

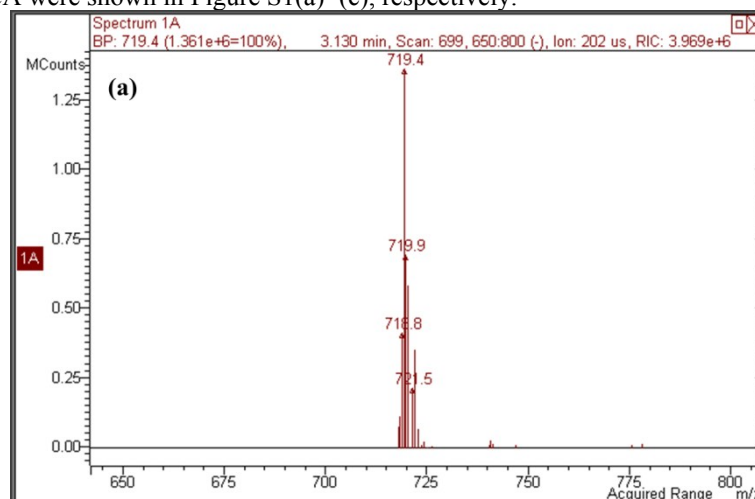
Support information

Synthesis of a thiacalix[4]arenetetrasulfonate-functionalized reduced graphene oxide adsorbent for the removal of lead(II) and cadmium(II) from aqueous solutions

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1. Synthesis of *p*-tert-butylthiacalix[4]arene (TCA)

TCA was synthesized referring to the literature.¹ A mixture of *p*-tert-butylphenol (32.25 g), elemental sulfur S₈ (13.75 g), and NaOH (4.43 g) in diphenyl ether (30 mL) was stirred under nitrogen. The stirred mixture was heated gradually to 230 °C over a period of 4 h and kept at this temperature for a further 4 h with concomitant removal of the evolving hydrogen sulfide with a slow stream of nitrogen. The product was cooled to ambient temperature and diluted with toluene (20 mL), and washed with sulfuric acid solution (0.5 mol·L⁻¹) and deionized water to give a grayish yellow suspension liquid. Then, the precipitate was collected by filtration, recrystallized from chloroform (170 mL) and dried in vacuum (60 °C, 4 h) to give a white powder product (yield 53%). Electrospray ionization mass spectrometry (ESI-MS): *m/z* 719.4 [M-H]⁻. Melting point (Mp): 320-324 °C. ¹H nuclear magnetic resonance (¹H NMR) (CDCl₃): δ 1.22 (s, 36H, C(CH₃)₃), 7.66 (s, 8H, ArH), 9.61 (s, 4H, OH). FTIR (KBr): 3324 (OH), 2961, 1395, 1364 (C(CH₃)₃). The ESI-MS, ¹H NMR, and FTIR spectrum of TCA were shown in Figure S1(a)~(c), respectively.



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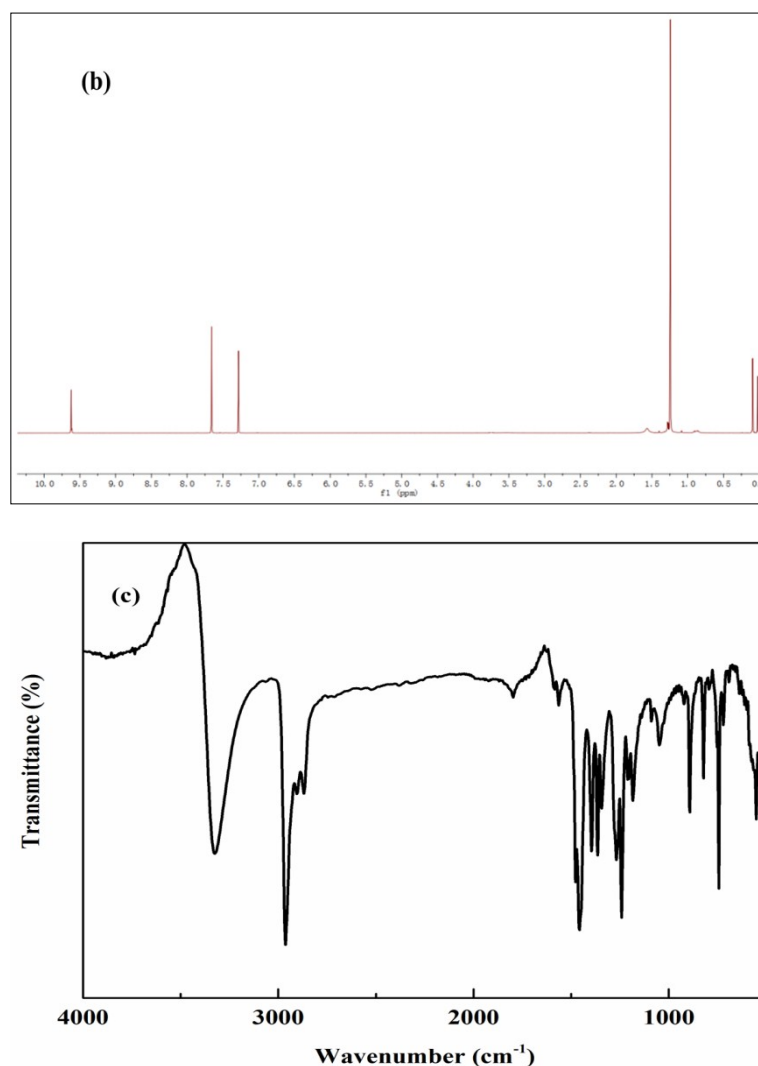


