Multivariate Synthesis of Tin Phosphide Nanoparticles: Temperature, Time, and Ligand Control of Size, Shape, and Crystal Structure

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Supporting Information

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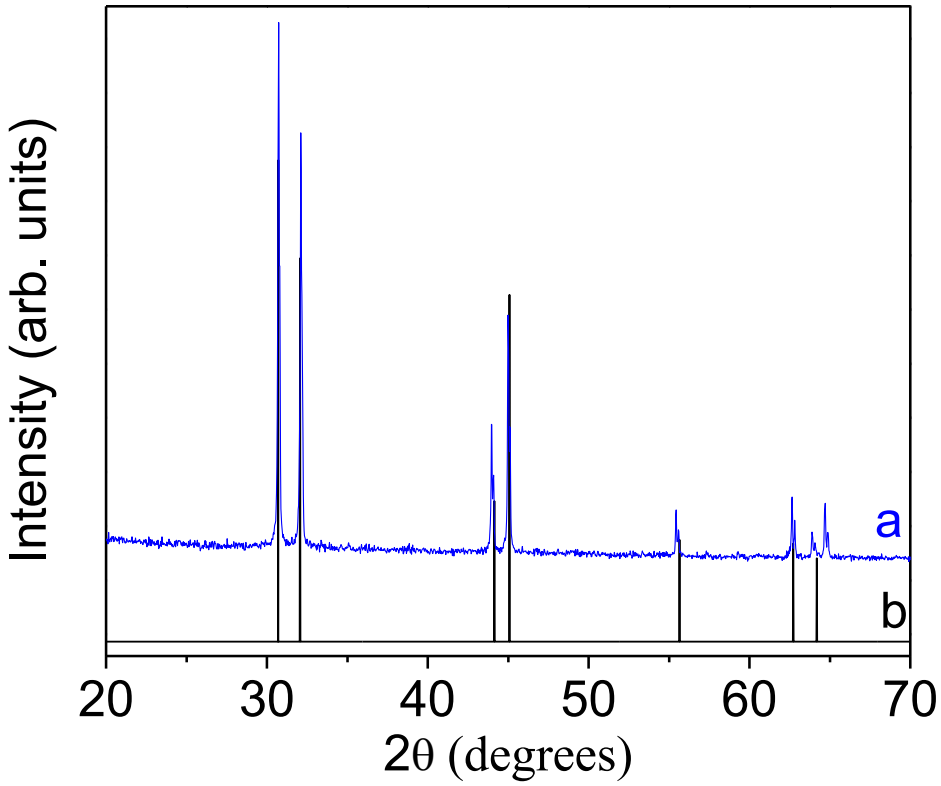


Figure S1. (a) Powder XRD pattern of the product obtained from the reaction of $SnCl_2$ and TOP in OLA/OA/ODE at 350 ºC for 3 h along with the (b) ICDD-PDF overlay of tetragonal Sn (JCPDS No. 00-004-0673).

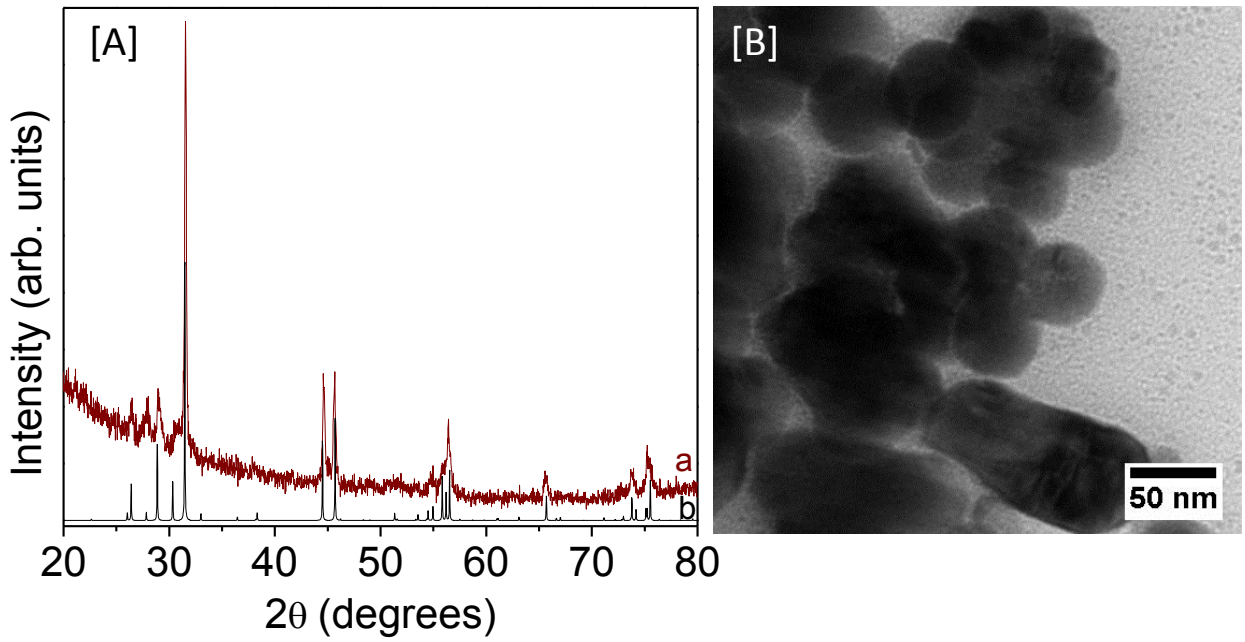


Figure S2. (A) (a) Powder XRD pattern of the product obtained from the reaction of $SnCl_2$ and $(TMSi)_3P$ in OLA/OA/ODE at 180 ºC for 3 min along with the (b) ICDD-PDF overlay of rhombohedral Sn_4P_3 (JCPDS No. 01-073-1820). (B) A representative TEM image of the as-prepared particles.

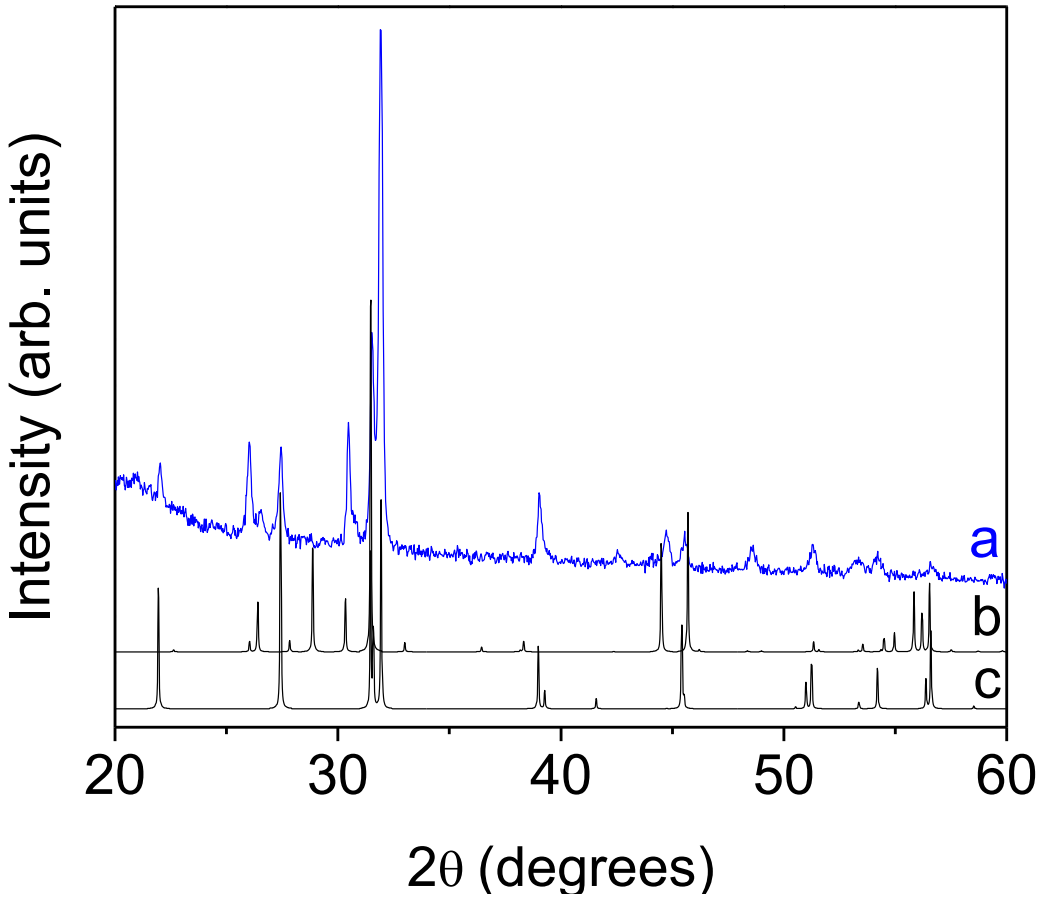


Figure S3. (a) Powder XRD pattern of the product obtained from the reaction of $SnCl_2$ and $(TMSi)_3P$ in OLA/OA/ODE with DDT at 180 ºC for 12 h along with the ICDD- PDF overlays of (b) rhombohedral Sn_4P_3 (JCPDS No. 01-073-1820) and (c) orthorhombic SnS (JCPDS No. 39-0354).

