## Submicron silica spheres decorated with silver nanoparticles as a new effective sorbent for inorganic mercury in surface waters

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## **Electronic Supplementary Material (ESI) for Analyst**

Table 1S. Instrumental parameters for Thermo Scientific, XSeries 2 ICP-MS spectrometer

| RF Power                       | 1.4 kW                              |  |  |  |  |
|--------------------------------|-------------------------------------|--|--|--|--|
| Argon flow rates:              |                                     |  |  |  |  |
| Cool gas                       | $14 \mathrm{L} \mathrm{min}^{-1}$   |  |  |  |  |
| Auxiliary gas flow             | $0.65 \mathrm{L} \mathrm{min}^{-1}$ |  |  |  |  |
| Nebulizer gas flow             | 0.85 L min <sup>-1</sup>            |  |  |  |  |
| Nebulizer                      | Concentric                          |  |  |  |  |
| Sample uptake                  | $0.6 \text{ mL min}^{-1}$           |  |  |  |  |
| Uptake and wash time           | 60 s                                |  |  |  |  |
| Integration time               | 0.3 s                               |  |  |  |  |
| Replicates                     | 3                                   |  |  |  |  |
| Dwell time per isotope         | 20 ms                               |  |  |  |  |
| Sample uptake<br>and wash time | 60 s                                |  |  |  |  |

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**Table 2S.** Sampling sites, Geographical coordinates: site 1 (river Iskar, 42°49'14"N,23°22'13"); site 2 (river Maritsa, 42°16'33'24.5N, 23°41'06.17E); site 3 (Black sea Krapets,43°36'60.0"N, 28°35'60.0"E); site 4 (Black sea Kamtchia (esuarine water): 43°00'60.0"N,27°53'60.0") and characteristics.

| Sample sites                | pН  | Dissolved $O_2$<br>(mg L <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup><br>(μM) | NO <sub>2</sub> <sup>-</sup><br>(μM) | HPO4 <sup>2-</sup><br>(µM) | $\frac{\text{DOC}}{(\text{mg } \text{L}^{-1})}$ |
|-----------------------------|-----|--|--------------------------------------|--------------------------------------|----------------------------|---|
| Site 1 river Iskar*         | 7.3 | 8.2                                      | 7                                    | 0.04                                 | 0.9                        | $4.5\pm0.1$                                     |
| Site 2 river Maritsa**      | 7.2 | 7.9                                      | 6                                    | 0.02                                 | 0.6                        | $5.6\pm0.2$                                     |
| Site 3 Black sea Krapets*** | 8.1 | 7.3                                      | 8                                    | 0.04                                 | 0.6                        | $2.5\pm0.2$                                     |
| Site 4 Black sea Kamtchia   | 8.0 | 7.7                                      | 9                                    | 0.03                                 | 0.5                        | $2.9\pm0.2$                                     |

\* Values of major chemical components:  $[Ca^{2+}] = 0.4 \text{ mM}$ ,  $[Mg^{2+}] = 0.2 \text{ mM}$ ,  $[Cl^{-}] = 0.2 \text{ mM}$ .

\*\* Values of major chemical components:  $[Ca^{2+}] = 0.95 \text{ mM}$ ,  $[Mg^{2+}] = 0.25 \text{ mM}$ ,  $[Cl^{-}] = 0.1 \text{ mM}$ .

\*\*\* The values of major chemical components of Black seawater have not varied significantly with sampling location; averaged concentrations:  $[Ca^{2+}] = 5.8 \text{ mM}$ ,  $[Mg^{2+}] = 0.026 \text{ M}$ ,  $[Cl^{-}] = 0.27 \text{ M}$ .

**Table 3S.** SAED data of SiO<sub>2</sub>/AgNPs sorbent particles after exposure to 1  $\mu$ g iHg solution;(hkl)<sub>f</sub>—double electron diffraction effects; SAED interpretation: accuracy 1%

| d (A° ) | Relative<br>intensity | Ag               | Ag                    | $Ag_2Hg_3$         | Hg           |
|---------|-----------------------|------------------|-----------------------|--------------------|--------------|
|         |                       | PDF 89-3722      | PDF 87-0598           | PDF 65-3156        | PDF 01-1017  |
|         |                       | a = 4.0855(1)  Å | a = 2.8862 Å,         | a = 10.0506 Å      | a = 3.459 Å, |
|         |                       | _                | $c=10.000~\text{\AA}$ |                    | c = 6.699 Å  |
|         |                       | SG Fm3m          | P6 <sub>3</sub> /mmc  | SG I23             | SG R         |
| 2.789   | m                     | -                | -                     | (320) <sub>f</sub> | 101          |
| 2.390   | S                     | 111              | 101                   | 330, 411           | -            |
| 2.063   | S                     | 200              | -                     | 422                | -            |
| 1.424   | m                     | -                | -                     | -                  | 021          |
| 1.255   | m                     | 311              | 008                   | 800                | -            |
| 1.035   | m-w                   | 400              | -                     | 932                | -            |
|         |                       |                  |                       |                    |              |

s — strong; m — middle; m-w — middle weak



**Scheme S1** Formation of silica-silver nanocomposite structure by functionalization of the core surface and chemisorption of preformed silver nanoparticles (colloid mixing method)



**Fig. S1** UV-Vis absorbance spectrum of starch-stabilized silver nanoparticles in colloidal solution (with inset of a photograph)



**Fig. S2** (A) TEM image (with inset of a size distribution histogram determined by counting of 150 particles using Image J software) and (B) HRTEM image of preformed starch-stabilized silver nanoparticles. Some polyhedral nanoparticles are surrounded by circles.



**Fig. S3** (A) SEM image and (B) particle size distribution histogram of SiO<sub>2</sub>-NH<sub>2</sub> determined by counting of 450 particles using Image J software



Fig. S4 UV-Vis absorption spectral changes observed for  $SiO_2/AgNPs$  aqueous dispersion upon the addition of iHg solution