Electronic Supplementary Information

The Precipitation, Growth and Stability of Mercury Sulfide Nanoparticles Formed in Presence of Marine Dissolved Organic Matter.

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Methodology for X-ray Absorption Near Edge Structure Studies (XANES)

S K-edge XANES data were collected on beamline 4B7A at the mid-energy X-ray station in Beijing Synchrotron Radiation Facilities, China. The beamline source is equipped with a Si (111) double-crystal monochromator. The storage ring was 2.2 GeV and ring current 100 mA. The dry NOM samples were prepared for analysis by rubbing a small amount onto sulfur free tape in the sample holder. Care was taken to form a thin layer to minimize self-adsorption effects. This was then mounted to the sample cell and flushed by He. The measurements were performed under high vacuum (10^{-6} to 10^{-8} mbar) at ambient temperature. The incident X-ray energy range scanned was 2462 to 2500 eV with a step size of 0.2 eV. The reference compounds included sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), elemental sulfur (S^0), cysteine (-SH), methionine (-S=), sodium methane sulfonate (CH_3SO_3Na), and iron sulfide (FeS). All chemicals were analysis grade purchased from Sigma-Aldrich except for FeS which was purchased from Alfa Aeser.

The sample spectrum was processed following the methods of Yekta et al.[1] First, a polynomial pre-edge function was subtracted from the spectrum, and the data were normalized between 2460 and 2490 ev using the software WinXAS97.[2] The corrected spectrum was deconvoluted into pseudo-components by a least-square fitting procedure in Microsoft Excel. Briefly, s → p transitions of S atoms in the standards were modeled by Gaussian peaks, which were then fit to the sample spectrum to quantify the relative S components. The absolute S species were calculated by multiplying the relative S composition by the S concentration of the sample. Total organic reduced sulfur was calculated as the sum of RSR(H) and RSSR. An approximate thiol concentration was calculated by multiplying the organic reduced S value by 30%.

Fig. S1. Map showing the location where dissolved organic matter used in the synthesis of β-HgS*(s)*$_{nano}$ was extracted from surface waters using a modified styrene divinyl polymer cartridge.

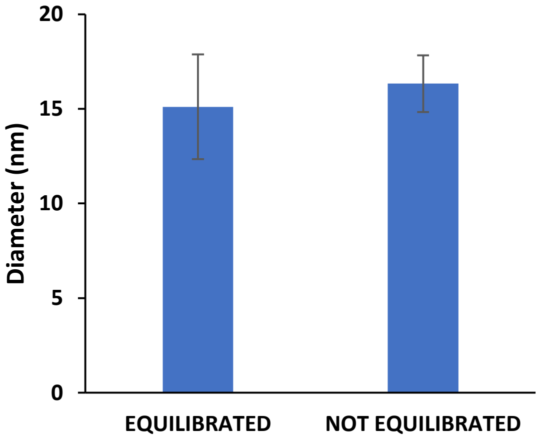

Fig. S2. The hydrodynamic diameter of β-HgS*(s)*$_{nano}$ (mean ± SD, n=2) recorded 5 min after the addition of Na_2S to a solution containing equilibrated and non-equilibrated mixtures of Hg^{II} and ELIS DOM. In the equilibrated β-HgS*(s)*$_{nano}$ vials, Hg^{II} and DOM were first allowed to react for 24 hours before HS^- was added. Solutions contained 150 µM $Hg(NO_3)_2$, 150 µM Na_2S and 10 mg C/L ELIS DOM in 2.2 mM $NaHCO_3$ (pH 7.8).

