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Studies in Micelle-Mediated Pd Nucleation

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Experimental

Block copolymer synthesis: Polystyrene-*b*-poly(*N*,*N*-dimethyl acrylamide), PS_{365}-$PDMA_{125}$ (the subscripts denote the repeating unit numbers of the corresponding blocks), was synthesized via sequence reversible addition-fragmentation chain transfer (RAFT) polymerizations. The molecular weight of the polymer is 54,800 g/mol and the polydispersity is 1.16.

Preparation of micelle solutions: 5.0 mg of PS_{365}-$PDMA_{125}$ was dissolved in 0.5 ml of tetrahydrofuran (THF) and then the solution was quickly injected via a syringe into 9.5 mL of isopropanol alcohol (IPA) to form micelles, or the polymers were directly mixed with IPA at 50 ^{o}C for 0.5 hour before cooling to room temperature. Sonication (10 min each time for 2-5 times) was also used to assist the dispersion of the copolymer. The hydrophobic PS chains collapsed to form micellar cores and the hydrophilic PDMA chains stretched into IPA to form micellar coronas.

Preparation of micelle/Pd complex solutions: Different amounts (0.2, 2.0 or 5.0 mg) of $Pd(PPh_3)_4$ was dissolved in 0.5 ml of toluene and the solution was quickly injected into 9.5 ml of the prepared micelle solution. The resulting mixture was stirred at room temperature for 3 days to yield fresh samples with amorphous Pd aggregates on the micellar cores. These samples were aged or heated to yield well-incubated samples with Pd NPs in the micellar cores.

Preparation of Pd NP suspensions: 5.0 mg of $Pd(PPh_3)_4$ was dissolved in 0.5 ml of toluene and the solution was quickly injected into 9.5 ml of pure IPA without polymeric micelles. The resulting mixture was stirred at room temperature for 3 days to yield pure Pd NP suspension. The color of this solution changed gradually from light yellow to dark brown.

Characterizations: $Pd(PPh_3)_4$ solutions in micellar solution were monitored by using UV-Vis spectroscopy (Jasco V-530, wavelength 280 - 700 nm) and by using ^{31}P-NMR (Bruker DRX 500, 500 MHz). The hydrodynamic diameters, D_h, of the micelles were investigated by using dynamic light scattering (DLS, Brookhaven Instrument, BI-200SM goniometer; He-Ne laser with wavelength of 632.8 nm) at $\theta = 90^{o}$ at room temperature. Samples for transmission electron microscope (TEM) study were prepared by drying a drop of the solutions onto carbon-coated copper grids. Morphology, element compositions, nanostructures of the Pd NPs and Pd/micelle hybrid colloids were investigated by using TEM (Philips CM10, 20 kV), high resolution transmission electron microscope (HR-TEM, FEI Tecnai TF20, 200 kV) with high angle annular dark field (HAADF) detector for dark field and HR-TEM (Philips CM200, 200 kV,) with resolution up to 0.24 nm and with electron energy loss spectroscopy (EELS) detector for element mapping.

