

Supporting information

When Ligand Exchange Leads to Ion Exchange: Nanocrystal Facets Dictate the Outcome

*Indika K. Hewavitharana and Stephanie L. Brock**

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, United States

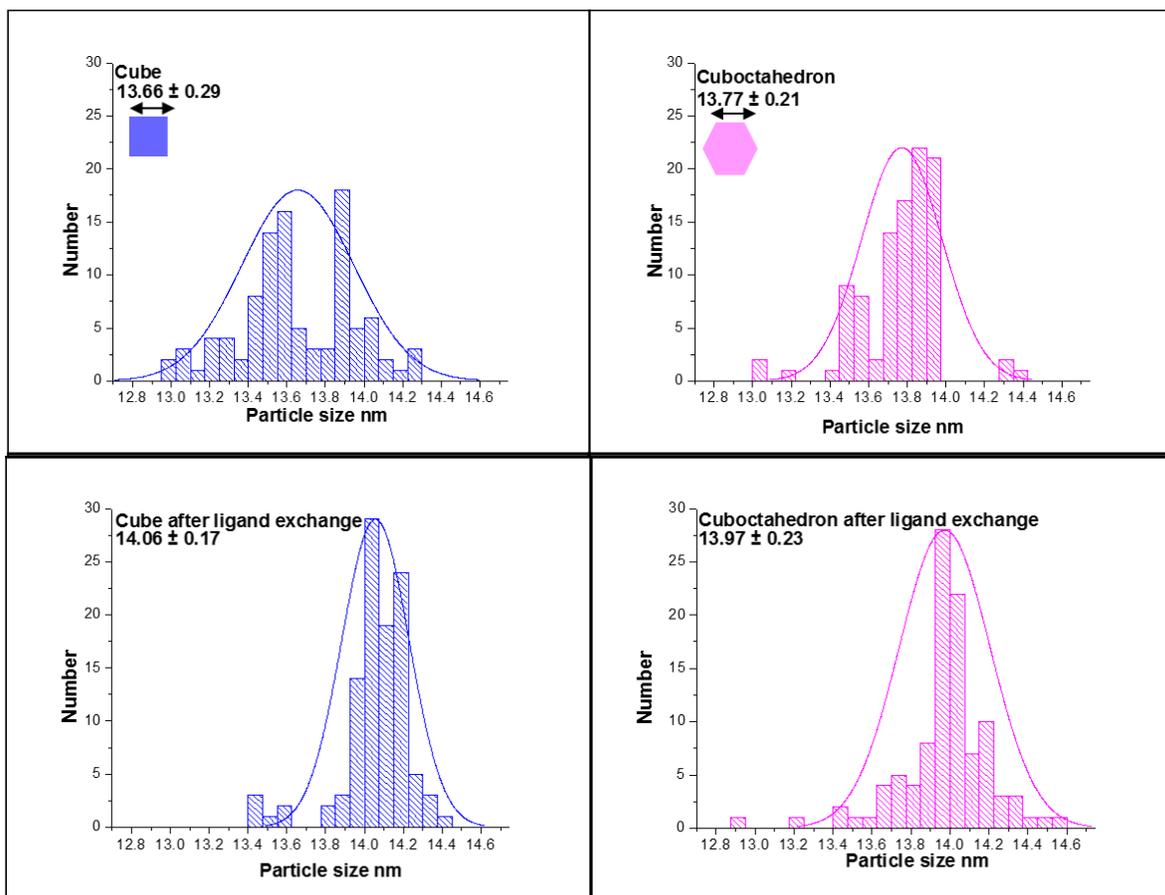


Figure S1. Histograms representing the cube size and cuboctahedron size as the facet edge-length distribution measured from TEM images of PbTe NCs ligand exchanged with Na₂S. (Molar ratio of Na₂S: PbTe = 5: 1). Note that while the size change is marginal after ligand exchange, the nature of the distribution becomes more symmetric than in the starting particles.