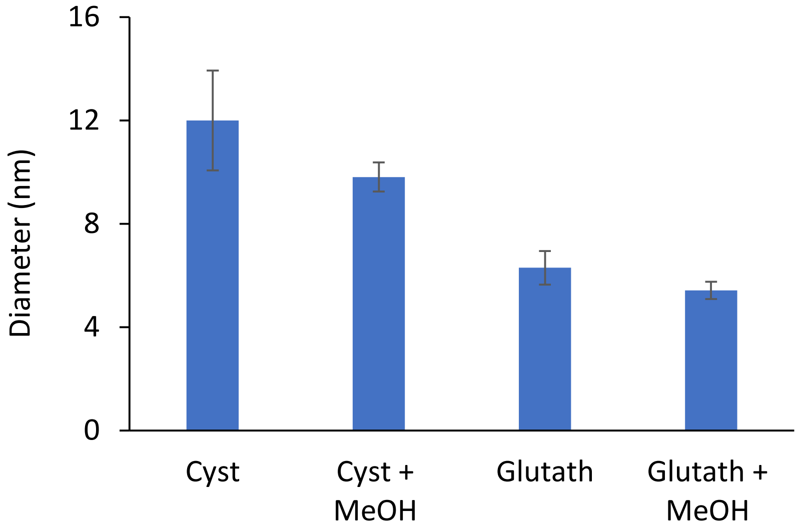

Fig. S3. The hydrodynamic diameter (mean ± SD, n=2) of β-HgS*(s)*$_{\text{nano}}$ capped with cysteine and glutathione taken 9 h after initiating precipitation. Solutions contained 150 µM $Hg(NO_3)_2$, 150 µM Na_2S and 300 µM cysteine or glutathione with and without methanol in 2.2 mM $NaHCO_3$ (pH 7.8).