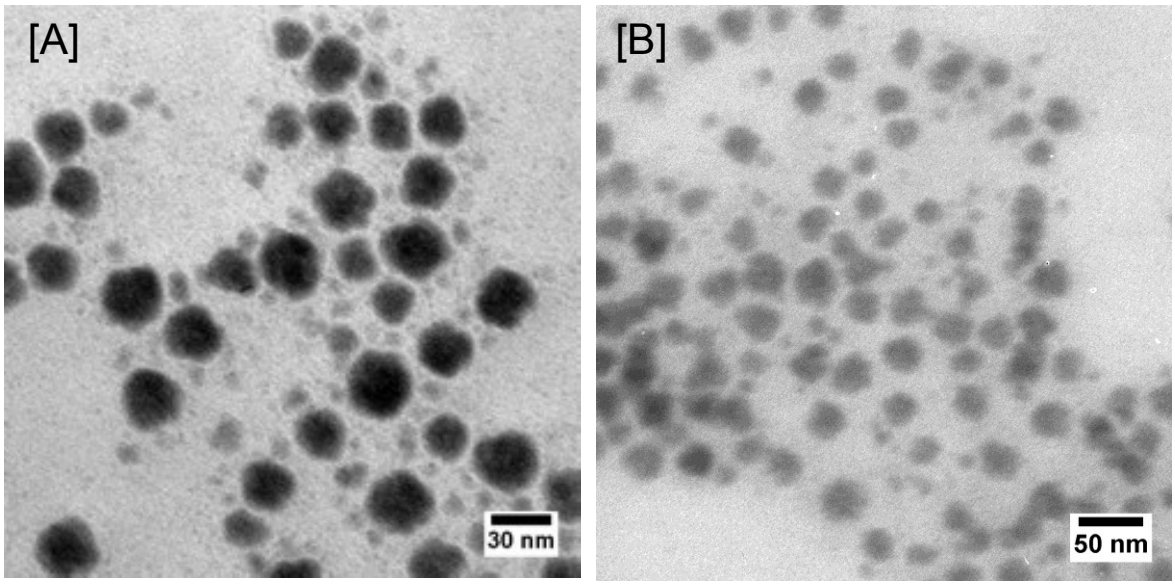


Figure S4. Representative TEM images of (A) rhombohedral Sn_4P_3 NPs synthesized at 180 °C and (B) hexagonal SnP NCs synthesized at 250 °C with no use of oleic acid.

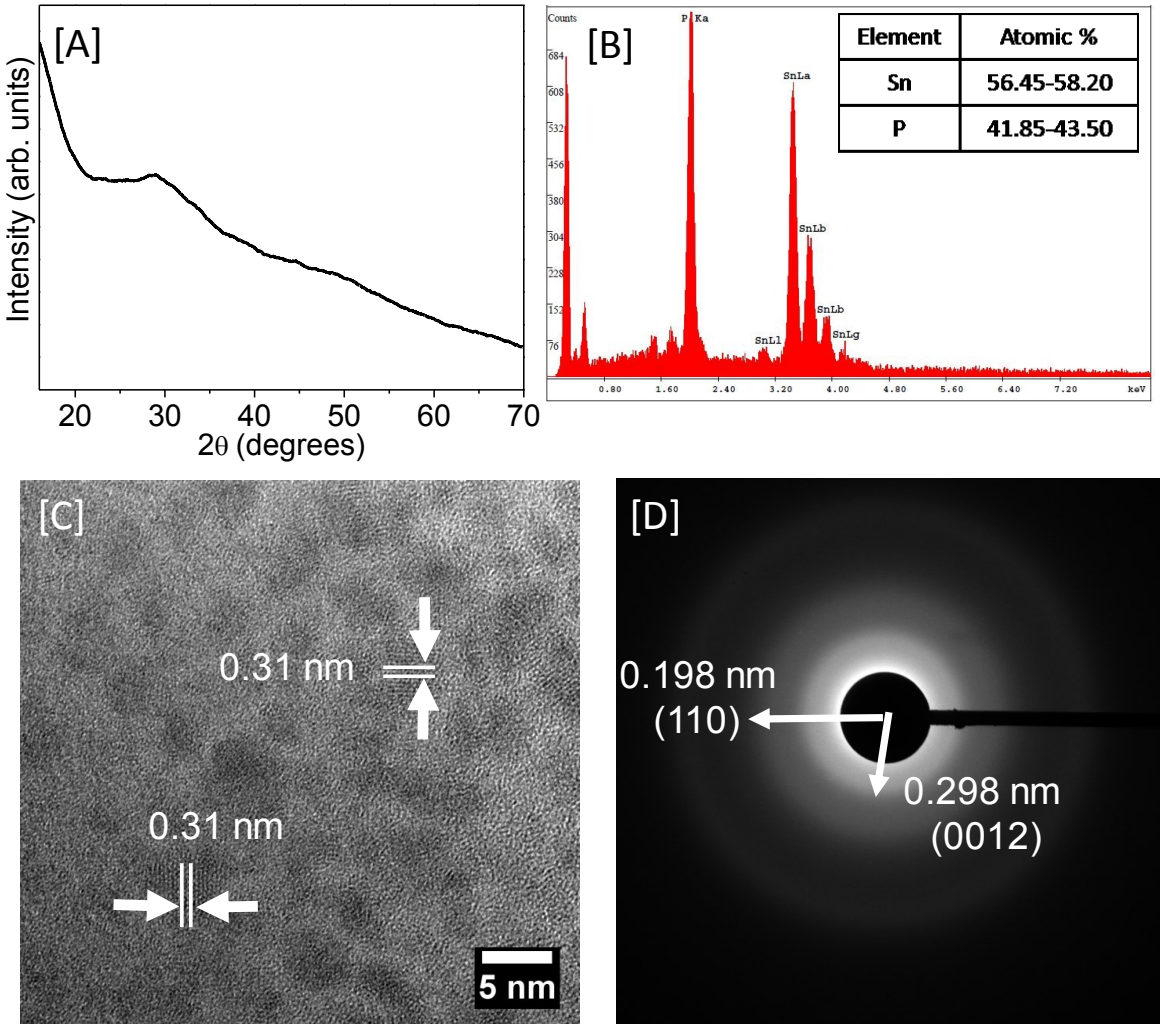


Figure S5. (A) A representative powder XRD pattern of amorphous to partially crystalline Sn_4P_3 NPs produced at 180 °C for 5 min using SnI_4 and $(TMSi)_3P$ precursors, without the use of alkylphosphines (TBP or TOP). (B) SEM/EDS spectrum of the corresponding Sn_4P_3 NPs along with (C) HRTEM, and (D) the selected area electron diffraction pattern recorded from 200 nm x 200 nm area of the sample indicating short-range crystalline order of rhombohedral Sn_4P_3. The broad and not well defined peaks in the PXRD is due to lack of long-range crystalline order. The average Sn: P atomic ratio obtained from 5 individual measurements of the same sample are also shown suggesting the growth of Sn_4P_3 particles.

