# Supporting Information

**Table S1**. EDX Elemental compositions of background (average over 3 areas) vs. a particle (average over 7 particles). Measurements taken from areas highlighted in **Figure S1**

| **Background** | | **Particle** | |
|---|---|---|---|
| **Element** | **Atomic %** | **Element** | **Atomic %** |
| C | 87.99 | C | 92.15 |
| O | 7.36 | O | 2.75 |
| Si | 4.28 | Si | 1.4 |
| Zn | 0 | Zn | 1.72 |
| Cu | 0.29 | Cu | 0.33 |
| S | 0.07 | S | 1.62 |

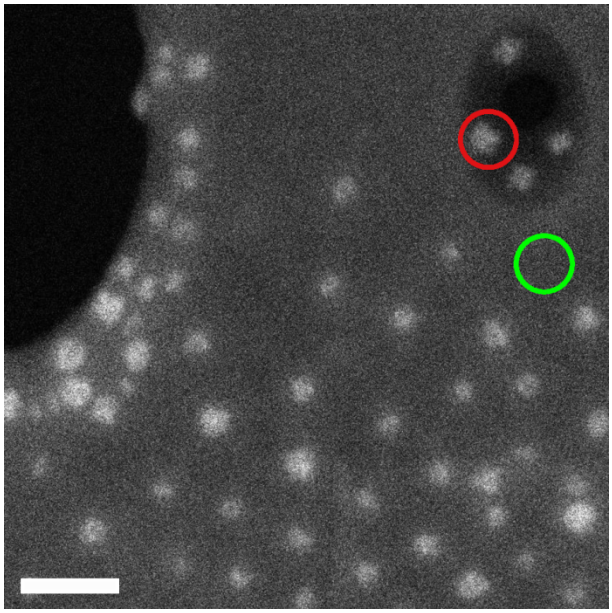


**Figure S1** - Scanning transmission electron micrograph (STEM) of typical ZnS particles, synthesized using polymer template PS(52,100)-*b*-P2VP(31,000) and 0.5 $Zn^{2+}$:P2VP loading, with the circles indicating an example region analyzed for EDX of particle (RED) and background (GREEN) (scale bar represents 100 nm)