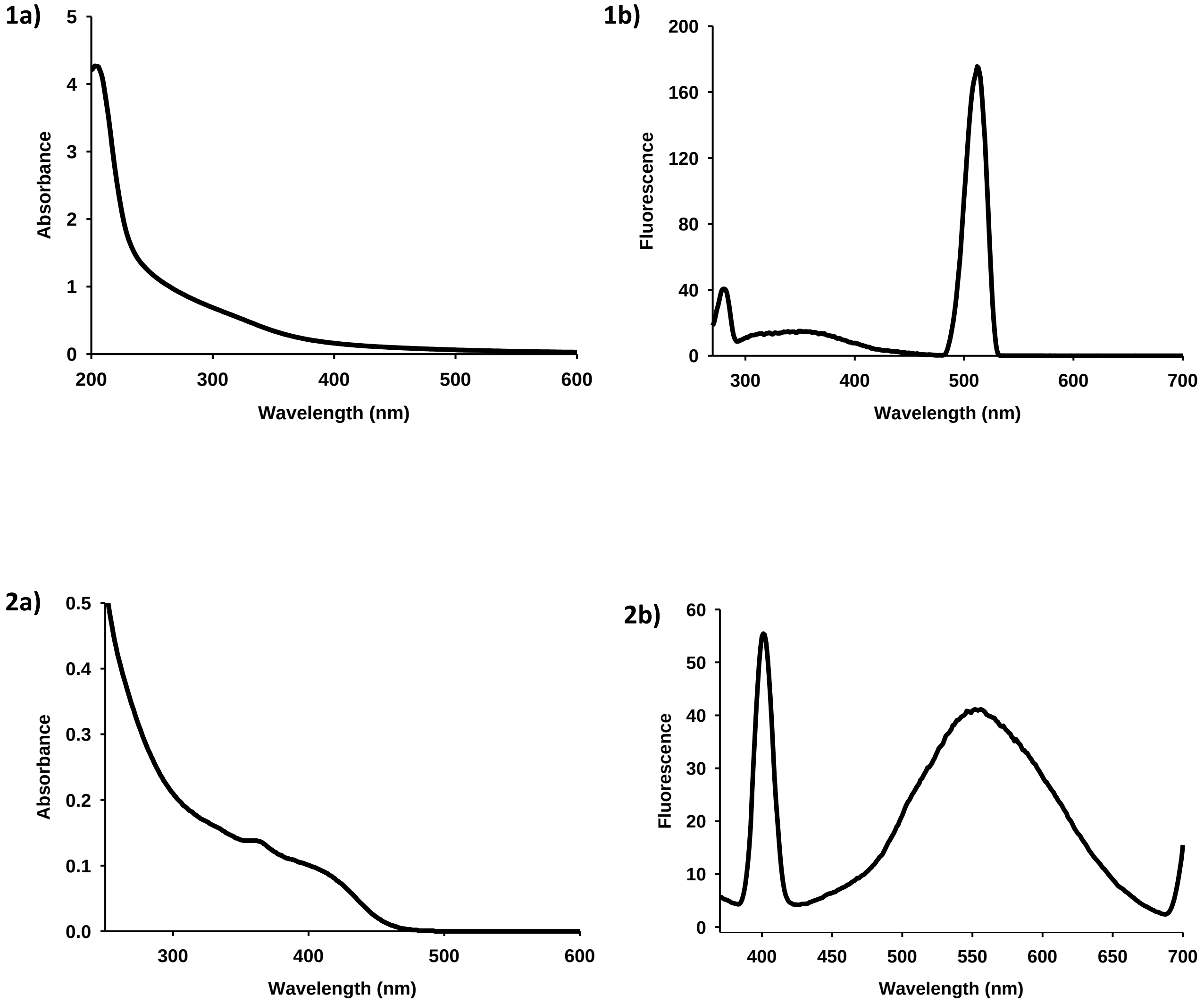

Fig. S4. The UV-Vis (a) and Fluorescence (b) spectra of cysteine capped β-HgS*(s)*$_{\text{nano}}$ (1) and CdS*(s)*$_{\text{nano}}$ (2). Fluorescence spectra were recorded at an excitation wavelength of 250 nm for β-HgS*(s)*$_{\text{nano}}$ and 350 nm for CdS*(s)*$_{\text{nano}}$. The x-axis on 1b and 2b correspond to the emission wavelength. The solutions contained 150 µM $Hg(NO_3)_2$ or $Cd(NO_3)_2$, 150 µM Na_2S and 600 µM cysteine in 2.2 mM $NaHCO_3$ (pH 7.8).

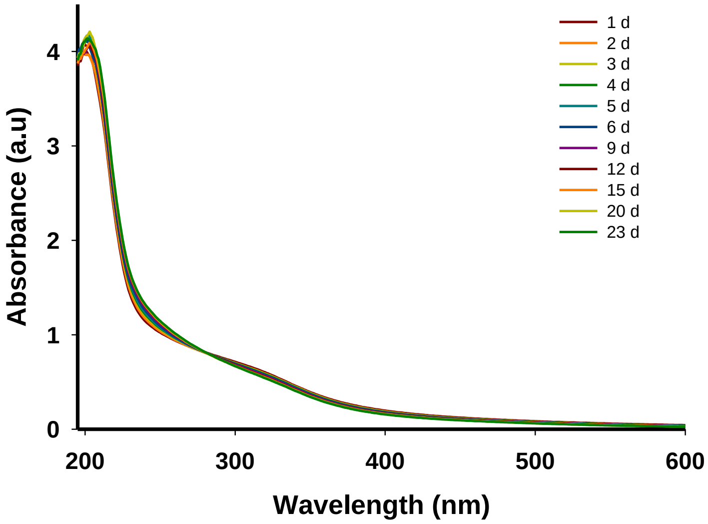

Fig. S5. The overlaid UV-Vis spectra of cysteine capped β-HgS*(s)*$_{nano}$. The solutions contained 150 µM $Hg(NO_3)_2$, 150 µM Na_2S and 300 µM cysteine in 2.2 mM $NaHCO_3$ (pH 7.8). Diameter over the 3 weeks was calculated to be 5.4 ± 0.02 nm using the effective mass approximation theory.

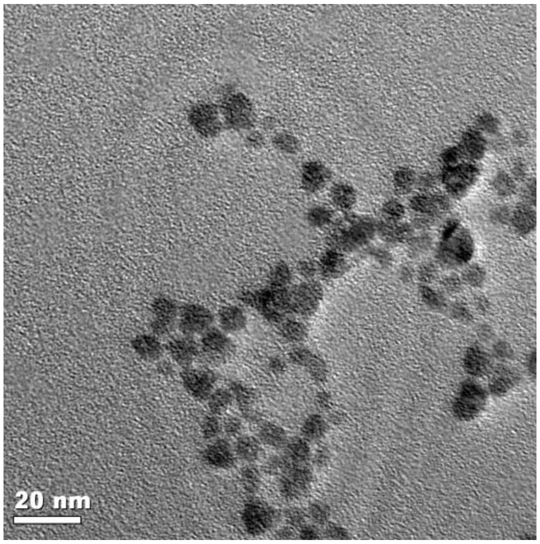

Fig. S6. TEM images of cysteine capped β-HgS*(s)*$_{nano}$. The solutions contained 150 µM $Hg(NO_3)_2$, 150 µM Na_2S and 300 µM cysteine in 2.2 mM $NaHCO_3$ (pH 7.8).