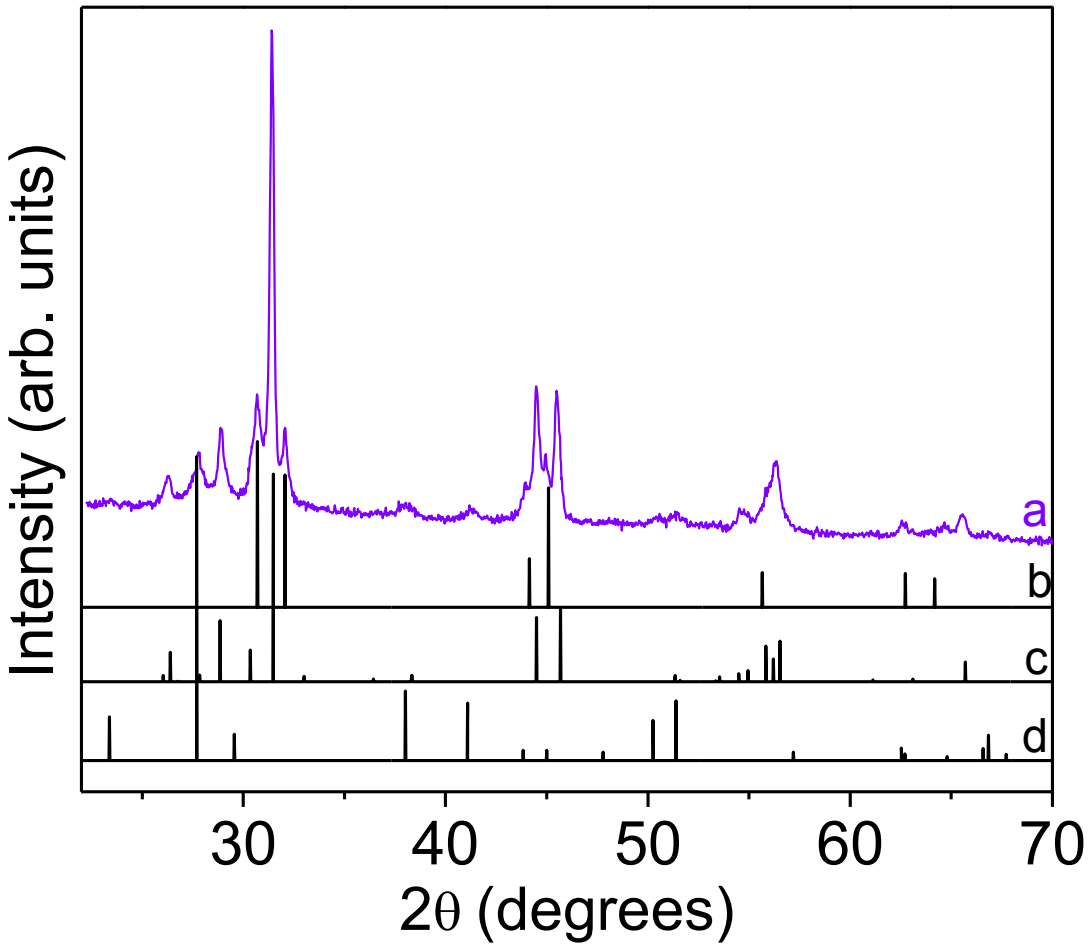


Figure S6. (a) Powder XRD pattern of the product obtained from the reaction of SnI_4 and $(TMSi)_3P$ in OLA/OA/ODE at 180 ºC for 3 min in the presence of 12 mM TBP. ICDD-PDF overlays of (b) tetragonal tin (JCPDS No. 00-004-0673), (c) rhombohedral Sn_4P_3 (JCPDS No. 01-073-1820), and (d) hexagonal SnP (JCPDS No. 03-065-9787) are also shown.

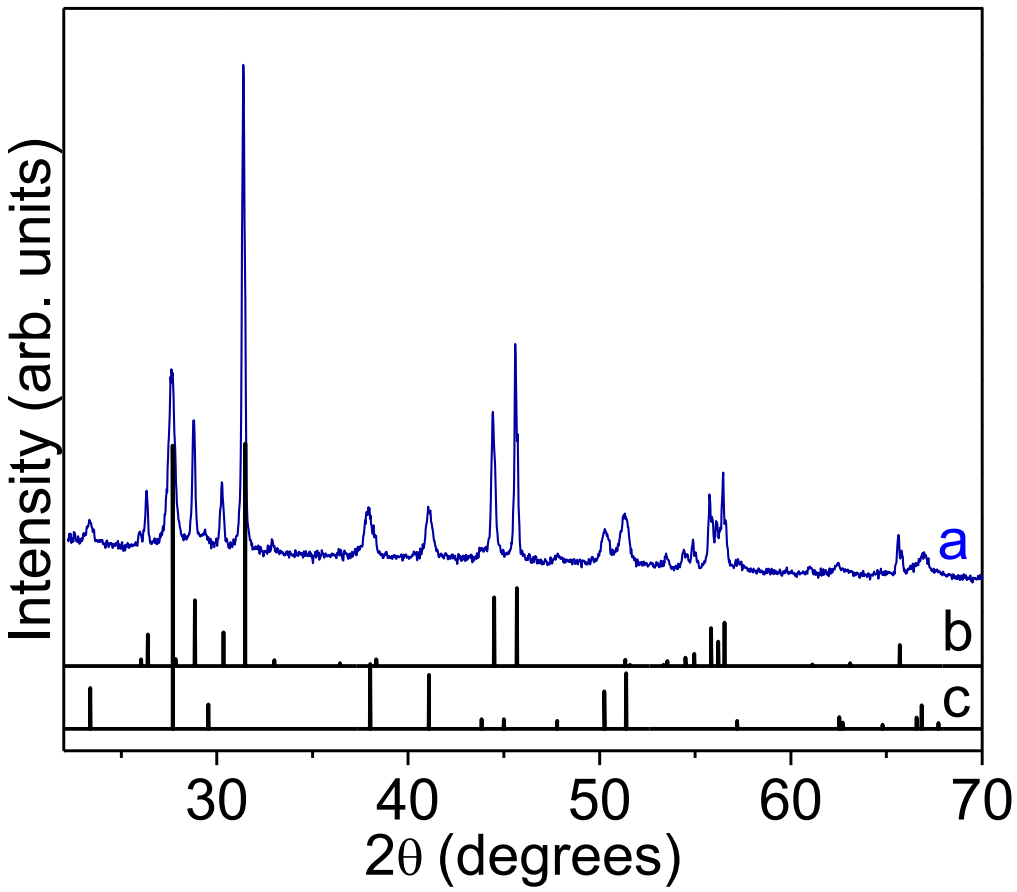


Figure S7. (a) Powder XRD pattern of the product obtained from the reaction of SnI_4 and $(TMSi)_3P$ in OLA/OA/ODE at 180 ºC for 3 min in the presence of 4 mM of TOP. ICDD-PDF overlays of (b) rhombohedral Sn_4P_3 (JCPDS No. 01-073-1820) and (c) hexagonal SnP (JCPDS No. 03-065-9787) are also shown.

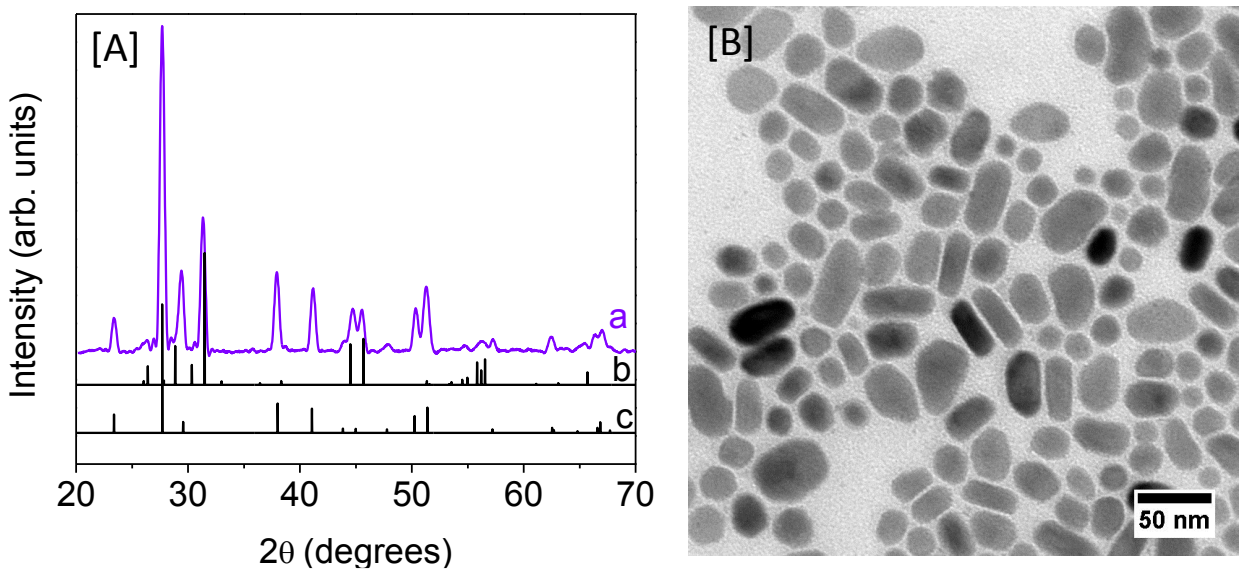


Figure S8. (A) Powder XRD pattern of (a) the product obtianed from the reaction of SnI_4 and $(TMSi)_3P$ in OLA/OA/ODE at 220 ºC for 15 min. ICDD-PDF overlays of (b) rhombohedral Sn_4P_3 (JCPDS No. 01-073-1820) and (c) hexagonal SnP (JCPDS No. 03-065-9787) are also shown. (B) A representative TEM image of the as-prepared particles.