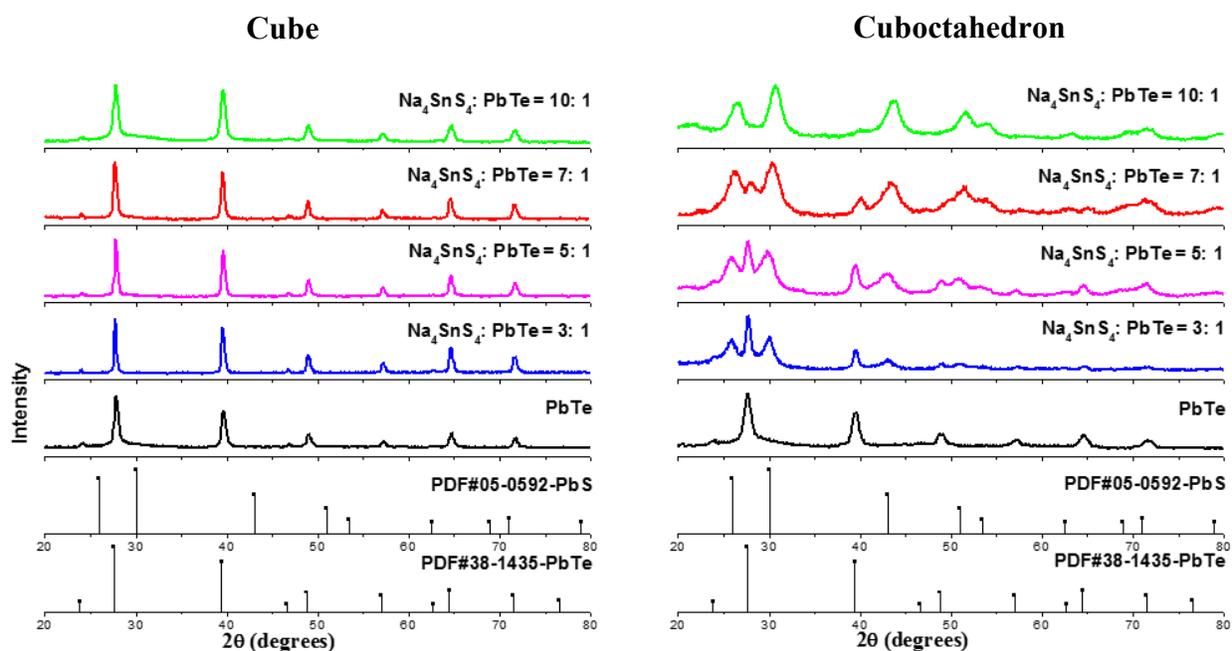


Figure S2. PXRD data for (a) cube-shaped (b) cuboctahedron-shaped PbTe NCs ligand exchanged with different molar ratios of Na_4SnS_4 . The reference patterns for PbS (JCPD: 05-592) and PbTe (JCPD: 38-1435) are shown.

Table S1. ICP-MS analysis of supernatants of the cube-shaped and cuboctahedron-shaped PbTe NCs ligand exchange with Na_2S . ([HEHe] = High Energy He)

Na ₂ S: PbTe molar ratio	PbTe cube		PbTe cuboctahedron	
	125 Te [HEHe] / Conc. [ppb]	208 Pb [HEHe] / Conc. [ppb]	125 Te [No Gas] / Conc. [ppb]	208 Pb [No Gas] / Conc. [ppb]
1:1	88.90	11.60	465.61	2.33
3:1	159.65	4.95	449.15	5.97
5:1	256.65	0.30	942.85	34.85
7:1	385.30	30.95	4238.09	35.56
10:1	664.95	20.40	2656.75	61.37

Table S2. TEM-EDS atomic % for cube-shaped and cuboctahedron-shaped PbTe NCs before and after ligand exchange with Na₄SnS₄

Na ₄ SnS ₄ : PbTe molar ratio		NaK	SK	SnL	TeL	PbL
Cube	5:1	2.2	46.3	13.8	19.1	18.7
Cuboctahedron	5:1	12.96	27.36	7.45	22.50	31.73
	5:1	14.22	24.75	6.59	24.23	30.21