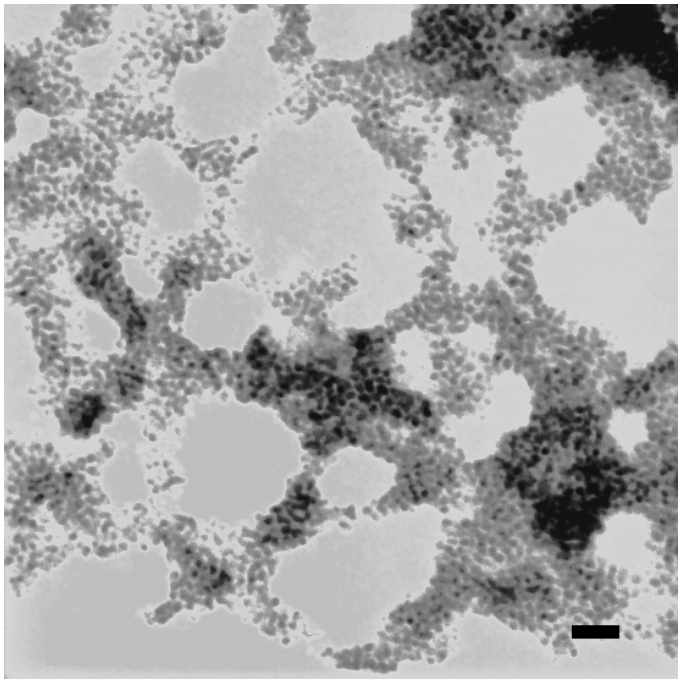

Figure S1. A TEM image of pure Pd nanocrystals generated from degradation of $Pd(PPh_3)_4$ in IPA without micelles. The Pd NPs settled down to the vial bottom as black precipitates. The scale bar here represents 20 nm.

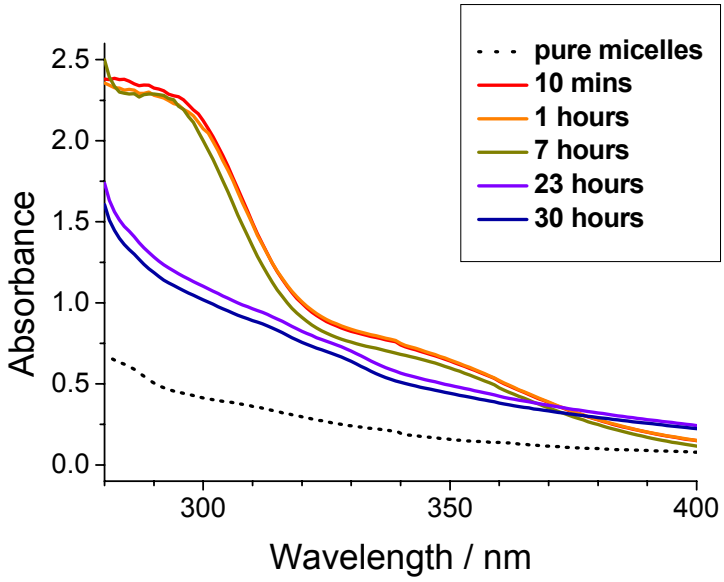

Figure S2. UV-Vis spectra as a function of time for a micellar solution in the presence of $Pd(PPh_3)_4$. The dot line indicates the absorption of a pure micellar solution. The intensity of the absorption peak (λ_{max} =

291 nm) of initial precursors decreased gradually within 30 hours, suggesting the dissociation of the $Pd(PPh_3)_4$ precursors.

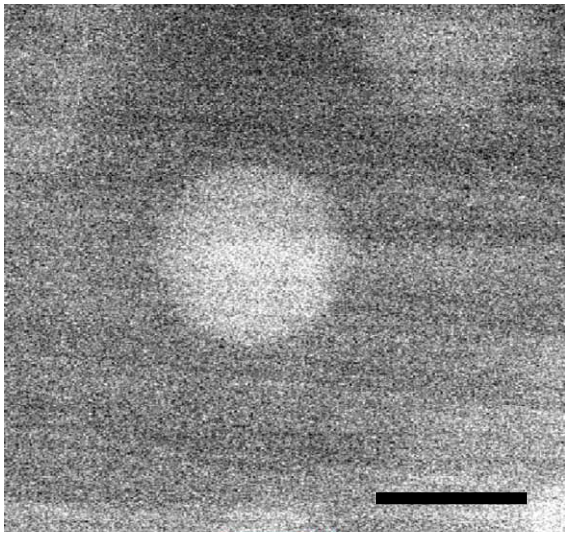

Figure S3. A micellar core deposited with amorphous Pd was observed by HR-TEM in the dark field mode (HAADF). The scale bar here represents 20 nm.

