Supplementary information

Metal-free SERS substrate based on rGO-TiO$_2$-Fe$_3$O$_4$ nanohybrid: Contribution from interfacial charge transfer and magnetic controllability

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The enhancement factor (EF) of rGO-TiO$_2$-Fe$_3$O$_4$ substrate is calculated according to the following equation:

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

in which the \(I_{\text{SERS}}\) and \(I_{\text{NR}}\) represent the SERS (1×10^{-6} mol/L of 4-MBA adsorbed on rGO-TiO$_2$-Fe$_3$O$_4$ substrate) and normal Raman (0.1 mol/L of 4-MBA ethanol solution) intensities at 1594 cm$^{-1}$ respectively, and here the ratio of \(I_{\text{SERS}}/I_{\text{NR}}\) is about 37.7. The \(N_{\text{NR}}\) and \(N_{\text{SERS}}\) represent the numbers of 4-MBA molecules in 0.1 mol/L of solution sample and on rGO-TiO$_2$-Fe$_3$O$_4$ substrate adsorbed from 1×10^{-6} mol/L of solution, which are lying in the laser spot. The \(S_{\text{laser}}\) is the area of laser focused on the sample (the diameter of laser spot is 1 \(\mu\)m), and \(h\) is the effective depth of laser (17.88 \(\mu\)m). The \(C_{\text{NR}}\) is the concentration of 4-MBA used in normal Raman spectrum (0.1 mol/L). \(S_{\text{MBA}}\) 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$_3$O$_4$ substrate is estimated to be about 2.7×10$^7$. 
Fig. S1 XRD patterns of rGO-TiO$_2$-Fe$_3$O$_4$ 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$_3$O$_4$ nanohybrid.
Fig. S3 UV-vis DRS spectra of TiO$_2$, rGO-TiO$_2$ and rGO-TiO$_2$-Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ substrates from $1 \times 10^{-3}$ mol/L solution (A); SERS spectra of 6-MP adsorbed on rGO-TiO$_2$-Fe$_3$O$_4$ 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$_3$O$_4$ substrates from 1 $\times$ 10$^{-3}$ mol/L solution (A); SERS spectra of BPE adsorbed on rGO-TiO$_2$-Fe$_3$O$_4$ 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$_3$O$_4$ substrates from $1 \times 10^{-3}$ mol/L solution (A); SERS spectra of PABA adsorbed on rGO-TiO$_2$-Fe$_3$O$_4$ substrates from different concentrations of PABA solution (B).