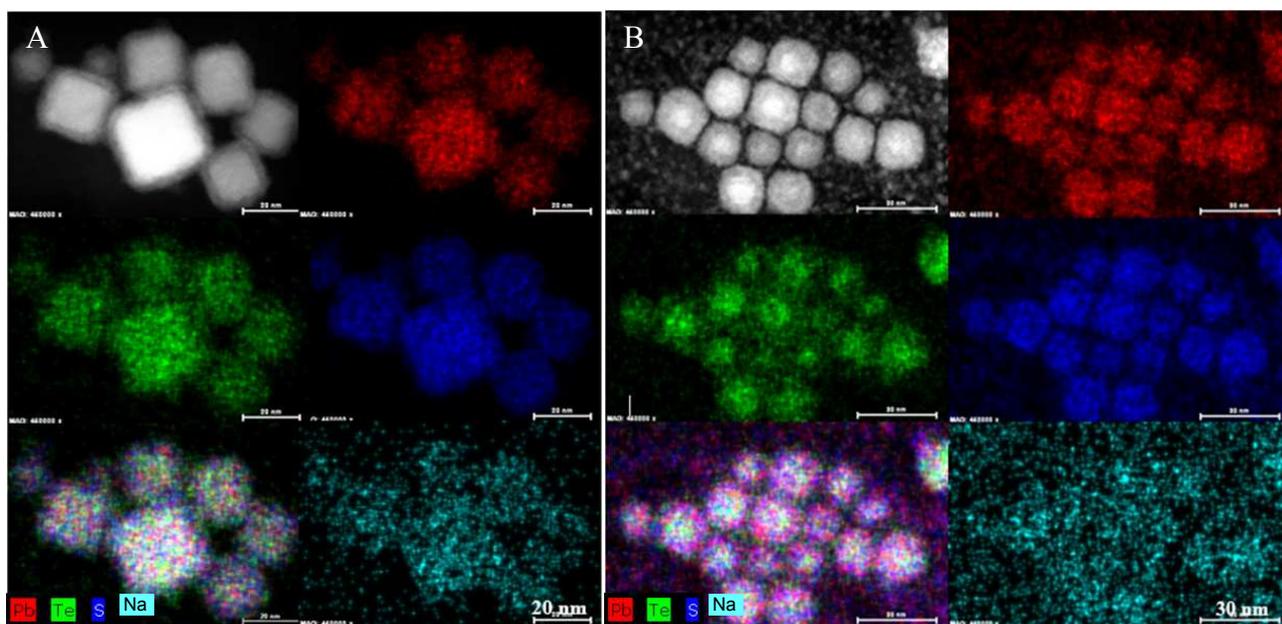


Figure S3. Atomic resolution HAADF-STEM images of (A) cube-shaped and (B) cuboctahedron-shaped PbTe NCs ligand exchanged with Na₂S. (Molar ratio of Na₂S: PbTe = 5:1). The scale bars in panel A are 20 nm and those in B are 30 nm.