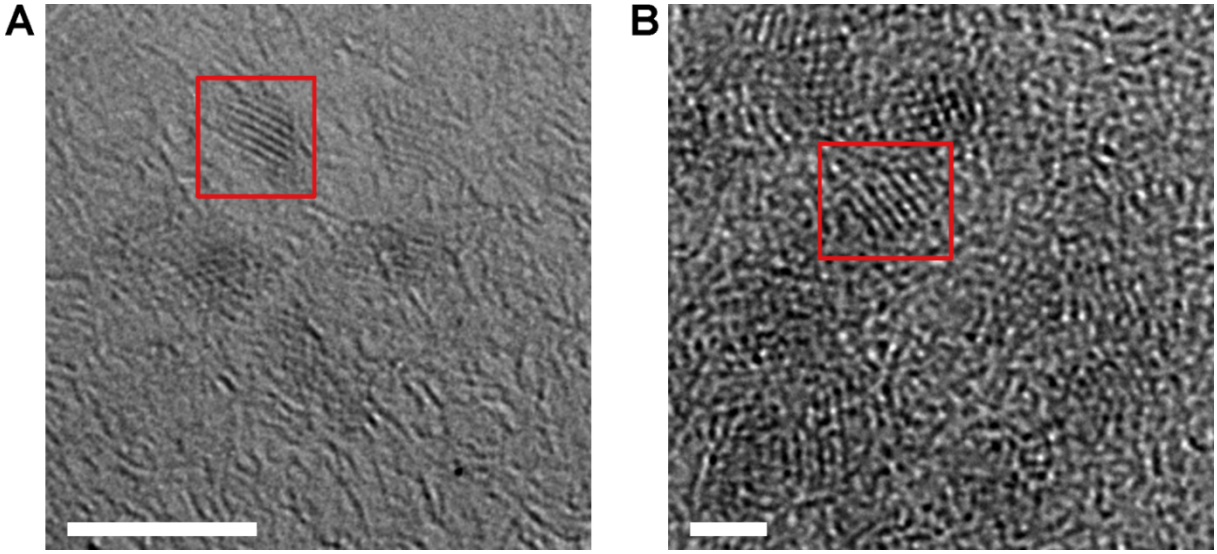



**Figure S2** - High resolution transmission micrographs (HR-TEM) of ZnS crystallites of ~4 nm diameter present in nanoparticles synthesized using (A) polymer template PS(16,000)-*b*-P2VP(3,500) with 0.5 $Zn^{2+}$:P2VP loading (scale bar represents 10 nm) and (B) polymer template PS(52,100)-*b*-P2VP(31,000) with 0.5 $Zn^{2+}$:P2VP loading (scale bar represents 5 nm)

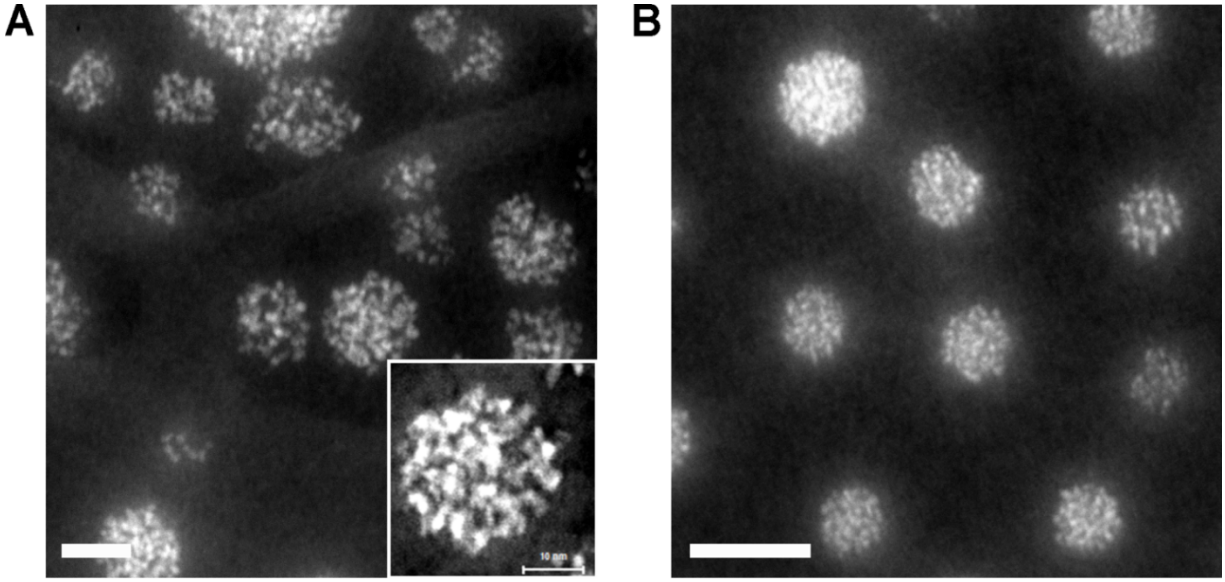



**Figure S3** - Nanoparticle substructure remains unchanged as a function of time and sulfur concentration. (A) Dark field scanning transmission electron micrograph (DF-STEM) image of nanoparticles synthesized using polymer template PS(52,100)-*b*-P2VP(31,000) and 0.5 $Zn^{2+}$:P2VP loading, imaged one year after particle synthesis, with the inset highlighting the presence of multiple crystallites ~4 nm in size (scale bars represent 20 nm and 10 nm for the main image and inset, respectively). (B) STEM image of nanoparticles synthesized using polymer template PS(34,000)-*b*-P2VP(18,000) and 0.5 $Zn^{2+}$:P2VP loading, with a 5x higher concentration of sulfur added to the system during synthesis (scale bar represents 50 nm).