Figure S1. The (a) ESI-MS, (b) ¹H NMR, and (c) FTIR spectrum of TCA

2. Synthesis of thiacalix[4]arenetetrasulfonate (TCAS)

TCAS was synthesized according to a previously reported procedure.² A mixture of TCA (1.5 g) and concentrated H₂SO₄ (80 ml) was heated at 80 °C for 5 h. The reaction mixture was cooled to ambient temperature and poured into ice-water (500 ml), and then the purple solid residue was filtered off. NaCl (100 g) was added to the clear filtrate to salt out the sodium salt. After the salt was filtered off and re-dissolved in water (8 mL), ethanol (50 mL) was added to the solution to give a white precipitate. The process was repeated for several times and dried in vacuum (80 °C, 48 h) to give a white powder (1.21 g, 63%). ESI-MS: *m/z* 1039.1 [M-H]⁻ (containing four water molecules and an ethanol molecule). ¹H NMR (D₂O): δ 7.93 (s, 8H, ArH), 3.48-3.53 (q, 2H, O-CH₂), 1.02-1.04 (t, 2H, -CH₃). IR (KBr): 3468, 3358 (OH), 1195, 1046 (SO₃). UV (water): 208, 303. These data are consistent with the results reported by Yuan et al.³ The ESI-MS, ¹H NMR, and UV-visible spectrum of TCAS were shown in Figure S2(a)~(c), respectively.

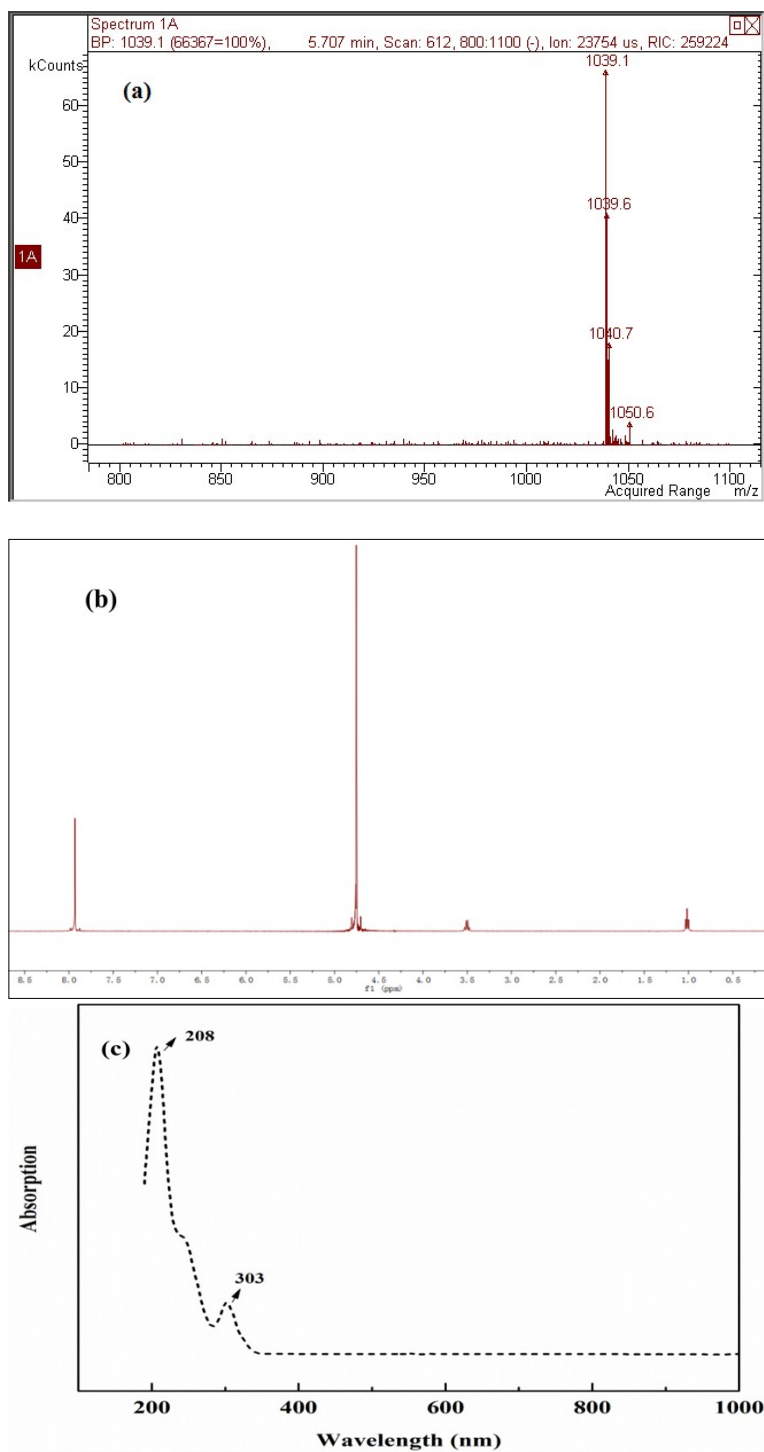


Figure S2. The (a) ESI-MS, (b) ¹H NMR, and (c) UV-visible spectrum of TCAS.