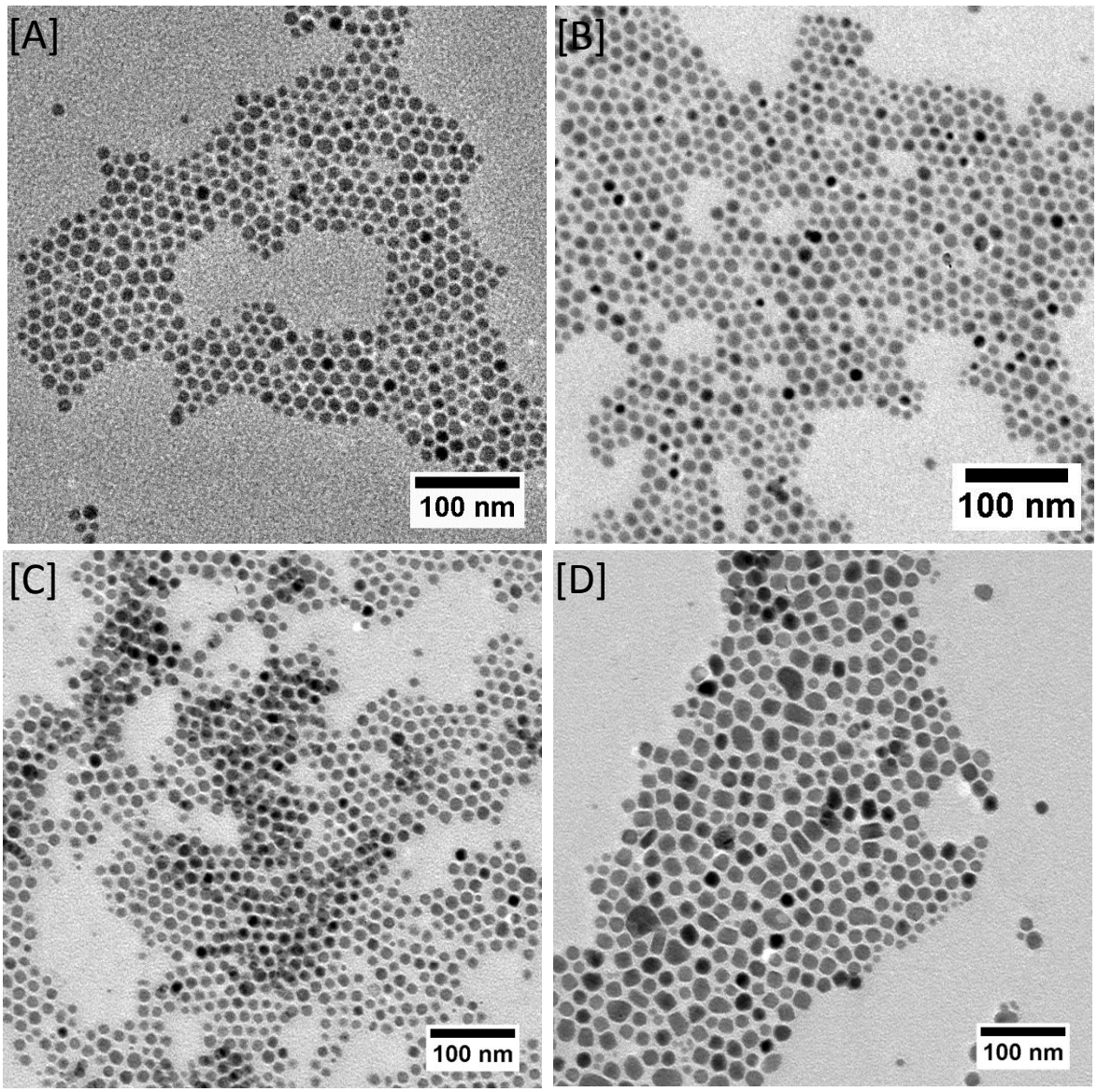


Figure S9. Representative TEM images of the phase pure hexagonal SnP NCs synthesized in OLA/OA/ODE at 250 ºC for (a) 5, (b) 30, (c) 60, and (c) 180 seconds.

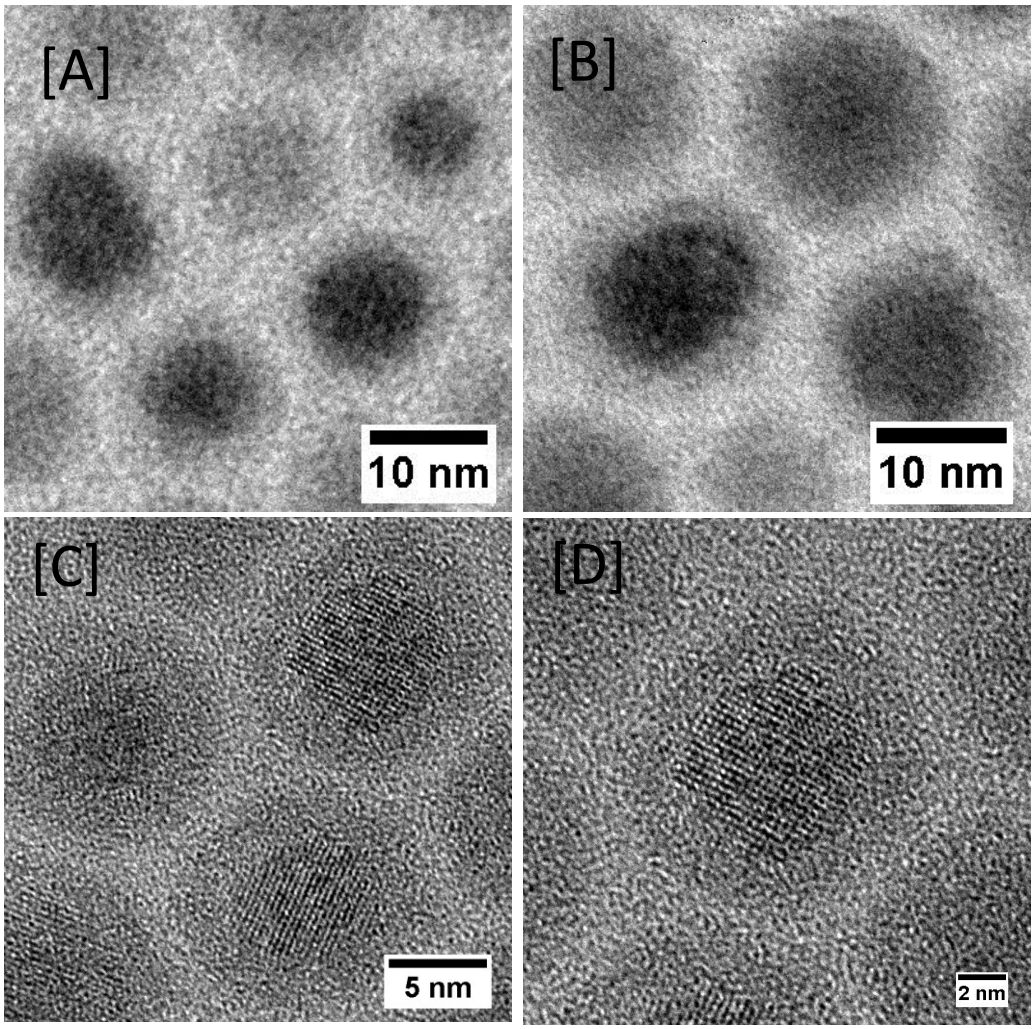
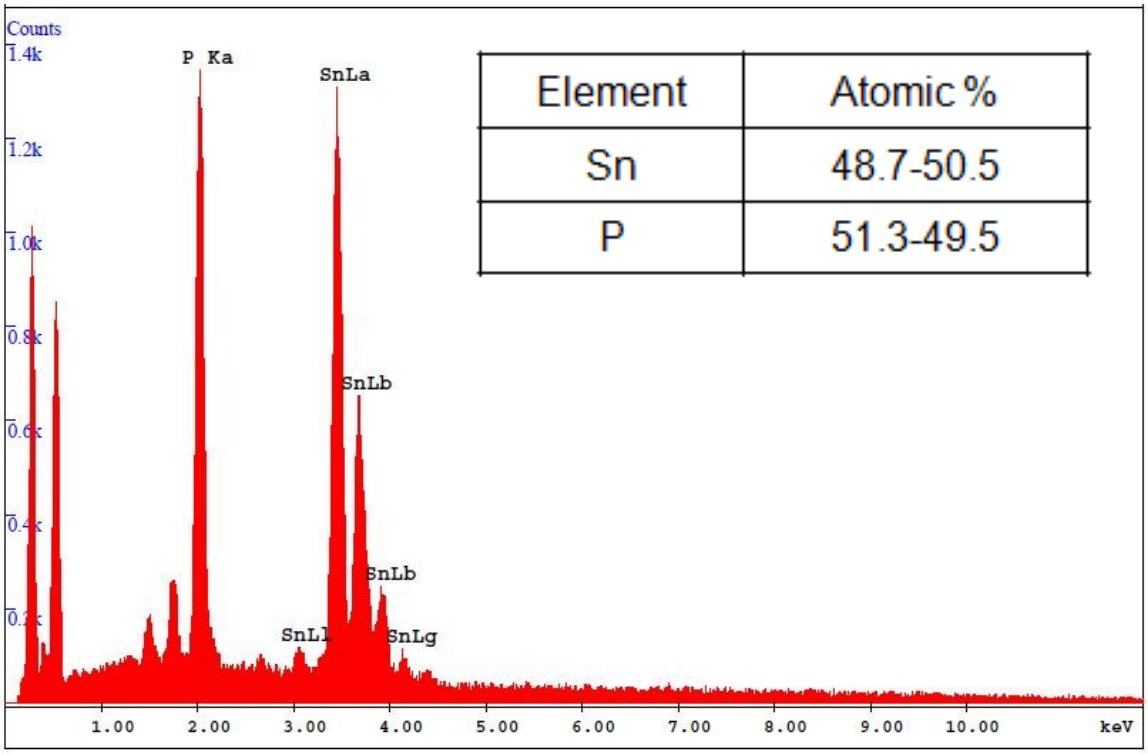


