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Supplementary information

Metal-free SERS substrate based on rGO-TiO_2-Fe_3O_4 nanohybrid: Contribution from interfacial charge transfer and magnetic controllability

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The enhancement factor (EF) of rGO-TiO_2-Fe_3O_4 substrate is calculated according to the following equation:

$$EF = (I_{SERS}/I_{NR}) \times (N_{NR}/N_{SERS}) = (I_{SERS}/I_{NR}) \times [(S_{laser} \times h \times C_{NR} \times N_A) / (S_{laser}/S_{MBA})]$$

in which the I_{SERS} and I_{NR} represent the SERS (1×10^{-6} mol/L of 4-MBA adsorbed on rGO-TiO_2-Fe_3O_4 substrate) and normal Raman (0.1 mol/L of 4-MBA ethanol solution) intensities at 1594 cm^{-1} respectively, and here the ratio of I_{SERS}/I_{NR} is about 37.7. The N_{NR} and N_{SERS} represent the numbers of 4-MBA molecules in 0.1 mol/L of solution sample and on rGO-TiO_2-Fe_3O_4 substrate adsorbed from 1×10^{-6} mol/L of solution, which are lying in the laser spot. The S_{laser} is the area of laser focused on the sample (the diameter of laser spot is 1 μm), and h is the effective depth of laser (17.88 μm). The C_{NR} is the concentration of 4-MBA used in normal Raman spectrum (0.1 mol/L). S_{MBA} is the area of 4-MBA molecule (6.9×10^{-13} m^2) and N_A is the Avogadro constant. Therefore, the EF of rGO-TiO_2-Fe_3O_4 substrate is estimated to be about 2.7×10^7.

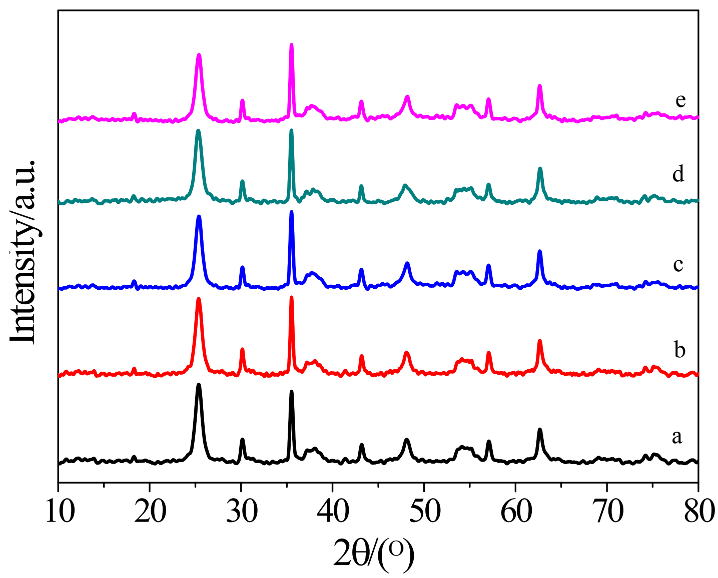

Fig. S1 XRD patterns of rGO-TiO_2-Fe_3O_4 samples with different addition amount of $FeSO_4$ (a: Ti/Fe=1/5, b: Ti/Fe=1/10, c: Ti/Fe=1/15, d: Ti/Fe=1/20, e: Ti/Fe=1/25).

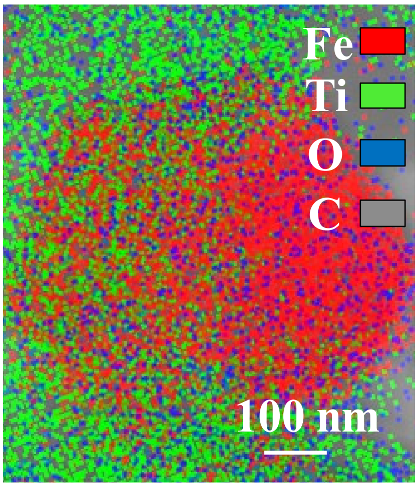

Fig. S2 The merged Fe, Ti, O and C elemental mapping image of single rGO-TiO_2-Fe_3O_4 nanohybrid.