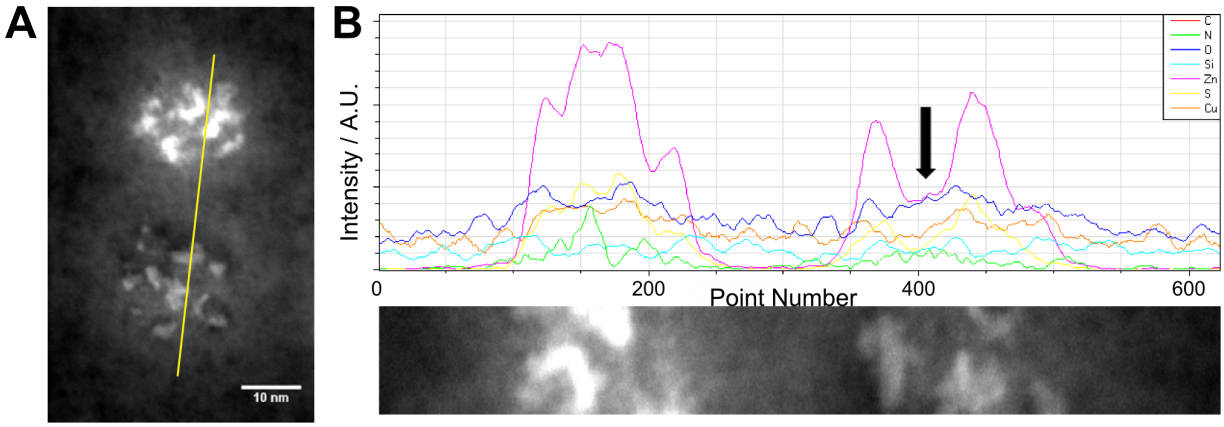



**Figure S4** - Zinc is present outside crystalline regions of ZnS nanoparticle. (A) Dark field scanning transmission electron micrograph (DF-STEM) image of nanoparticles synthesized using polymer template PS(52,100)-*b*-P2VP(31,000) and 0.5 $Zn^{2+}$:P2VP loading and (B) EDX elemental line profile taken along the yellow line in (A), showing the distribution of Zn, S, N and O within the two nanoparticles. Black arrow highlights the non-zero presence of Zn outside of the crystalline regions.

## Small angle X-ray scattering (SAXS): absolute-value scattering intensity plots and notes on fitting

In fitting, we have opted in all cases for spherical core-shell fits, as the simplest possible model to generate reliable radii that can be directly compared between samples. Deviations from these models at high Q for some samples can be attributed to the presence of small quantities of large aggregate phases in solution. The existence of such phases is confirmed by a slight cloudiness (Figure S7), that is common with this block copolymer system, however it is clear from SEM images (Figure S8) that spherical micelle-like structures are by far the numerically dominant species at all stages of the reaction. With the smallest ZnS, there is some deviation from the spherical fit at high Q, which must reflect fine structure, e.g. a roughness in the nanoparticle surface. We have not fitted this to preserve a simple model for SAXS that is comparable for all samples, and since the nanoparticle substructure is better investigated by TEM.

**Table S2** – X-Ray Scattering Length Densities (SLD) used for the analysis of SAXS data

| **Substance** | **Density / g.cm$^{-3}$** | **SLD / x10$^{-6}$ Å$^{-1}$** |
|---|---|---|
| Polystyrene (PS) | 1.05 | 9.6 |
| Poly(2-vinylpyridine) (P2VP) | 0.977 | 8.85 |
| P-Xylene | 0.861 | 8.0 |
| Zinc | 7.14 | 54.45 |
| Zinc Sulfide (ZnS) | 4.09 | 32.5 |
| Gold Chloride ($HAuCl_4$) | 3.90 | 29.0 |
| Gold (Au) | 19.3 | 126.5 |

