/ZnO/RGO and Si/ZnO/RGO/Au substrate. (b) Raman spectrum of Si/ZnO/RGO/Au substrate.

5. The Raman spectra of RGO in the process of fabrication of ZnO/RGO/Au composites

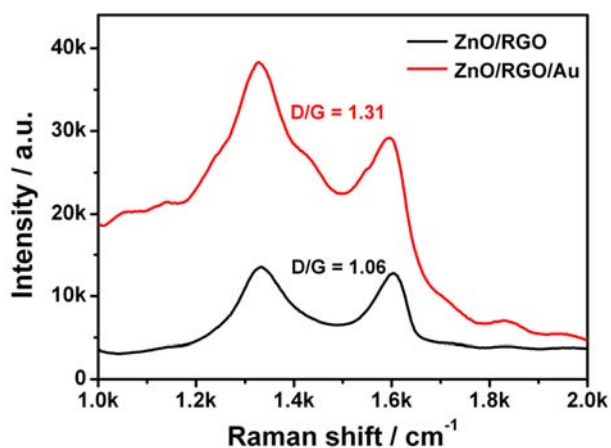


Figure S4. The Raman spectra of RGO in ZnO/RGO and ZnO/RGO/Au composites.

Compared with the Raman spectrum of RGO in ZnO/RGO composite, there is no obvious change in peak position for RGO in ZnO/RGO/Au composite. However, the D/G ratio increases from 1.06 to 1.31, which indicates the more defects was introduced the RGO during the growth of Au nanoparticles [S3-S5].

6. The solid UV-vis spectra of ZnO nanorod array and ZnO/RGO/Au substrate

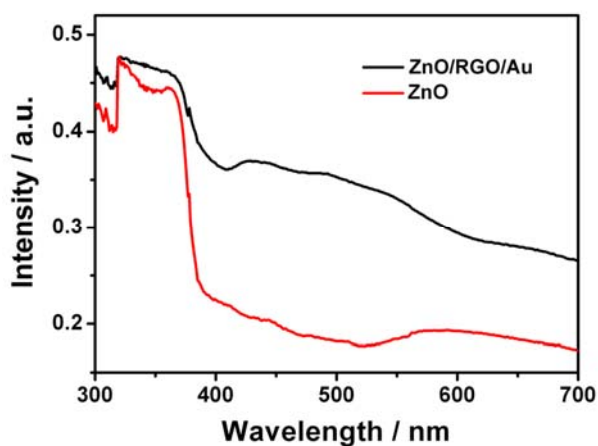


Figure S5. The UV-vis spectra of ZnO nanorod arrays and ZnO/RGO/Au substrate showed higher absorbance of the latter than the former in the visible light range.

7. The uniformity and stability of SERS substrate

An important feature showed in the Figure S6a is the excellent uniformity of the SERS signals. The SERS contour was plotted for the line-mapping mode at 1 μm increment. Significantly, each spot showed distinctive Raman intensity, revealing excellent capability to enhance the Raman signals of the R6G molecules. The Figure S6b shows the excellent stability.

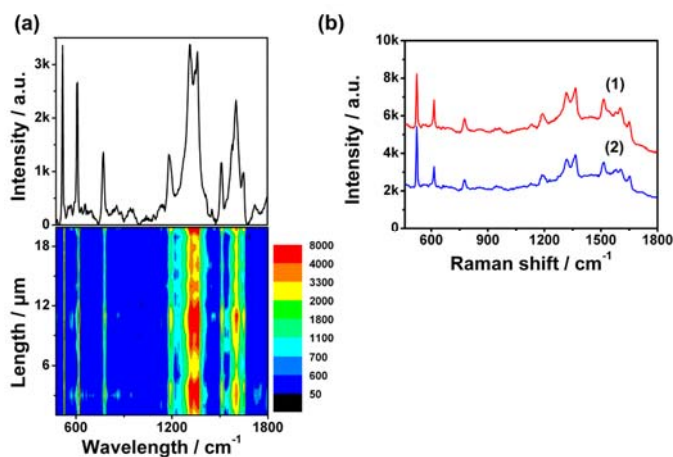


Figure S6. (a) SERS mapping of R6G collected from random area of as-prepared Au/RGO/ZnO substrate. Data acquisition time 2 s, $C_{\text{R6G}}=1 \times 10^{-5}$ M; (b) SERS spectra of R6G molecules collected from the freshly prepared substrate (Curve 1) and the substrate exposed at air for 15 days (Curve 2).

8. The relationship between the peak intensity and concentration of R6G

The work curves of peak intensity and concentration of R6G were obtained, finding out the linear relationship between intensity and concentration. In this process, the peak intensity of Si wafer at 520 cm^{-1} was chosen as reference value.