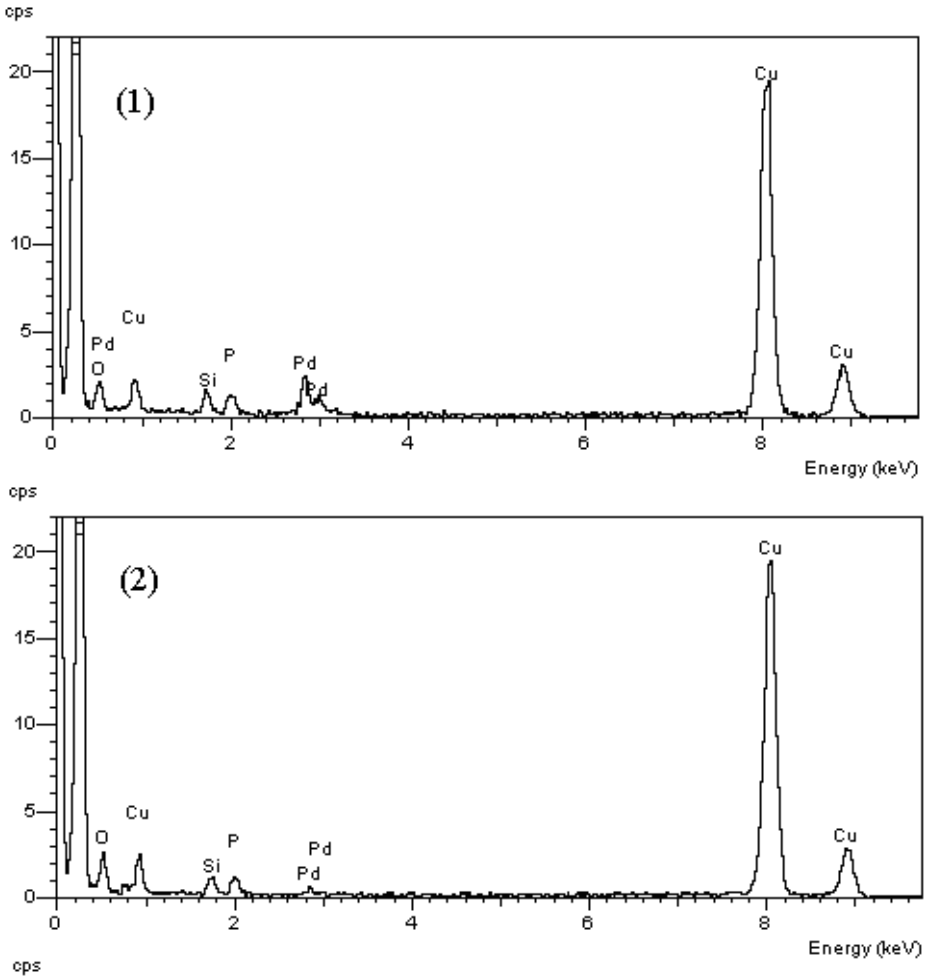

Figure S4. Pd analysis for the areas (1) and the area (2) in the HR-TEM image of Figure 2e. Pd atoms were detected from the surface of micellar core (area 2, Pd%=2.2%), although the signal intensity is much lower than that of Pd NP (area 1, Pd%=46%).