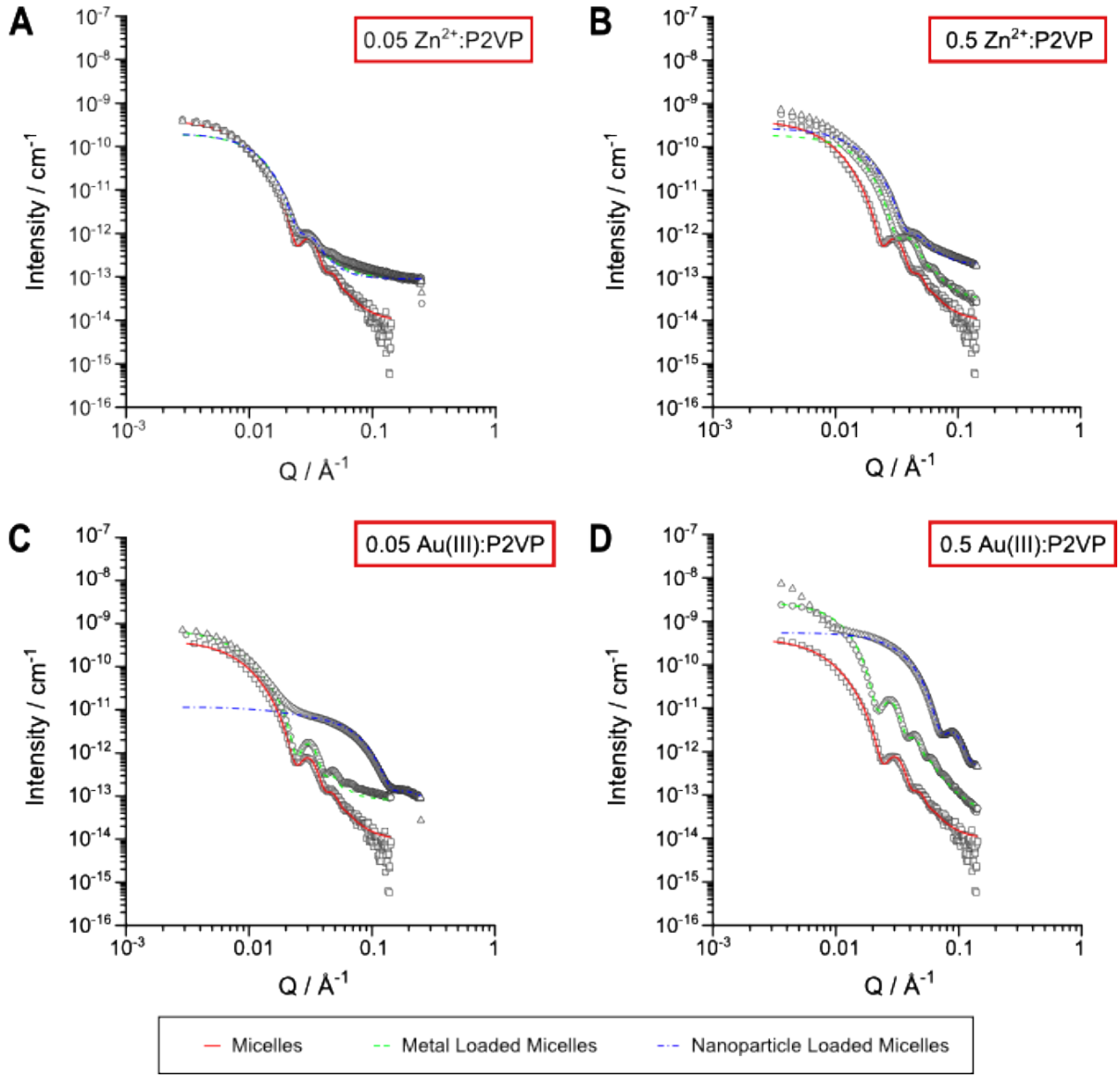



**Figure S5** - SAXS curves and the corresponding fitting curves for PS(52,100)-*b*-P2VP(31,000) micelles, showing the effect of loading on particle size where A) represents 0.05 $Zn^{2+}$:P2VP loading and B) represents 0.5 $Zn^{2+}$:P2VP loading. C) Represents 0.05 Au(III):P2VP loading and D) represents 0.5 Au(III):P2VP loading. Data was fitted to a core-shell model with a Schulz distribution and every 5$^{th}$ point is shown.