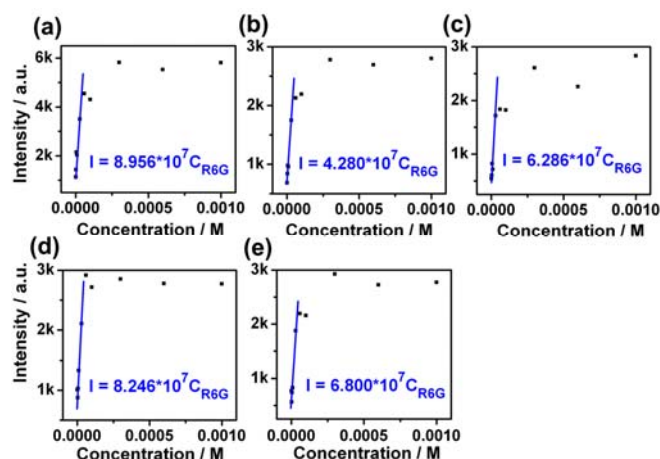


Figure S7. The work curves of Raman peak intensity and concentration of R6G at (a) 614 cm^{-1} , (b) 775 cm^{-1} , (c) 1186 cm^{-1} , (d) 1515 cm^{-1} , and (e) 1650 cm^{-1} .

The peak at 775 cm^{-1} corresponding to C-H bend out of plane can be also chosen as marker peak, obtaining the linear relationship between peak intensity at 775 cm^{-1} and the concentration of R6G, expressed as $I_{\text{R6G}} = 4.280 \times 10^7 C_{\text{R6G}}$ in the range of 1×10^{-7} - 1×10^{-4} M.

9. The UV-vis spectra of RGO and R6G solution

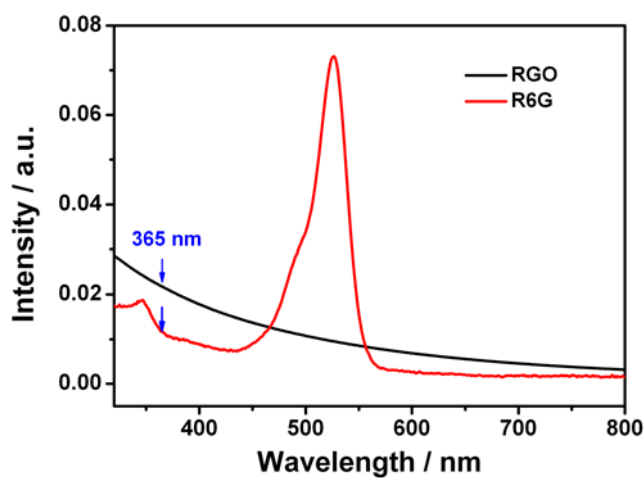


Figure S8. The UV-vis spectra of RGO and R6G solution. There is no obvious absorption band at 365 nm.

For the purpose of photocatalytic degradation reaction, the ZnO under the RGO layer and Au layer must receive UV light irradiation to generate holes and electrons. The UV-vis spectra of RGO and R6G showed that there is no obvious absorption band at 365 nm, which is beneficial to the transmission of UV light. Therefore, the whole system is practicable for photocatalytic degradation of R6G molecules.

9. The linear relationship between the concentration of R6G and photocatalytic time

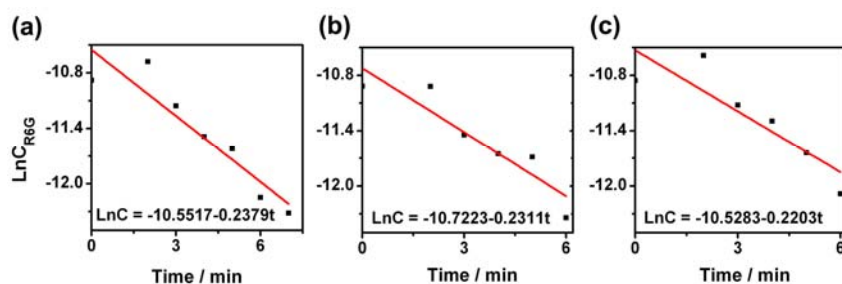


Figure S9. The curves of linear relationship between the concentration of R6G and photocatalytic time according to the peaks of (a) 1186 cm^{-1} , (b) 1515 cm^{-1} , and (c) 1650 cm^{-1} .