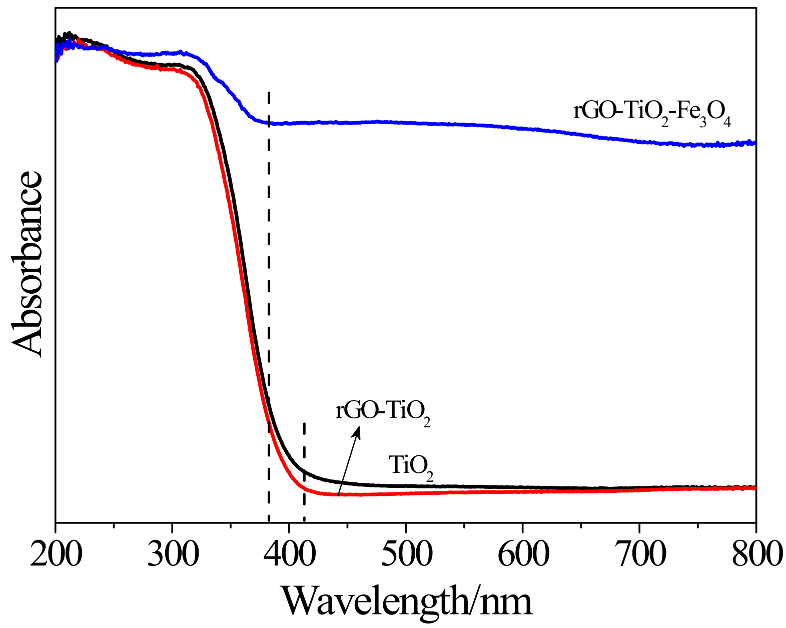

Fig. S3 UV-vis DRS spectra of TiO_2, rGO-TiO_2 and rGO-TiO_2-Fe_3O_4 samples.

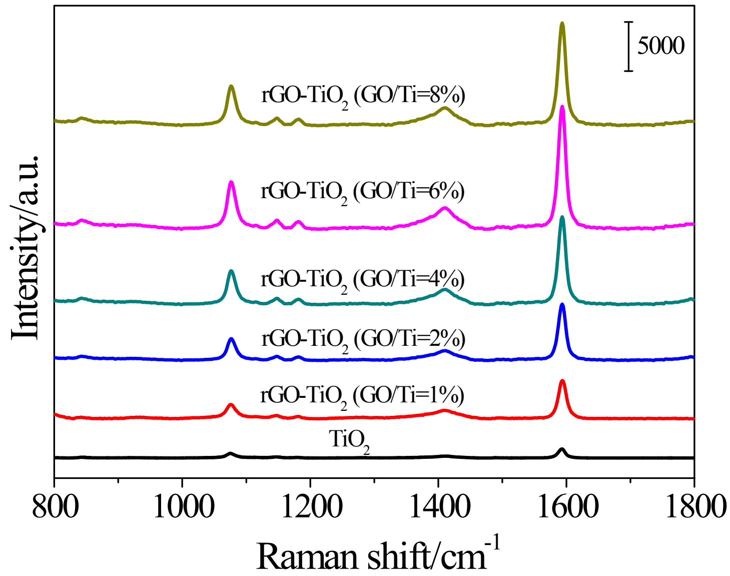

Fig. S4 SERS spectra of 4-MBA adsorbed on TiO_2 and different rGO-TiO_2 substrates.

