## Electronic Supplementary Information

## Direct observation of liquid pre-crystallization intermediates during the reduction of aqueous tetrachloroaurate by sulfide ions

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**Fig. S1** *In situ* tapping-mode AFM height (left panel) and phase images of the products formed with  $Na_2S/AuCl_4$  ratio of 3 and condensed on HOPG support acquired in about 15 min (upper panels) and about 2 h after mixing the reactants.



**Fig. S2** Tapping-mode AFM height (left) and phase images acquired *in situ* at HOPG areas free from large droplets after 90 min reaction with Na<sub>2</sub>S/AuCl<sub>4</sub><sup>-</sup> ratio of 3 (upper panels) and *ex situ* from the products dried in air (lower panels).



Fig. S3 Typical TEM image and electron diffraction pattern of the products afforded with  $Na_2S/AuCl_4$  ratio of 3.



Fig. S4 *Ex situ* (left) and *in situ* (right panels) tapping-mode AFM height and phase (lower panels) images of the products formed with  $Na_2S/AuCl_4^-$  ratio of 1.8 on HOPG support.



**Fig. S5** Distance distribution functions determined from SAXS data for solutions with Na<sub>2</sub>S/AuCl<sub>4</sub><sup>-</sup> ratio of 3 for various reaction times.



Fig. S6 Typical autocorrelation functions of dynamic light scattering measured in the medium with  $Na_2S/AuCl_4$  ratio of 3 at different reaction times.



Fig. S7 Particle size and relative volume distribution derived from dynamic light scattering measured in the medium with  $Na_2S/AuCl_4$  ratio of 3 at selected reaction times.