Figure S10. Low resolution and high resolution TEM images of the hexagonal SnP NCs prepared in OLA/OA/ODE at 250 ºC for (a) 5, (b) 30, (c) 60, and (c) 180 seconds showing the presence of a crystalline SnP core and amorphous shell with varying thickness.



Element	Atomic %
Sn	48.7-50.5
P	51.3-49.5

Figure S11. A representative SEM/EDS spectrum of the hexagonal SnP NCs synthesized at 250 ºC without the use of TBP for 60 seconds. The average Sn: P atomic ratio obtained from 5 individual measurements of the same sample are also shown.

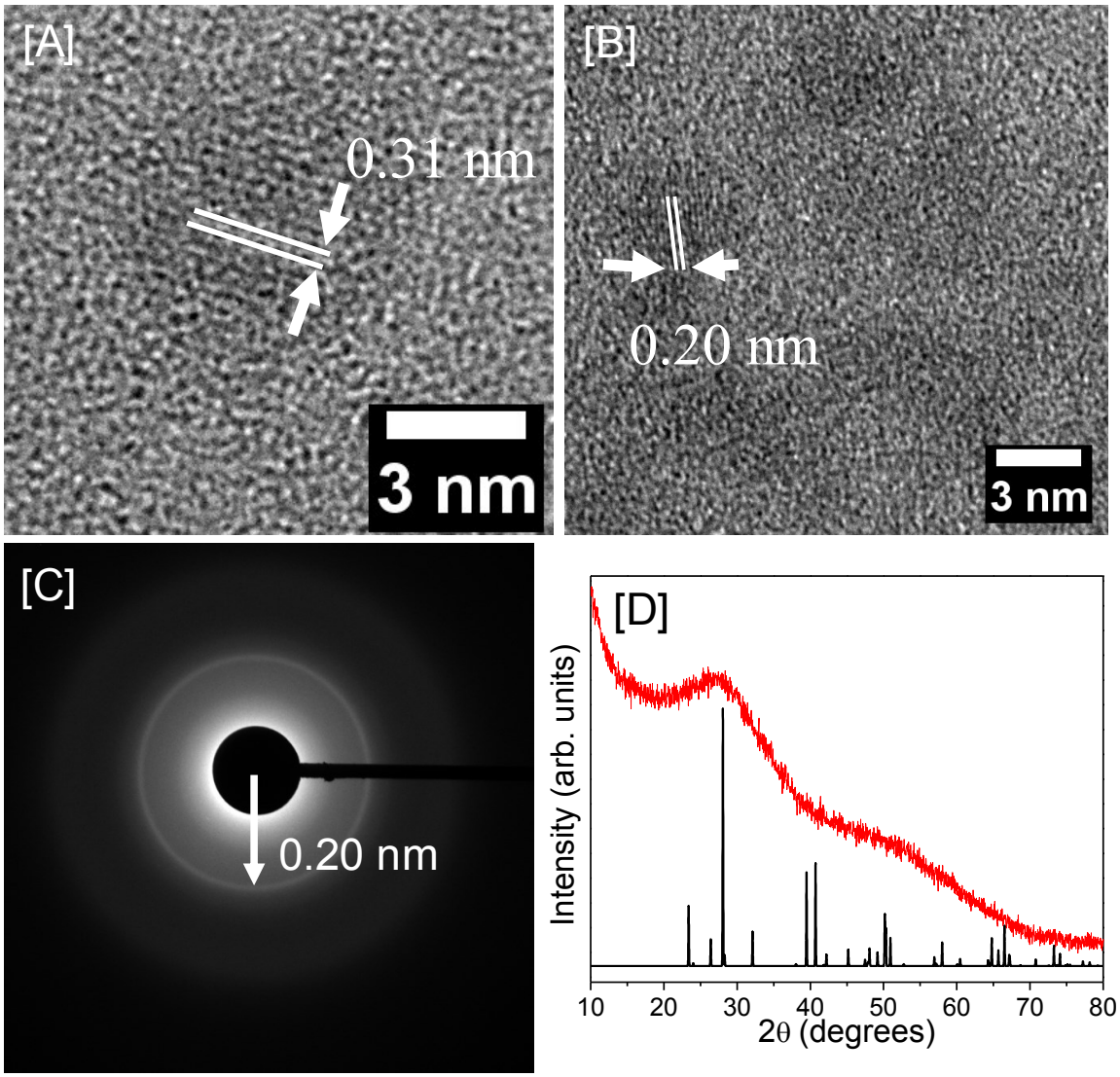
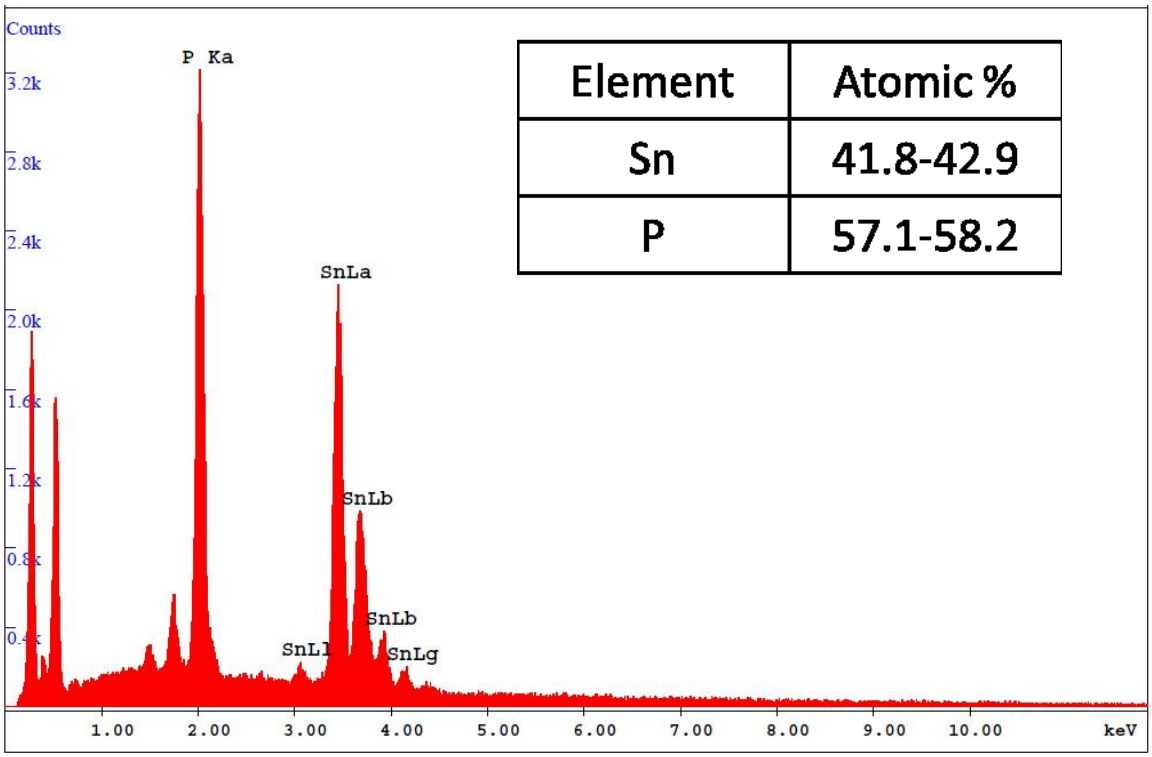