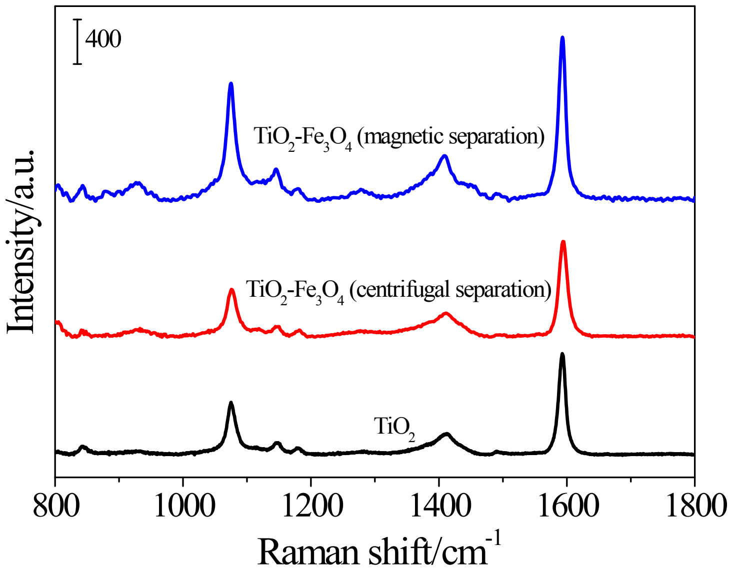

Fig. S5 SERS spectra of 4-MBA adsorbed on TiO_2 and TiO_2-Fe_3O_4 with the centrifugal separation treatment and magnetic separation treatment.

