

## **Metallothionein isoforms for the selective biosorption and preconcentration of cadmium at ultra-trace level**

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## Electronic Supplementary Information

Before performing characterizations, e.g., FT-IR, SEM-EDX and adsorption, the materials were thoroughly washed with diluted nitric acid to remove any of the physically adsorbed proteins.

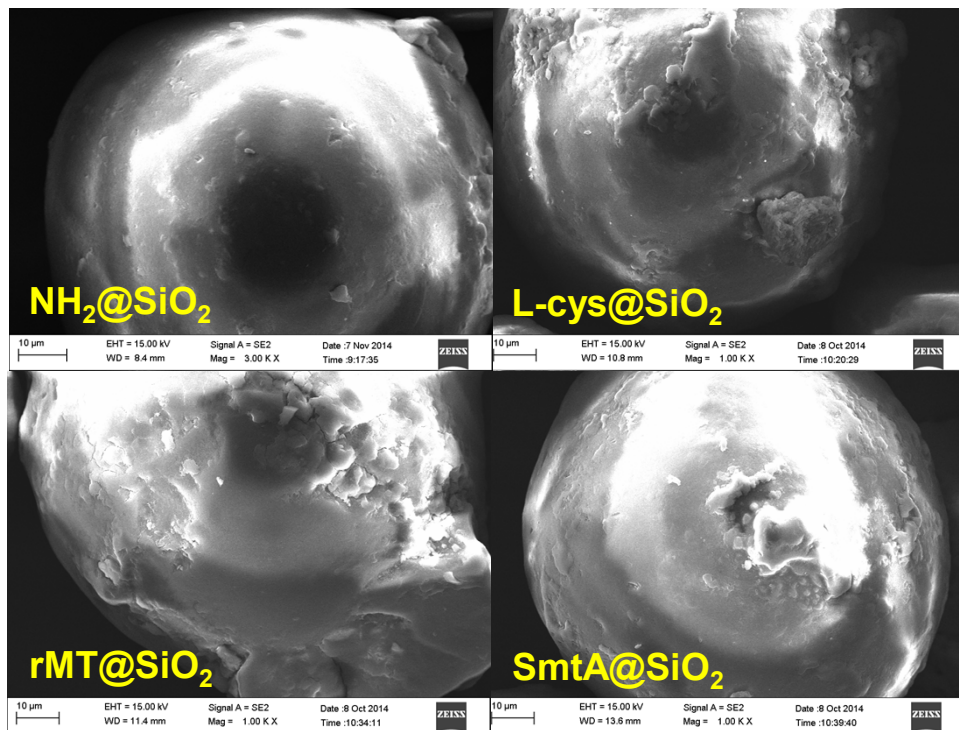


Figure S1. SEM images of aminated SiO<sub>2</sub> (NH<sub>2</sub>@SiO<sub>2</sub>), L-cys@SiO<sub>2</sub>, rMT@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub>.

×1000 magnifications

The change of surface morphology for the three composites (from smooth to rough) illustrates the grafting of L-cys, rMT or SmtA onto SiO<sub>2</sub> particles.