Figure S12. (A-B) HRTEM images of trigonal Sn_3P_4 NPs synthesized at 100 °C for 3 min using SnI_4 and $(TMSi)_3P$ in OLA/OA/ODE in the presence of TBP. (C) SAED and (D) PXRD patterns of the corresponding sample along with ICDD-PDF overlay of trigonal Sn_3P_4 generated from crystal maker (black lines).[1]



Element	Atomic %
Sn	41.8-42.9
P	57.1-58.2

Figure S13. Representative SEM/EDS spectrum of trigonal Sn_3P_4 NPs synthesized in OLA/OA/ODE at 100 ºC with 4 mM TBP for 60 sec. The average Sn: P atomic ratio obtained from 5 individual measurements of the same sample are also shown.

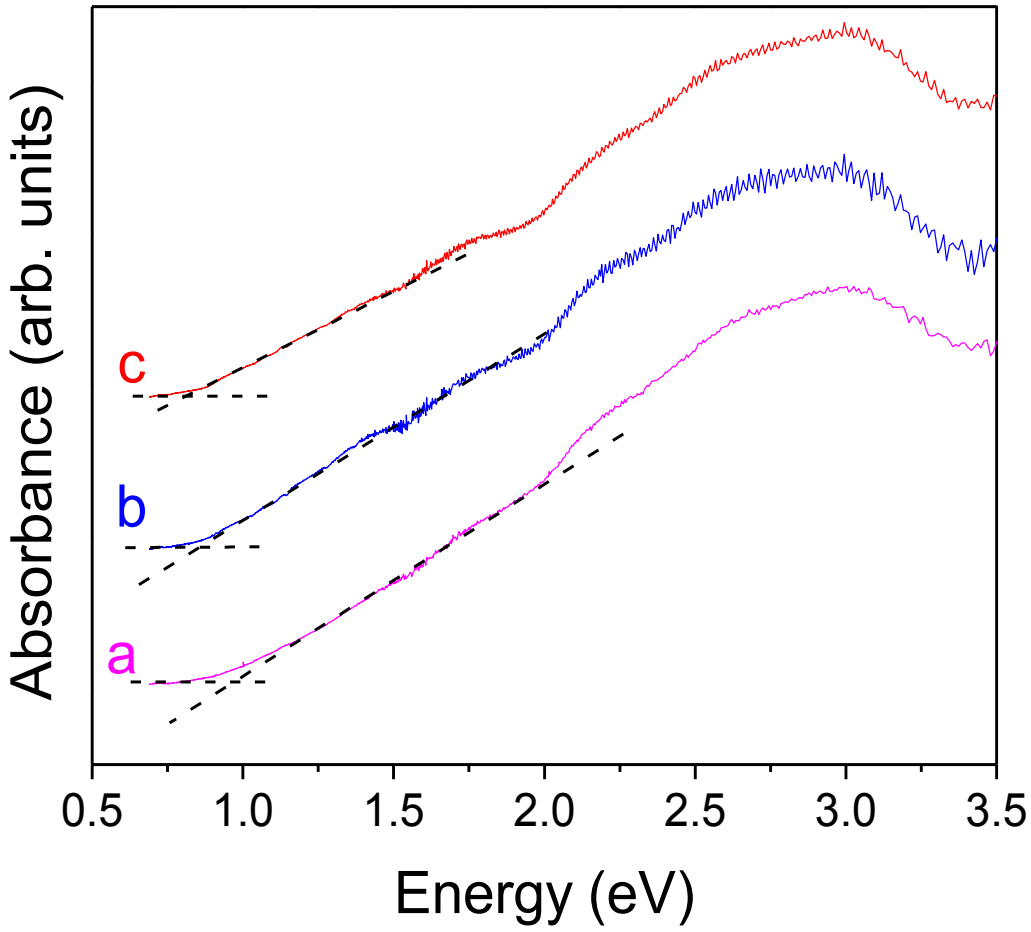


Figure S14. Diffuse reflectance spectra (converted to absorption using Kubelka-Munk remission function) of trigonal Sn_3P_4 NPs synthesized in OLA/OA/ODE without TBP at 100 ºC for (a) 1, (b) 2, and (c) 3 minutes.

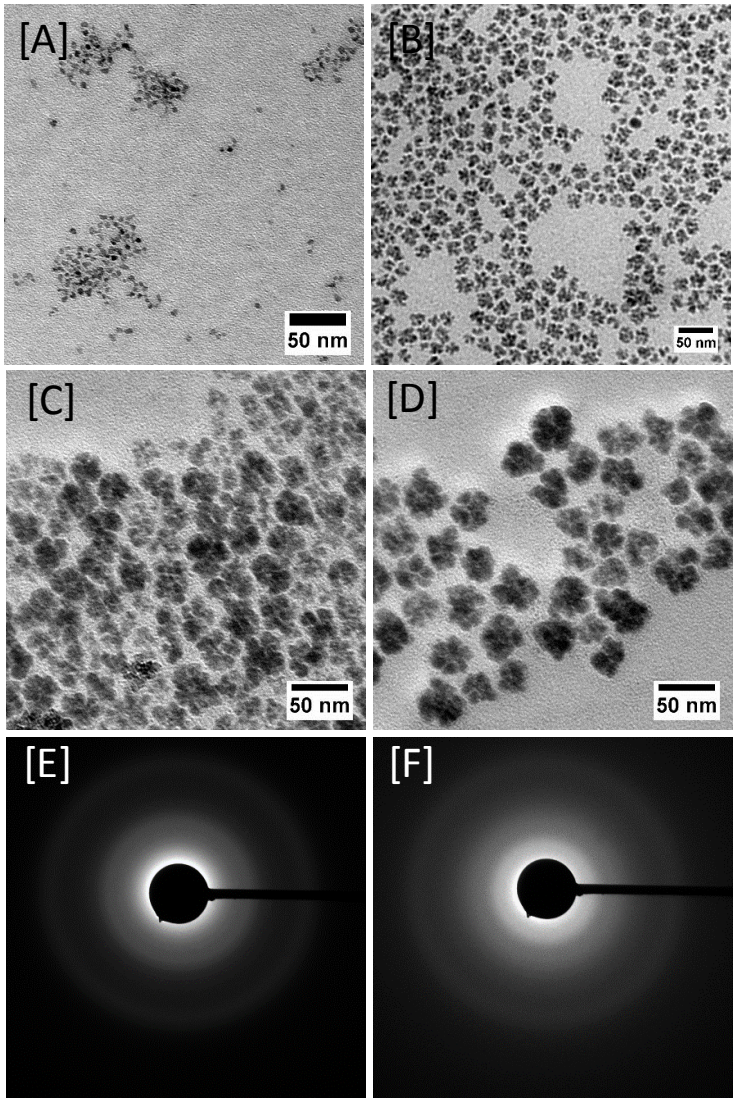


Figure S15. Representiavtive TEM images of trigonal Sn_3P_4 NPs synthesized in OLA/OA/ODE at 100 ºC without TBP for (A) 5 sec, (B) 1 min, (C) 2 min, and (D) 3 min. (E) and (F) are electron diffraction patterns of NPs shown in (C) and (D), respectively.