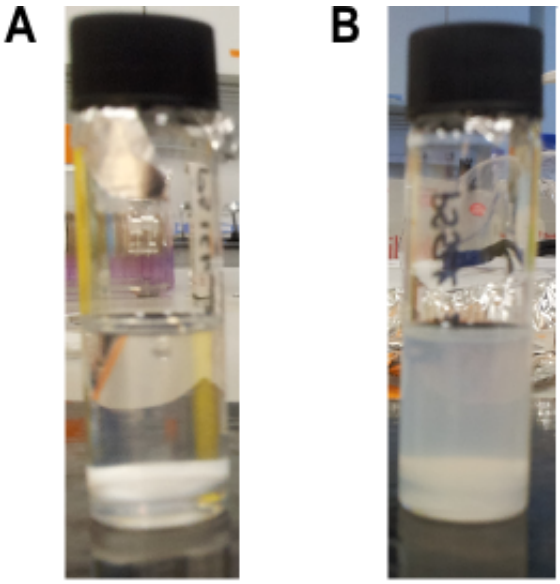



**Figure S6** – Presence of large aggregate phases in solution confirmed by slight cloudiness. (A) Typical micelle solution of PS(16,000)-*b*-P2VP(3,500) dissolved at 5mg/ml in p-xylene, compared to (B) a solution of PS(52,100)-*b*-P2VP(31,000) dissolved at 5mg/ml in p-xylene

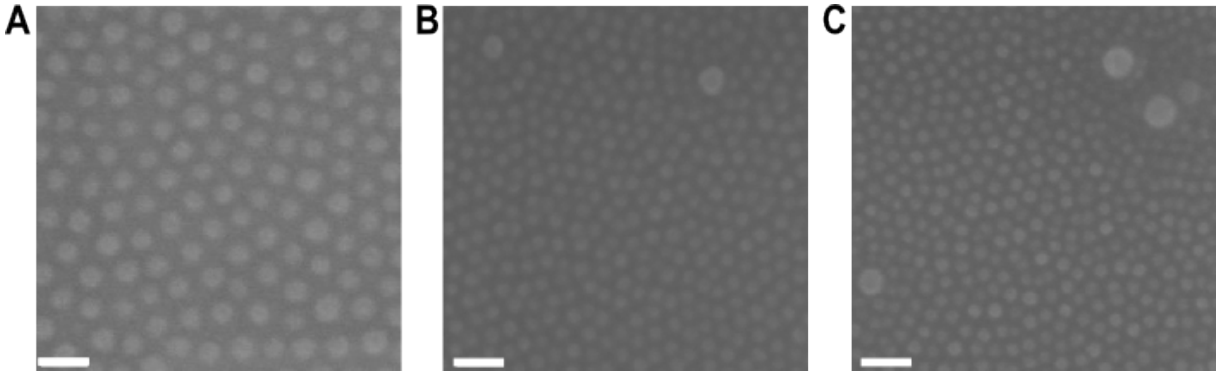



**Figure S7 –** Spherical micelle-like structures are by far the numerically dominant species at all stages of the ZnS nanoparticle synthesis reaction. Scanning electron micrographs (SEM) of (A) unloaded PS(52,100)-*b*-P2VP(31,000) micelles, (B) PS(52,100)-*b*-P2VP(31,000) micelles with 0.5 zinc acetate:P2VP loading and (C) PS(52,100)-*b*-P2VP(31,000) micelles with 0.5 ZnS:P2VP loading, deposited onto a Si wafer using dip-coating. Scale bar is 100nm in all 3 figures.