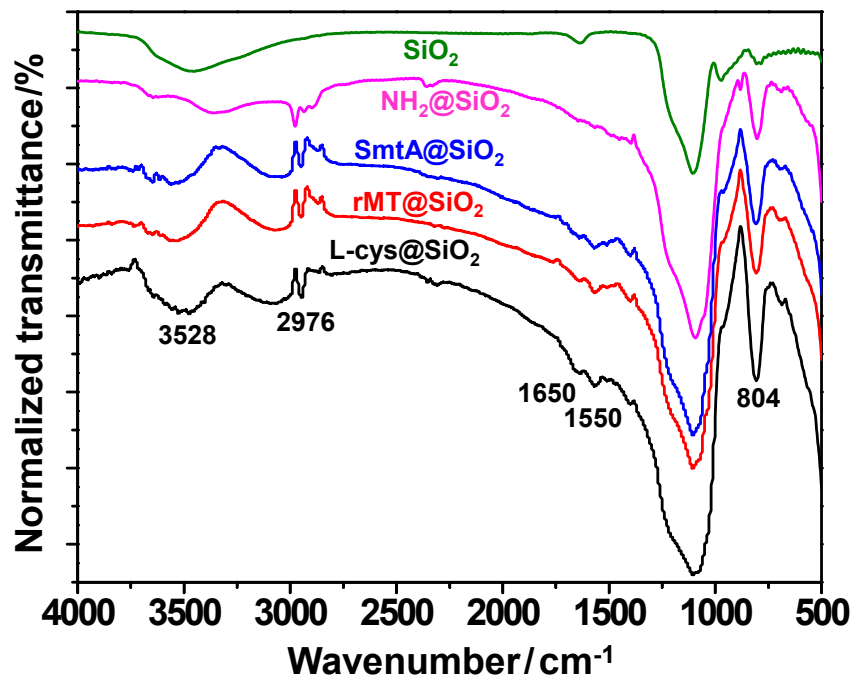


Figure S2. FT-IR spectra of SiO<sub>2</sub>, NH<sub>2</sub>@SiO<sub>2</sub>, L-cys@SiO<sub>2</sub>, rMT@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub>.

The successful amination of SiO<sub>2</sub> can be confirmed by the bending vibration of C-H (2976 cm<sup>-1</sup>) and the bending vibration of N-H (804 cm<sup>-1</sup>) originates from APTE in the spectra of NH<sub>2</sub>@SiO<sub>2</sub>.

As for L-cys@SiO<sub>2</sub>, rMT@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub>, the new absorption band at 1650 cm<sup>-1</sup> corresponds to the amide I (the -C=O stretch of amino acid) and that at 1550 cm<sup>-1</sup> is assigned to amide II (the -C-N stretch and -C-N-H deformation), indicating the binding of L-cys, rMT or SmtA onto the surface of SiO<sub>2</sub> particles.

Table S1. The temperature program for the determination of cadmium with GFAAS

| Step        | Temperature<br>/°C | Ramp<br>/s | Hold<br>/s |
|-------------|--------------------|------------|------------|
| Drying      | 100                | 15         | 10         |
| Pyrolysis   | 350                | 15         | 10         |
| Atomization | 1900               | 1          | 3          |
| Cleaning    | 2100               | 1          | 3          |

Table S2. Atom% of elements in SiO<sub>2</sub>, NH<sub>2</sub>@SiO<sub>2</sub>, L-cys@SiO<sub>2</sub>, MT(II)@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub> samples by SEM-EDX.

| Sample                            | O(%)  | Si (%) | C (%) | N (%) |
|-----------------------------------|-------|--------|-------|-------|
| SiO <sub>2</sub>                  | 76.87 | 23.13  | 0     | 0     |
| NH <sub>2</sub> @SiO <sub>2</sub> | 63.91 | 20.21  | 13.46 | 2.42  |
| L-cys@SiO <sub>2</sub>            | 55.26 | 17.86  | 24.08 | 2.80  |
| MT(II)@SiO <sub>2</sub>           | 54.34 | 13.60  | 28.86 | 3.20  |
| SmtA@SiO <sub>2</sub>             | 47.67 | 13.78  | 34.27 | 4.29  |

The increased C and N content for L-cys@SiO<sub>2</sub>, MT(II)@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub> in comparison with SiO<sub>2</sub> and NH<sub>2</sub>@SiO<sub>2</sub> can be a clear supplementary evidence confirming the grafting of L-cysteine and MTs onto SiO<sub>2</sub> particles. In addition, the maximum adsorption capacity of cadmium by NH<sub>2</sub>@SiO<sub>2</sub>, L-cys@SiO<sub>2</sub>, MT(II)@SiO<sub>2</sub> and SmtA@SiO<sub>2</sub> are derived to be 1.80 mg g<sup>-1</sup>, 3.09 mg g<sup>-1</sup>, 13.70 mg g<sup>-1</sup> and 18.94 mg g<sup>-1</sup>, respectively, this provide an indirect evidence confirming the immobilization of L-cysteine, SmtA or rMT onto SiO<sub>2</sub> particles.