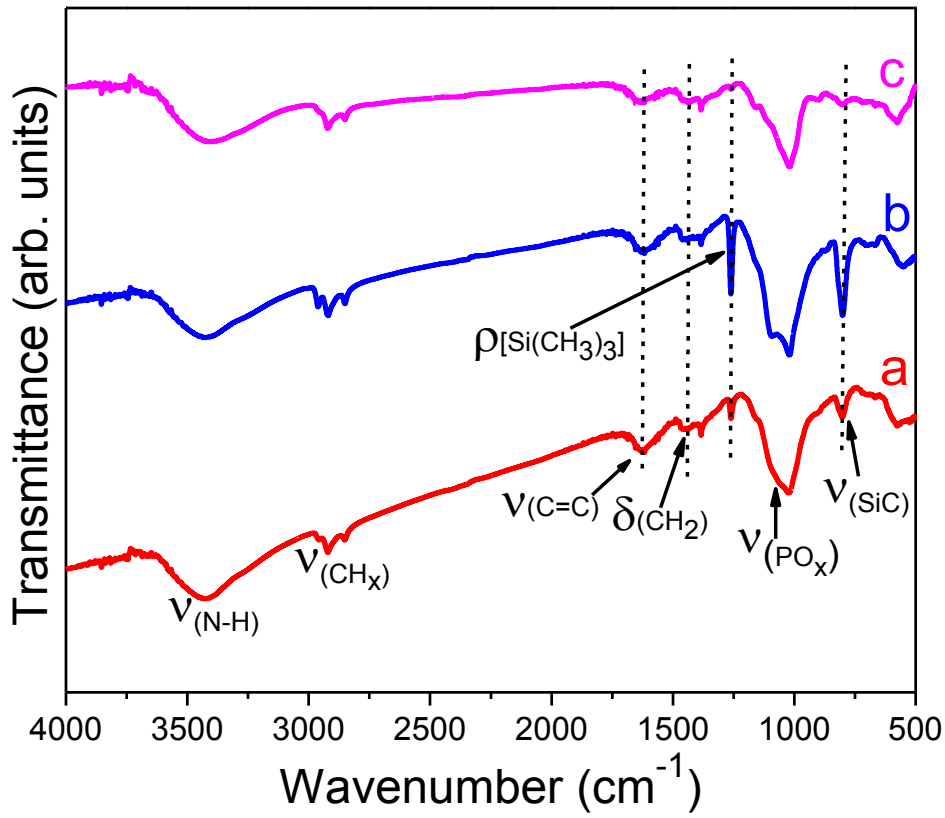


Figure S16. FT-IR spectra of tin phosphide NPs synthesized OLA/OA/ODE. (a) rhombohedral Sn_4P_3 NCs produced at 180 °C for 3 min, (b) hexagonal SnP NCs at 250 °C for 5 seconds, and (c) trigonal Sn_3P_4 NPs produced at 100 °C for 3 min.

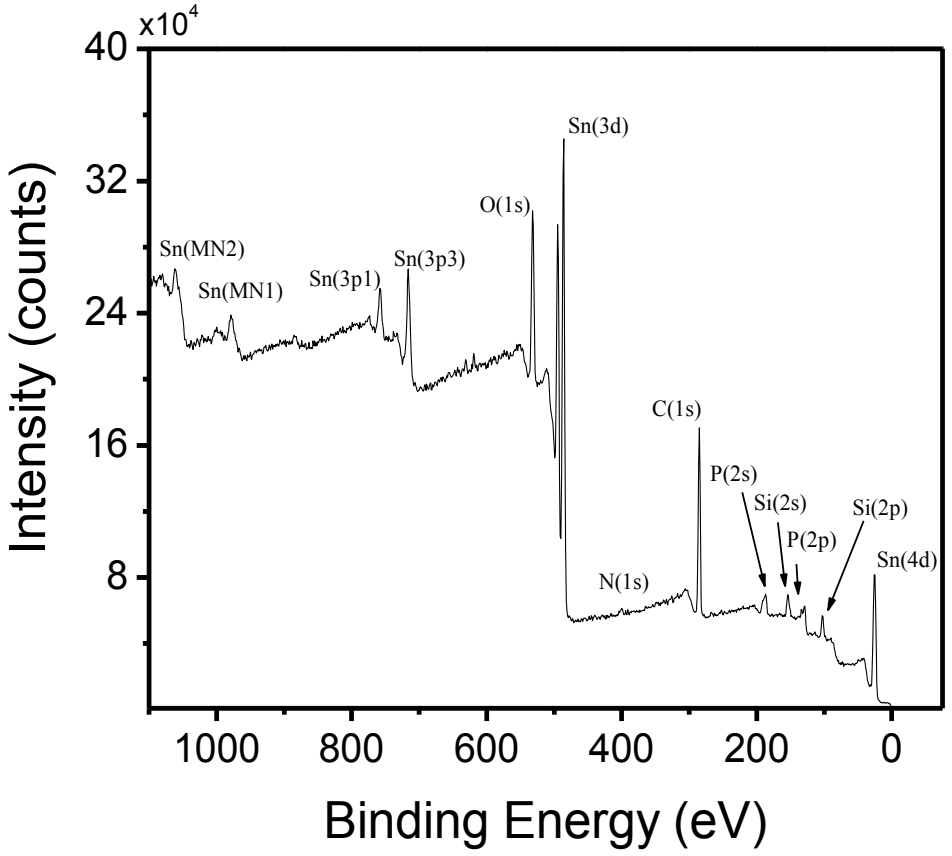


Figure S17. X-ray photoelectron spectrum (survey scan) of rhombohedral Sn_4P_3 NCs produced at 180 ºC for 3 min.

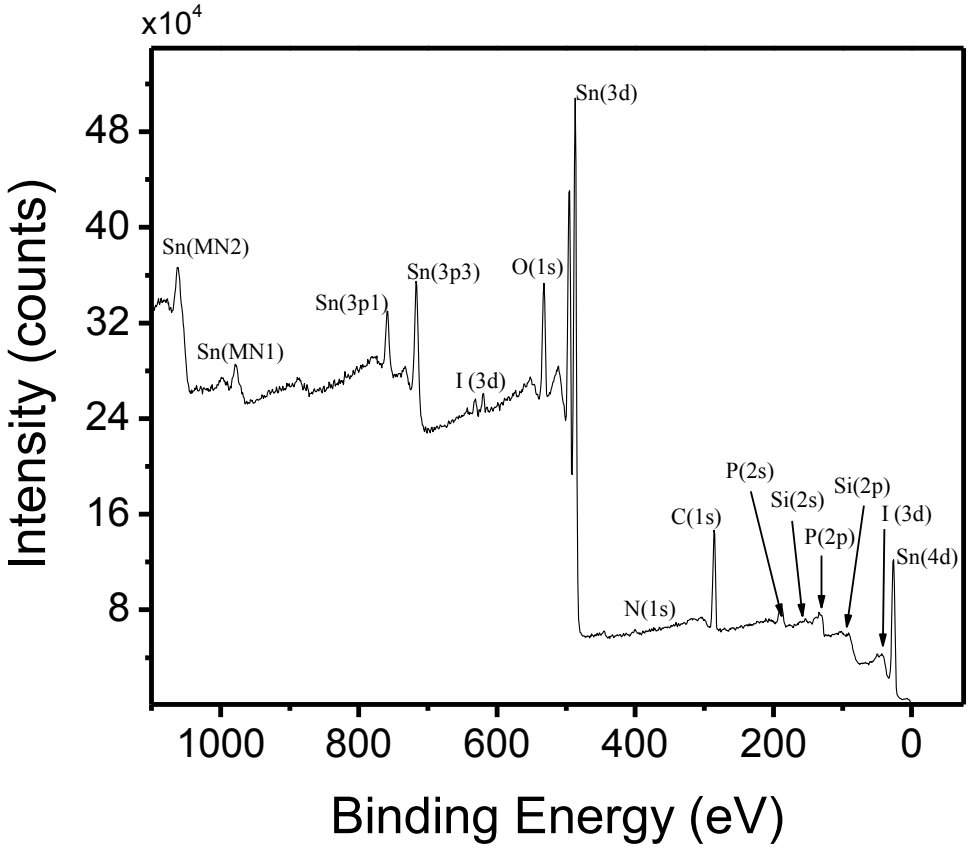


Figure S18. X-ray photoelectron spectrum (survey scan) of hexagonal SnP NCs produced at 250 °C for 5 seconds.