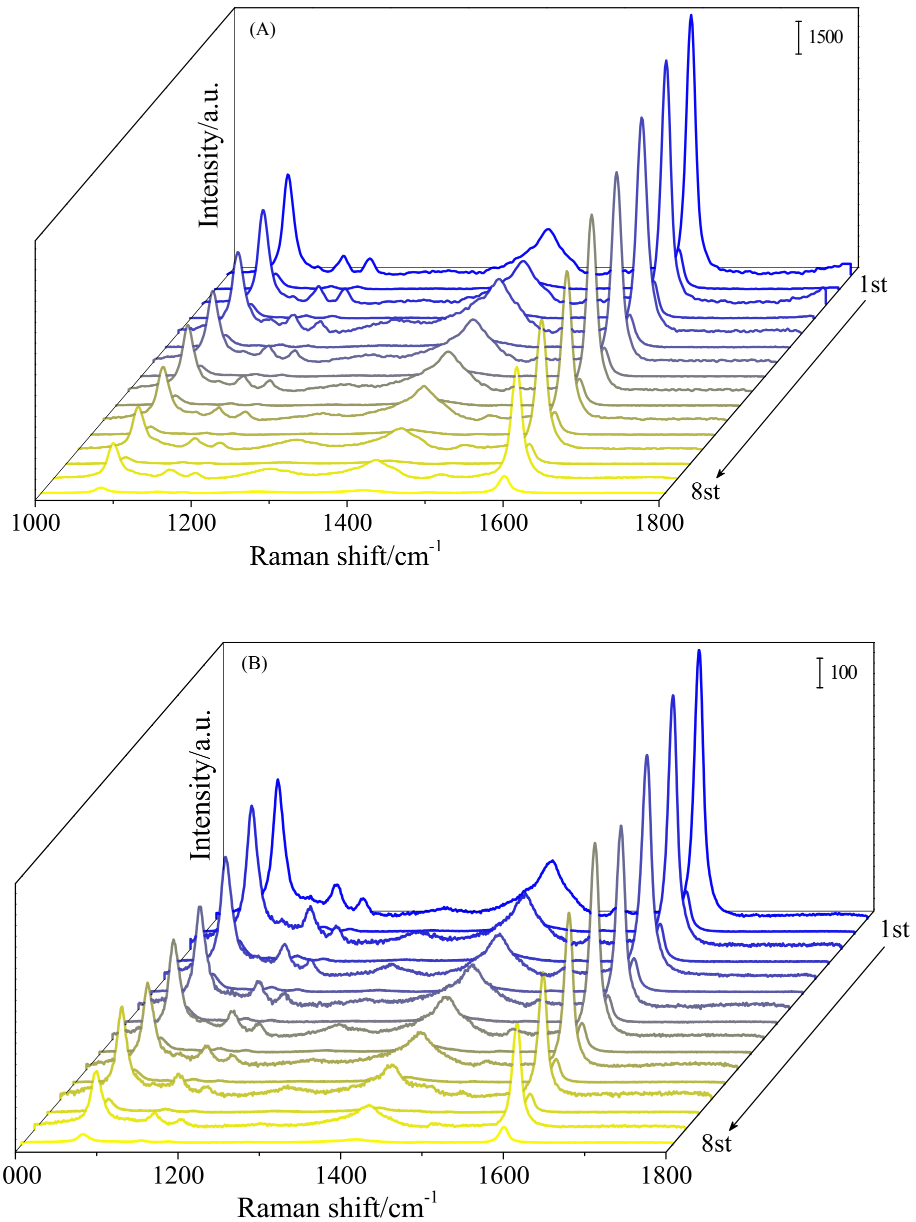

Fig. S6 SERS spectra of 4-MBA adsorbed on the recycled rGO-TiO_2 (A) and TiO_2 (B) substrates (eight adsorption/UV-cleaning cycles).

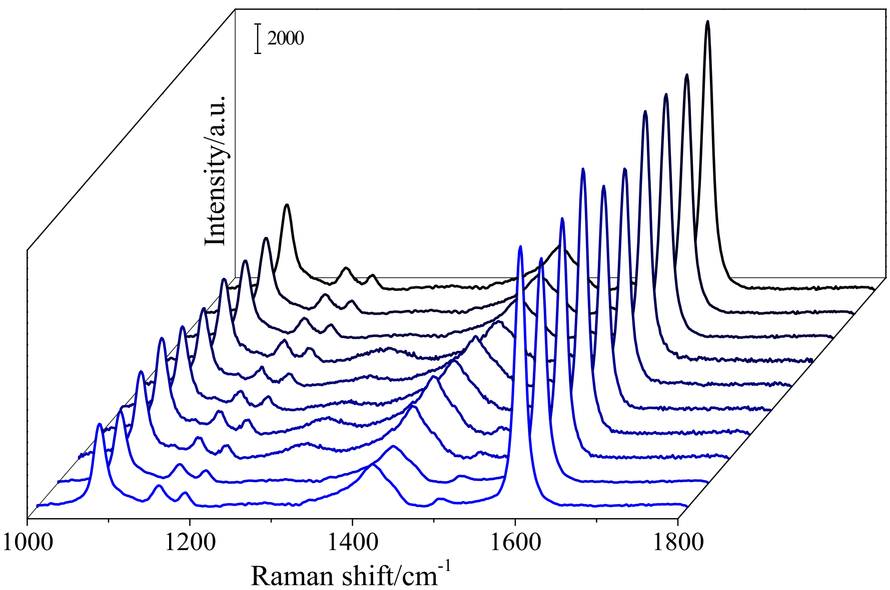

Fig. S7 SERS spectra of 4-MBA adsorbed on ten identical rGO-TiO_2-Fe_3O_4 substrates with the centrifugal separation treatment.

