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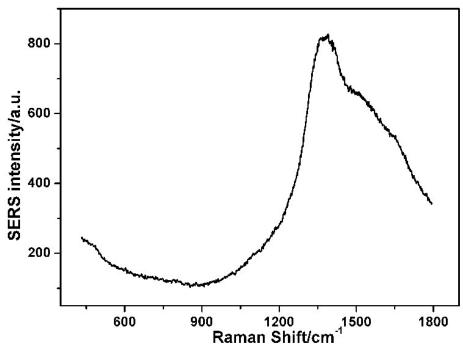


Fig. S1 Average background spectra of glass container used for SERS measurement.

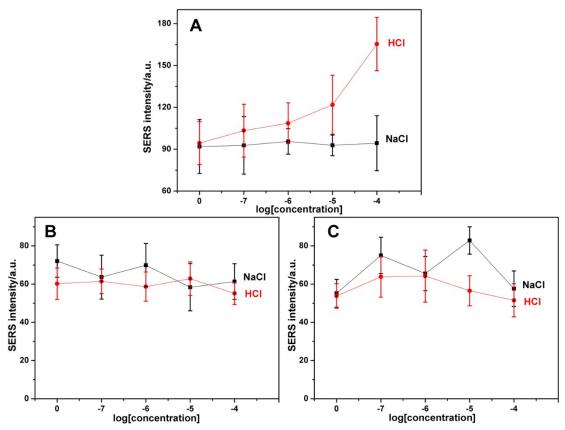


Fig. S2 SERS intensity of the peak at 1095 cm<sup>-1</sup> [mean  $\pm$  SD, n = 3] from GNPs modified with 4-MPy after 90 min of addition of serial concentrations of HCl or NaCl (A), and SERS intensity of the peak at 1095 cm<sup>-1</sup> [mean  $\pm$  SD, n = 3] from Au/TiO<sub>2</sub> core-shell nanocomposites after 90 min (B) and 24 h (C) of addition of serial concentrations of HCl or NaCl. The results from GNPs modified with 4-MPy show that hydrions will increase the SERS intensity while chloridions less than 10<sup>-4</sup> M will not significantly influence the SERS intensity. Meanwhile the results from the samples of Au/TiO<sub>2</sub> core-shell nanocomposites with added HCl exhibit that the added HCl will not affect the SERS of the nanocomposites, suggesting that only the HCl generated in the TiO<sub>2</sub> shell will improve the SERS intensity.

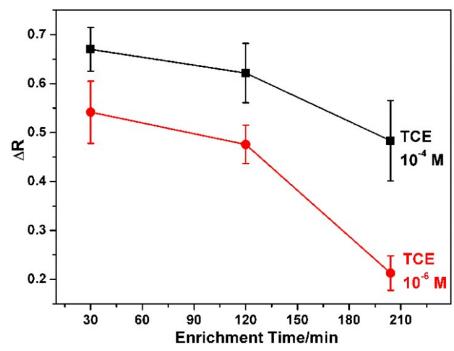


Fig. S3. SERS intensity change of the peak at 1095 cm<sup>-1</sup> [mean  $\pm$  SD, n = 3] in the samples with 10<sup>-4</sup> and 10<sup>-6</sup> M of TCE for different duration of enrichment.

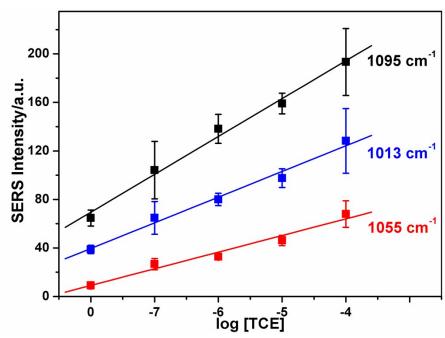


Fig. S4 Calibration plot in response to serial concentration TCE based on SERS intensity of the peak at 1095, 1055 and 1013 cm<sup>-1</sup>.

Table S1. LOD and R2 based on the peaks at 1095, 1055 and 1013 cm<sup>-1</sup>

Peak position	$LOD/\mu M$	LOD/ppb	$\mathbb{R}^2$
1095 cm <sup>-1</sup>	0.038	5.0	0.993
1055 cm <sup>-1</sup>	0.068	8.9	0.968
1013 cm <sup>-1</sup>	0.060	7.9	0.985

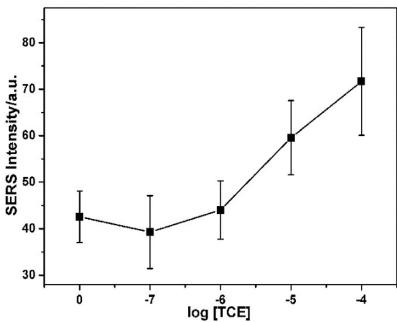
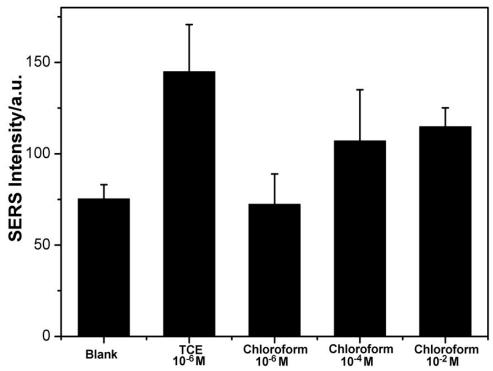


Fig. S5. SERS intensity of the peak at  $1095 \text{ cm}^{-1}$  [mean  $\pm$  SD, n = 3] from unpurified water samples from river purposefully contaminated with TCE. The dust and other suspended solid in unpurified river water are believed to influence the TCE absorption of the TiO<sub>2</sub> shell and thus the detection of TCE less than  $10^{-6} \text{ M}$ .



Blank TCE Chloroform Chloroform 10-6 M Chloroform  $10^{-6}$  M Chloroform  $10^{-6}$  M  $10^{-6}$  M  $10^{-6}$  M TCE,  $10^{-6}$ ,  $10^{-4}$ ,  $10^{-2}$  M chloroform.