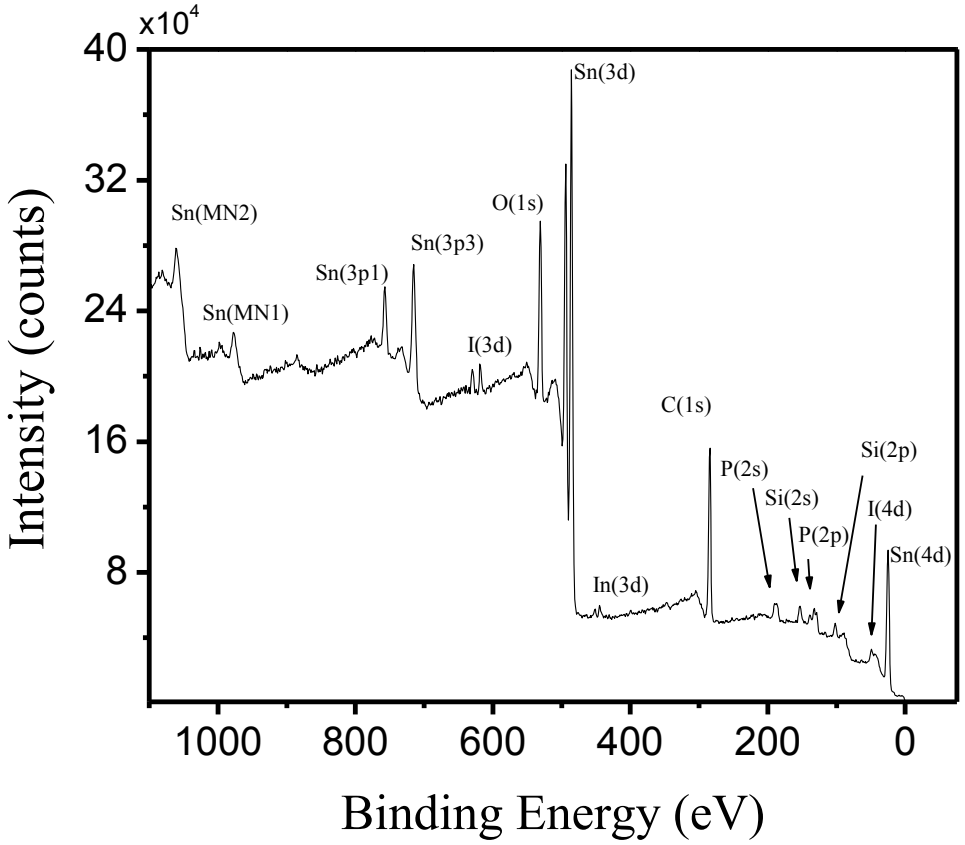


Figure S19. X-ray photoelectron spectrum (survey scan) of trigonal Sn_3P_4 NPs produced at 100 ºC for 3 min.

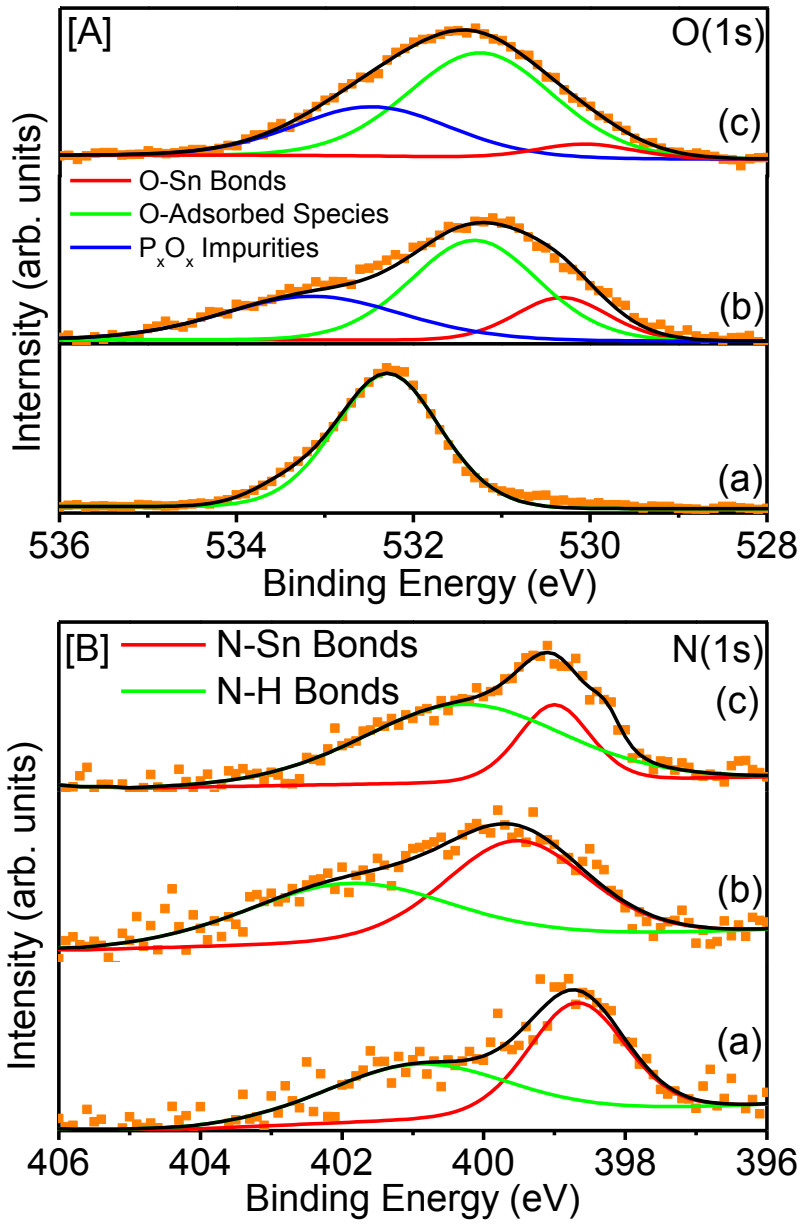


Figure S20. X-ray photoelectron spectra of (A) O(1s) and (B) N(1s) regions of (a) rhombohedral Sn_4P_3 NCs produced at 180 °C for 3 min., (b) hexagonal SnP NCs produced at 250 °C for 5 seconds, and (c) trigonal Sn_3P_4 NPs produced at 100 °C for 3 min.

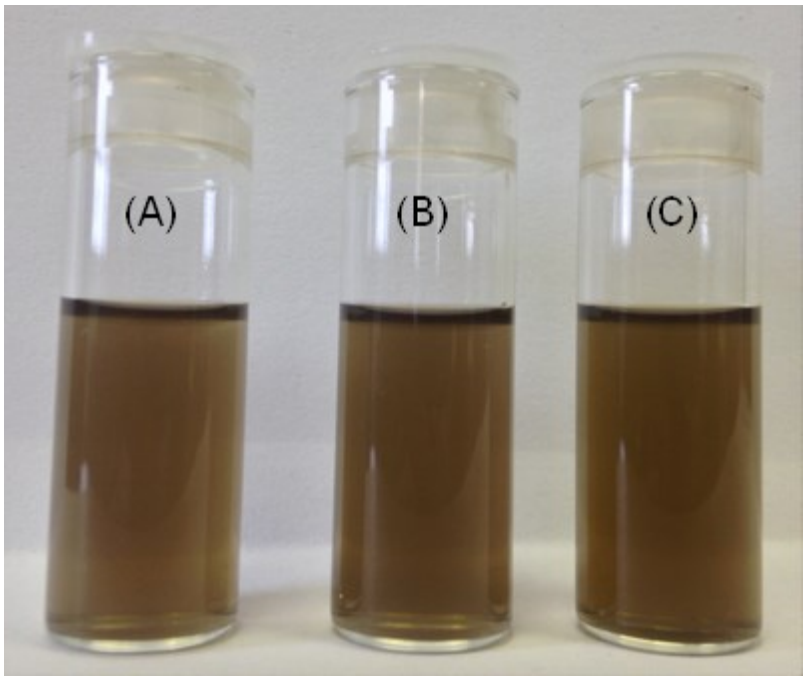


Figure S21. A photograph showing the colloidal stability of tin phosphide NPs in hexane. (A) trigonal Sn_3P_4 NPs synthesized at 100 °C, (B) rhombohedral Sn_4P_3 NCs synthesized at 180 °C, and (C) hexagonal SnP NCs synthesized at 250 °C.

References

(1) Ganesan, R.; Richter, K. W.; Schmetterer, C.; Effenberger, H.; Ipser, H. Synthesis of Single-Phase Sn_3P_4 by an Isopiestic Method. *Chem. Mater.* **2009**, *21*, 4108–4110.