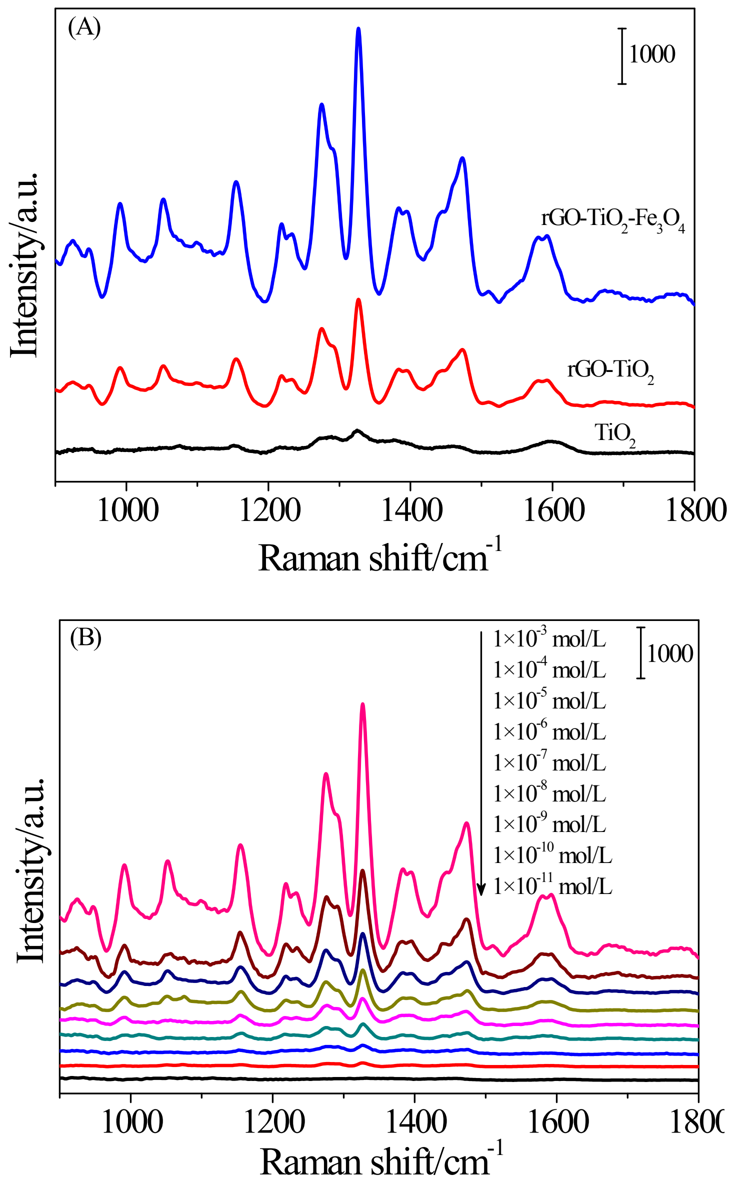

Fig. S8 SERS spectra of 6-MP adsorbed on TiO_2, rGO-TiO_2 and rGO-TiO_2-Fe_3O_4 substrates from 1×10^{-3} mol/L solution (A); SERS spectra of 6-MP adsorbed on rGO-TiO_2-Fe_3O_4 substrates from different concentrations of 6-MP solution (B).