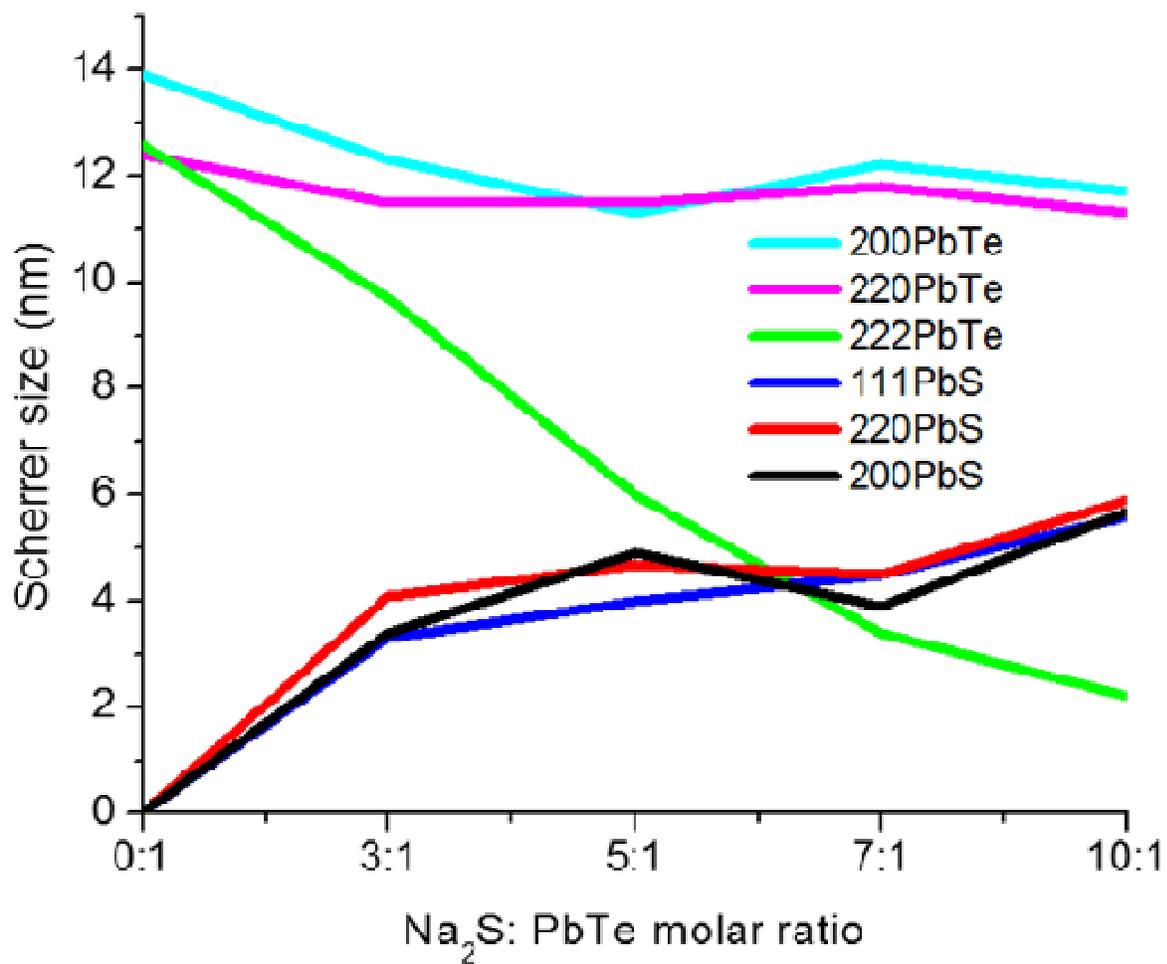


Figure S4. Graphical illustration of the data in Table 1 for PbTe cuboctahedra exchange with sulfide showing the etching of the (222) PbTe facets and the growth of polycrystalline PbS with increasing Na₂S:PbTe molar ratio.

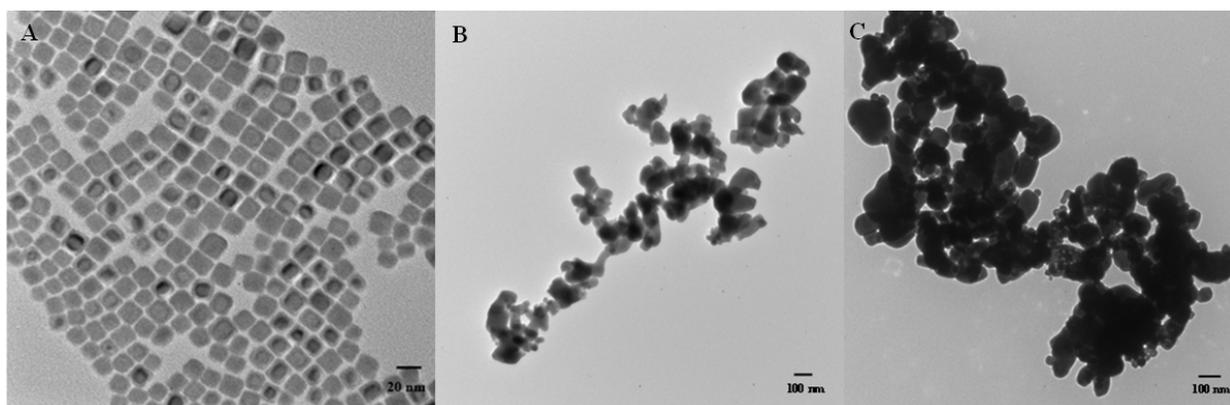


Figure S5. TEM images of (A) cube-shaped PbTe NCs after cation exchange with AgNO₃ (molar ratio of AgNO₃: PbTe= 20: 1); (B) cuboctahedron-shaped PbTe NCs after cation exchange with AgNO₃ (molar ratio of AgNO₃: PbTe= 10: 1) and (C) cuboctahedron-shaped PbTe NCs after cation exchange with AgNO₃ (molar ratio of AgNO₃: PbTe= 20: 1). Note that under strongly forcing conditions (Figure S4(C)) Ag⁺ ion exchange results in dramatic morphological changes (ripening) and aggregation due to the energetic nature of the process and the innate reactivity of Ag⁺ terminated surfaces.^{1,2}

References

1. Kim, Y. D.; Ishizaki, S.; Kato, A., Preparation of Ag₂S-Coated ZnS Particles by an Ion Exchange Method - Effect of Reaction Conditions on the Morphology of Coated Particles. *J. Mater. Sci. Lett.* **1996**, *15*, 943-947.
2. Zhang, W. J.; Cai, Y.; Qian, R.; Zhao, B.; Zhu, P. Z., Synthesis of Ball-Like Ag Nanorod Aggregates for Surface-Enhanced Raman Scattering and Catalytic Reduction. *Nanomat.* **2016**, *6*, 99-1-11.