10. The calculation method of conversion relationship of peak intensity and time and concentration of R6G

According to the formula above, the intensity of Raman peaks at 614 cm^{-1} , 775 cm^{-1} , 1186 cm^{-1} , 1515 cm^{-1} , and 1650 cm^{-1} obtained from the photocatalytic process (Figure 3a) is transformed into corresponding concentration of R6G. Because the intensity of

Raman peaks is time-dependent, the relationship between concentration of R6G and time is determined as follows:

$$\text{Ln}C_{\text{R6G}} = -10.3084 - 0.2067t \quad 614 \quad (\text{S1})$$

$$\text{Ln}C_{\text{R6G}} = -10.3135 - 0.1854t \quad 775 \quad (\text{S2})$$

$$\text{Ln}C_{\text{R6G}} = -10.5517 - 0.2379t \quad 1186 \quad (\text{S3})$$

$$\text{Ln}C_{\text{R6G}} = -10.7223 - 0.2311t \quad 1515 \quad (\text{S4})$$

$$\text{Ln}C_{\text{R6G}} = -10.5283 - 0.2203t \quad 1650 \quad (\text{S5})$$

11. The controlled experiments of photocatalytic performance for ZnO, ZnO/Au, ZnO/RGO, and RGO/Au

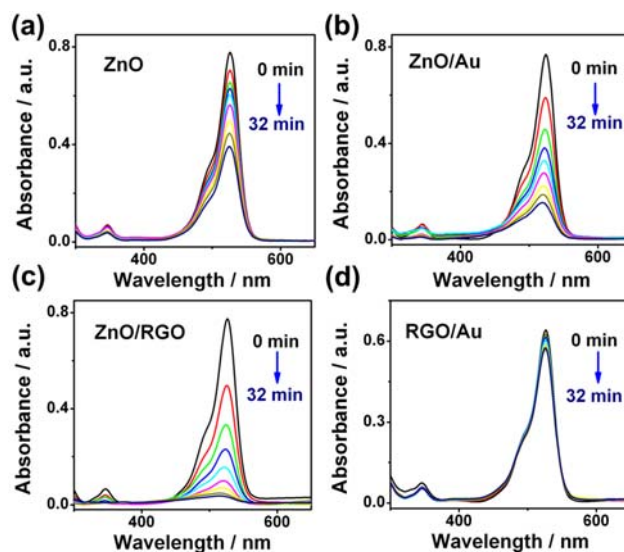


Figure S10. The UV-vis spectra of photo-degradation of R6G using (a) ZnO, (b) ZnO/Au, (c) ZnO/RGO, and (d) RGO/Au as catalysts.

In the controlled tests, Au nanoparticles also increased the catalytic activity. The control experiments showed better catalytic performance of ZnO/Au than ZnO.

Therefore, the Au nanoparticles have a dual role, both providing the needed SERS effect and acting as reduction centers in the photocatalytic reaction.

11. The reproducibility of ZnO/RGO/Au substrates

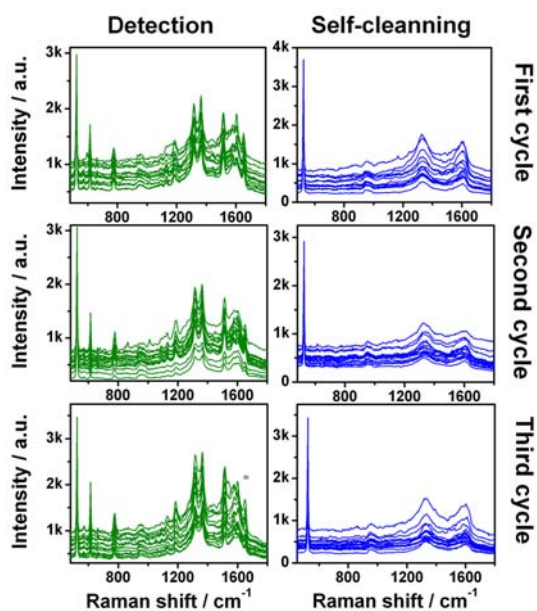


Figure S11. Reversible SERS behavior of ZnO/RGO/Au substrates with three cycles (1×10^{-5} M R6G).

In the recycle test, it can be found that the main Raman peaks of R6G molecule lose intensity after self-cleaning of the ZnO/RGO/Au substrate under UV irradiation, only the peaks of Si wafer and RGO remained. The shrinking intensity of SERS signals indicates the target molecules were degrading into CO_2 and H_2O or other small molecules.

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- S2. G. Williams, P. V. Kamat, *Langmuir*, 2009, **25**, 13869.
- S3. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- S4. Z. H. Ni, H. M. Wang, Y. Ma, J. Kasim, Y. H. Wu, and Z. X. Shen, *ACS Nano*, 2008, **2**, 1033.
- S5. A. Gupta, G. Chen, P. Joshi, S. Tadigadapa, and P. C. Eklund, *Nano Lett.*, 2006, **6**, 2667