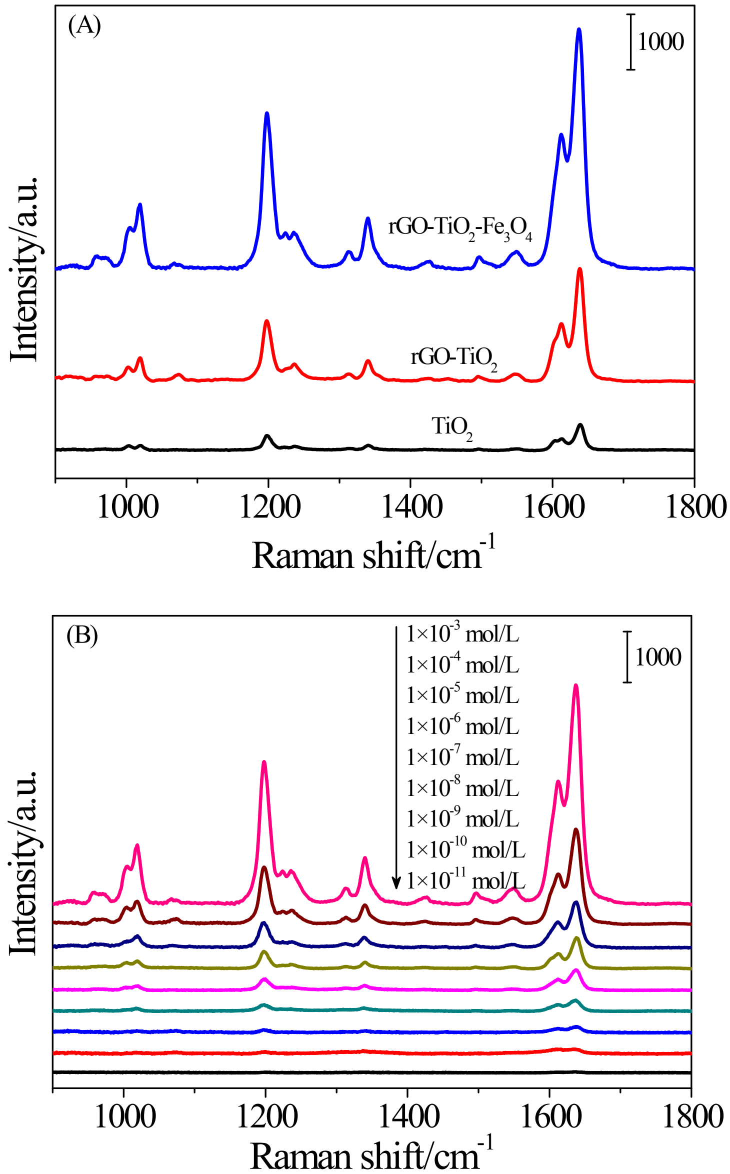

Fig. S9 SERS spectra of BPE adsorbed on TiO_2, rGO-TiO_2 and rGO-TiO_2-Fe_3O_4 substrates from 1 × 10^{-3} mol/L solution (A); SERS spectra of BPE adsorbed on rGO-TiO_2-Fe_3O_4 substrates from different concentrations of BPE solution (B).

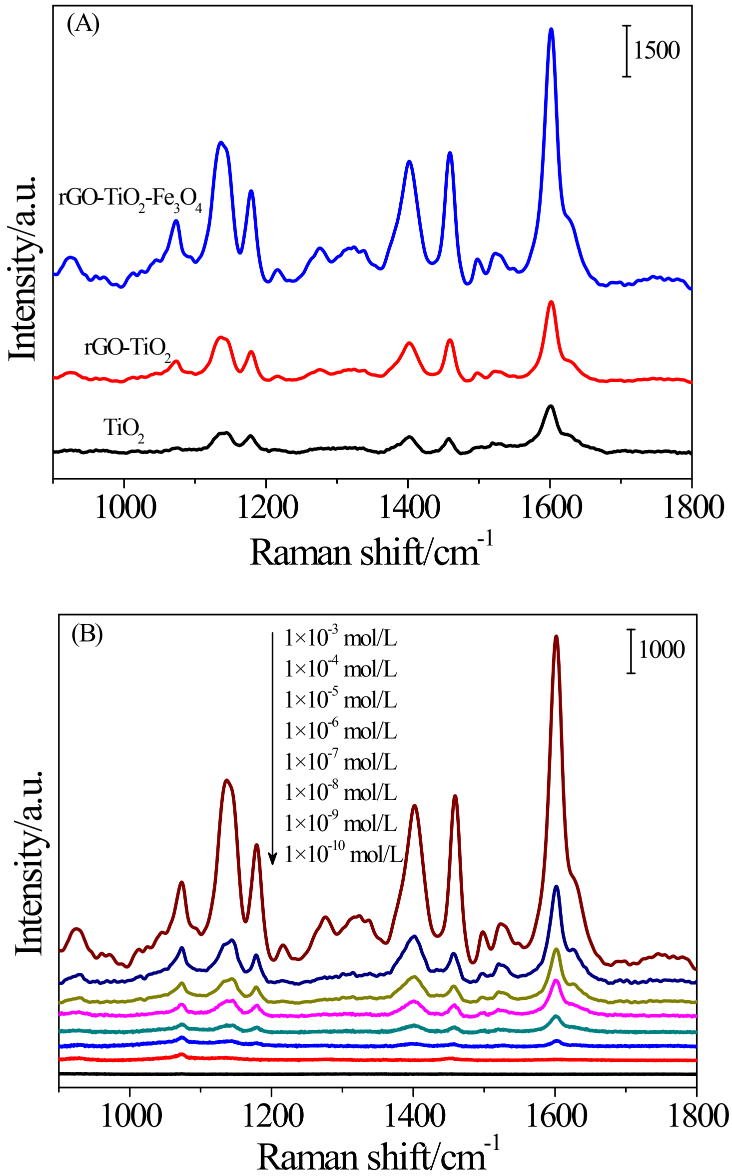

Fig. S10 SERS spectra of PABA adsorbed on TiO_2, rGO-TiO_2 and rGO-TiO_2-Fe_3O_4 substrates from 1×10^{-3} mol/L solution (A); SERS spectra of PABA adsorbed on rGO-TiO_2-Fe_3O_4 substrates from different concentrations of PABA solution (B).