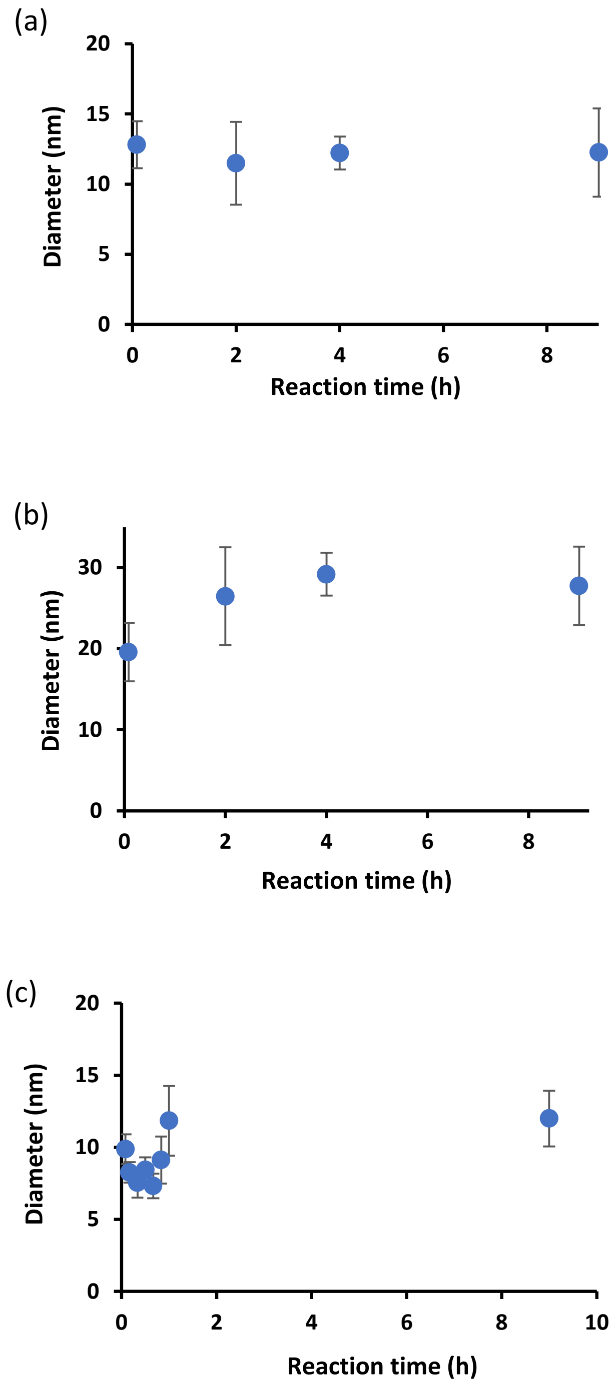

Fig. S7. The hydrodynamic diameter (mean ±SD, n=3) of β-HgS*(s)*$_{\text{nano}}$ recorded over time from 0 – 9h of reaction. Solutions contained 150 µM $Hg(NO_3)_2$, 150 µM Na_2S and 10 mg C/L ELIS DOM (a); SB DOM (b); or 300 µM cysteine (c), in 2.2 mM $NaHCO_3$ (pH 7.8).

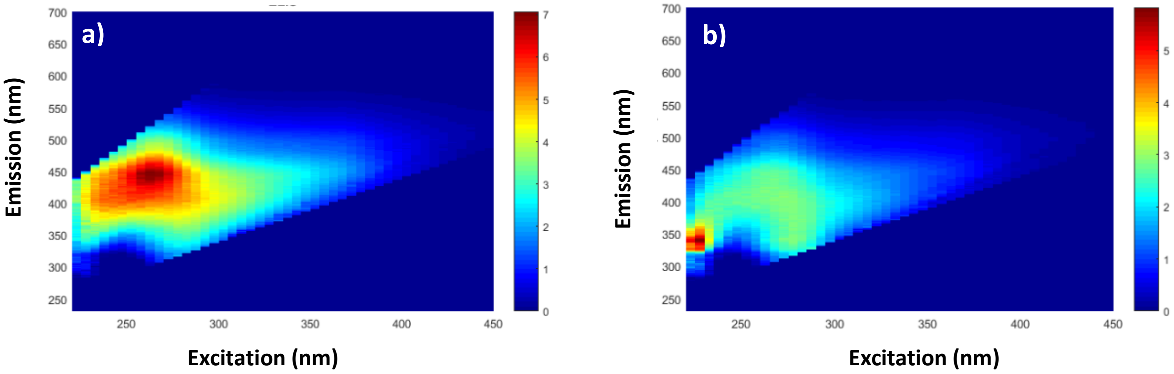

Fig. S8. Excitation and emission matrices (EEM) of dissolved organic matter extracted from surface waters collected from (a) Eastern Long Island Sound (ELIS) and (b) at the shelf break of the North Atlantic Ocean (SB). Fluorescence intensities are given in Raman Units (R.U).