3. Transmission electron microscope (TEM) images of rGO.

TEM images of rGO were shown in Figure S3.

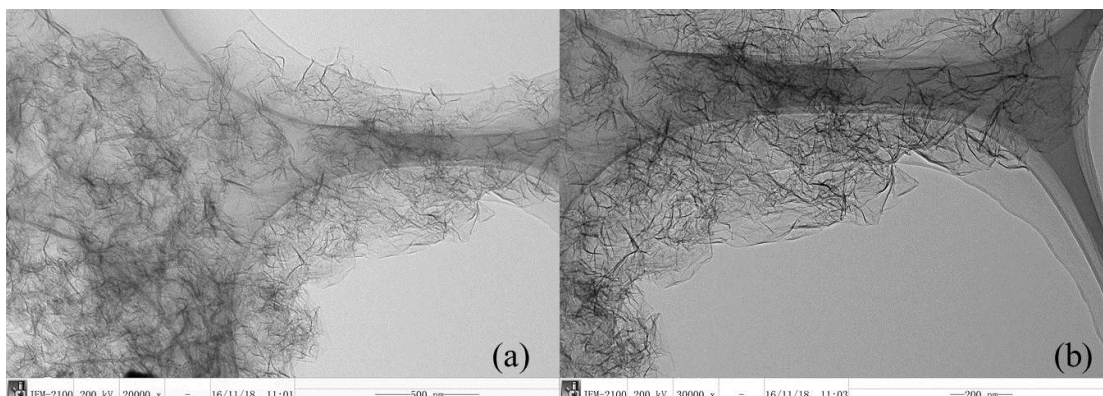


Figure S3. TEM images of rGO. (a) magnification \times 20000 and (b) magnification \times 30000.

4. Scanning electron microscopy (SEM) images of adsorbed species.

SEM images of TCAS-rGO after adsorption of Pb(II) and Cd(II), and the corresponding EDX pattern and element mapping are shown in Figure S4.

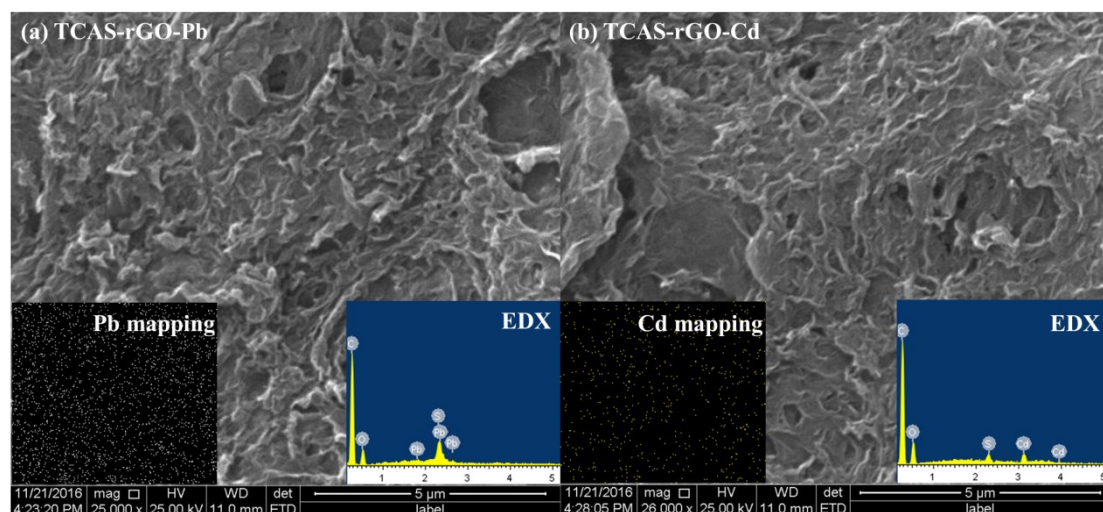


Figure S4. SEM images of (a) TCAS-rGO-Pb, the corresponding EDX pattern and element mapping of Pb, (b) TCAS-rGO-Cd, the corresponding EDX pattern and element mapping of Cd.

References

1. H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Letters*, 1997, 38, 3971-3972.
2. N. Iki, T. Fujimoto and S. Miyano, *Chemistry Letters*, 1998, 27, 625-626.
3. D. Yuan, W. X. Zhu, S. Ma and X. Yan, *Journal of Molecular Structure*, 2002, 616, 241-246.