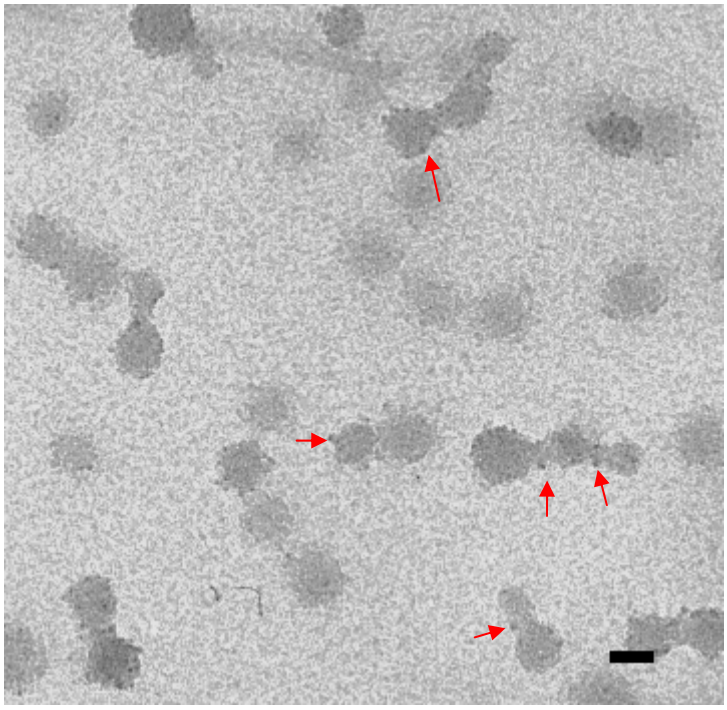

Figure S5. After ageing the Pd/micelle NPCs (prepared from 2 mg Pd precursor/5 mg polymer micelles in 10 ml solution) for 18 days, small Pd NPs started to be observed in a TEM image. The red arrows indicate some of the fresh-formed Pd NPs. The scale bar here represents 20 nm.

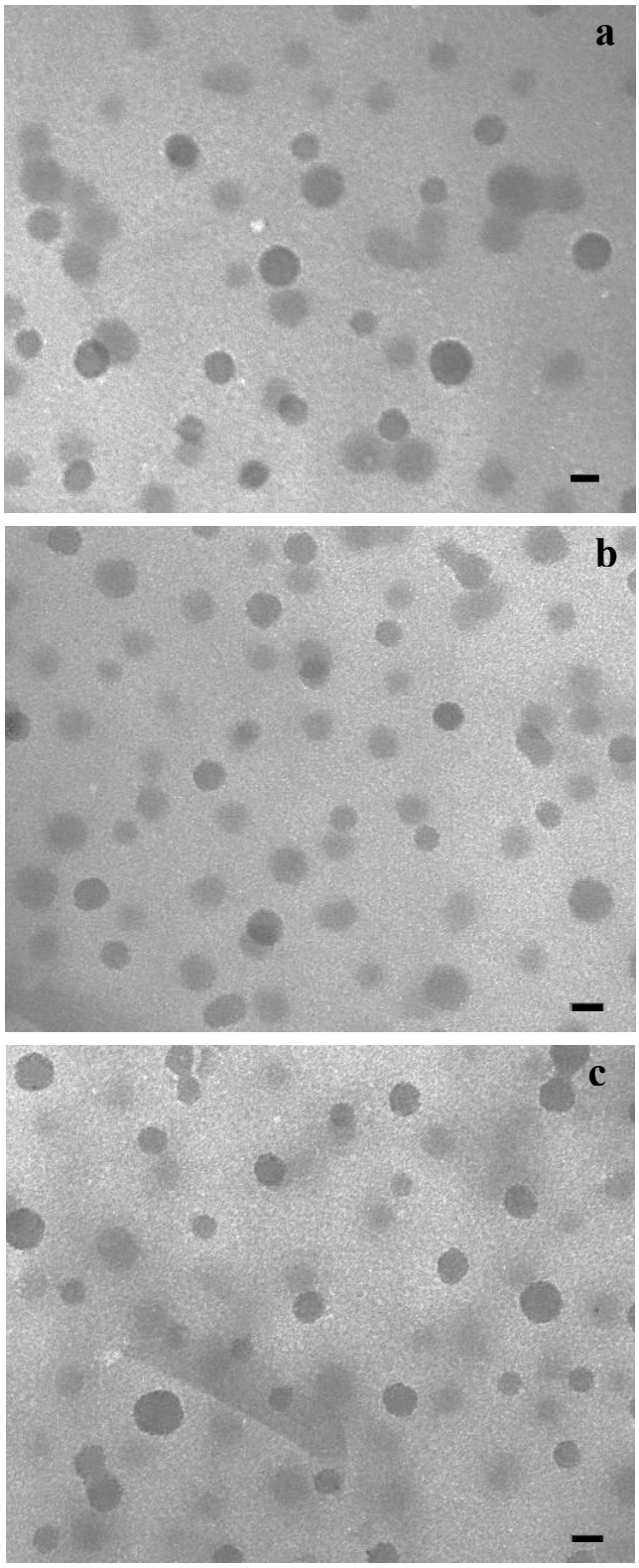

Figure S6. TEM images for fresh prepared Pd/micelle NPCs with different adding amount of Pd precursor (a) 0.5 mg; (b) 2.0 mg; and (c) 5.0 mg. The amount of polymer is 5.0 mg in all systems. The scale bars present 20 nm.