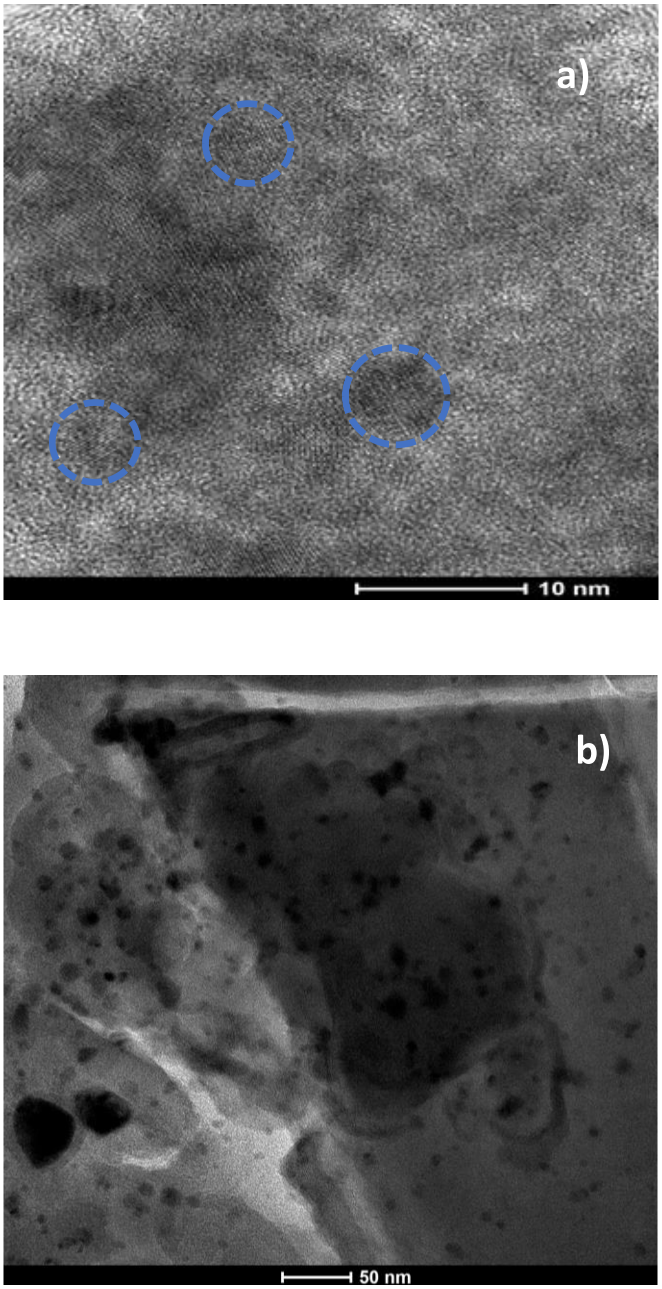

Fig. S9. Transmission Electron Microscopy (TEM) images of β-HgS*(s)*$_{\mathrm{nano}}$ precipitated at a Hg^{II}:DOM ratio of 1.5 nmol /mg C. Solutions contained 1 µM $Hg(NO_3)_2$, 1 µM Na_2S and 0.67 g C/L ELIS DOM in 2.2 mM $NaHCO_3$ (pH 7.8).

References

1. Shakeri Yekta, S.; Gustavsson, J.; Svensson, B.H.; Skyllberg, U. Sulfur K-edge XANES and acid volatile sulfide analyses of changes in chemical speciation of S and Fe during sequential extraction of trace metals in anoxic sludge from biogas reactors. *Talanta* **2012,** *89*, 470-477; 10.1016/j.talanta.2011.12.065.

2. Ressler, T. WinXAS: A program for X-ray absorption spectroscopy data analysis under MS-Windows. *J. Synchrotron Radiat.* **1998,** *5* (2), 118-122; 10.1107/S0909049597019298.