

## Hydrogen Bonding-Assisted Self-Assembly: Monodisperse Hollow Nanoparticles Made Easy

Zaicheng Sun<sup>1</sup>, Feng Bai<sup>1</sup>, Huimeng Wu<sup>2</sup>, Samantha K. Schmitt<sup>1</sup>, Daniel M. Boye<sup>3</sup>, and Hongyou Fan<sup>1,2\*</sup>

<sup>1</sup>*The University of New Mexico/NSF Center for Micro-Engineered Materials, Chemical and Nuclear Engineering Department, Albuquerque, NM 87131, USA*

<sup>2</sup>*Sandia National Laboratories, Advanced Materials Lab, 1001 University Blvd. SE, Albuquerque, NM 87106, USA*

<sup>3</sup>*Physics Department, Davidson College, Davidson, NC 28035, USA*

*Correspondence and requests for materials should be addressed to H.F. (e-mail: [hfan@sandia.gov](mailto:hfan@sandia.gov)).*

**1. Synthesis of monodisperse hollow nanoparticles:** In general, 2 ml of 2-4wt% block copolymers (purchased from Polymer Source Inc.) in organic solvents such as dioxane, toluene, or mixture, etc. was added to 2 ml solutions containing varied amount of HBBA in same solvents. After stirring and heating, the nanoparticles were collected by centrifuging. For TEM and SEM characterization, samples were prepared by drop-casting of a small amount of solutions on TEM grids or Si wafer. For films, specimens were prepared by dip- or spin-coated on substrates such as Si wafer, microscope glass, and carbon films, etc. To synthesize hollow nanoparticles, HBBA were removed using an alcohol (methanol, ethanol, etc) wash.

**2. Characterizations:** SEM images were taken using a Hitachi 5200 FEG microscope. TEM was performed on a JEOL 2010 with 200kV acceleration voltage, equipped with a Gatan slow scan CCD camera. A surface acoustic wave (SAW) technique was used to characterize nitrogen sorption isotherms of hollow nanoparticle films. In a typical SAW device, an alternating voltage applied to an interdigital transducer on a piezoelectric substrate generates an alternating strain, which launches an acoustic wave. The samples of thin film for SAW measurement were deposited onto ST-cut quartz SAW substrates followed by carbonization as described above. The SAW devices (97 MHz) on ST-quartz with Ti-primed Au transducers were designed and fabricated at Sandia National Laboratories. An ASAP 2020 instrument was combined with the SAW device to control the relative pressure; while the SAW device was used to determine the resonant frequency. Mass change was monitored ( $\sim 80 \text{ pg cm}^{-2}$  sensitivity) as a function of relative pressure, assuming that the SAW frequency is only perturbed by mass loading variation.

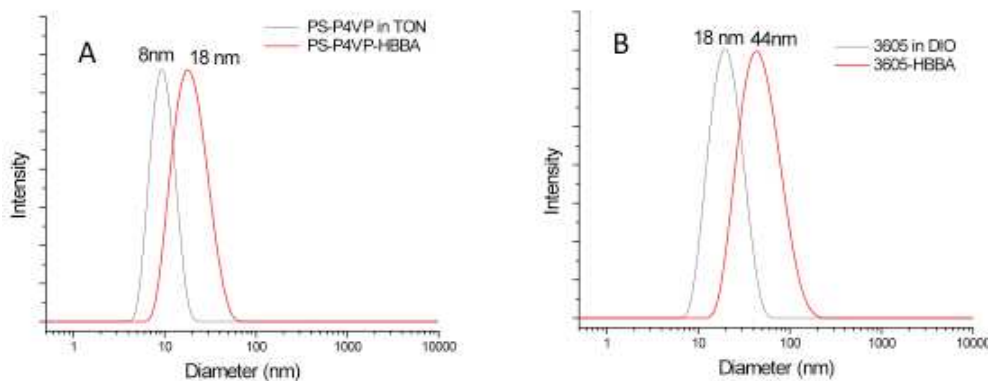


Figure S1. Dynamic light scattering results. A, PS<sub>12k</sub>-PVP<sub>11.8k</sub> in toluene (black) and after addition of HBBA (red). B, PS<sub>12k</sub>-PVP<sub>11.8k</sub> in dioxane and after addition of HBBA (red). Size increases after addition of HBBA in both cases clearly indicated the formation of PS<sub>12k</sub>-PVP<sub>11.8k</sub>/HBBA nanoparticles.

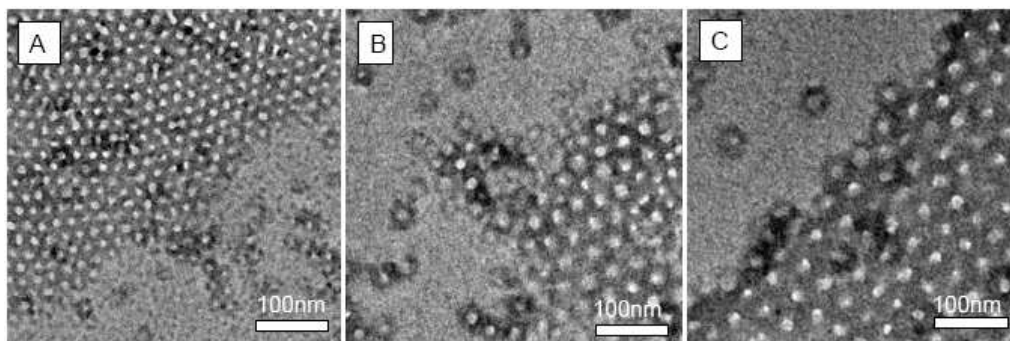


Figure S2. TEM images of hollow polymer nanoparticles with different hollow cavity sizes controlled by PVP chain size. A, monodisperse hollow nanoparticles prepared using 2wt % PS<sub>12k</sub>-PVP<sub>11.8k</sub> and 2wt % HBBA,  $D_h \sim 10\text{nm}$ ,  $D_s \sim 7\text{nm}$ . B, monodisperse hollow nanoparticles prepared using 2wt % PS<sub>20K</sub>-PVP<sub>19k</sub> and 2wt % HBBA,  $D_h \sim 14\text{nm}$ ,  $D_s \sim 10\text{nm}$ . C, monodisperse hollow nanoparticles prepared using 2wt % PS<sub>19.9k</sub>-PVP<sub>29.4k</sub> and 2wt % HBBA,  $D_h \sim 20\text{nm}$ ,  $D_s \sim 11\text{nm}$ .

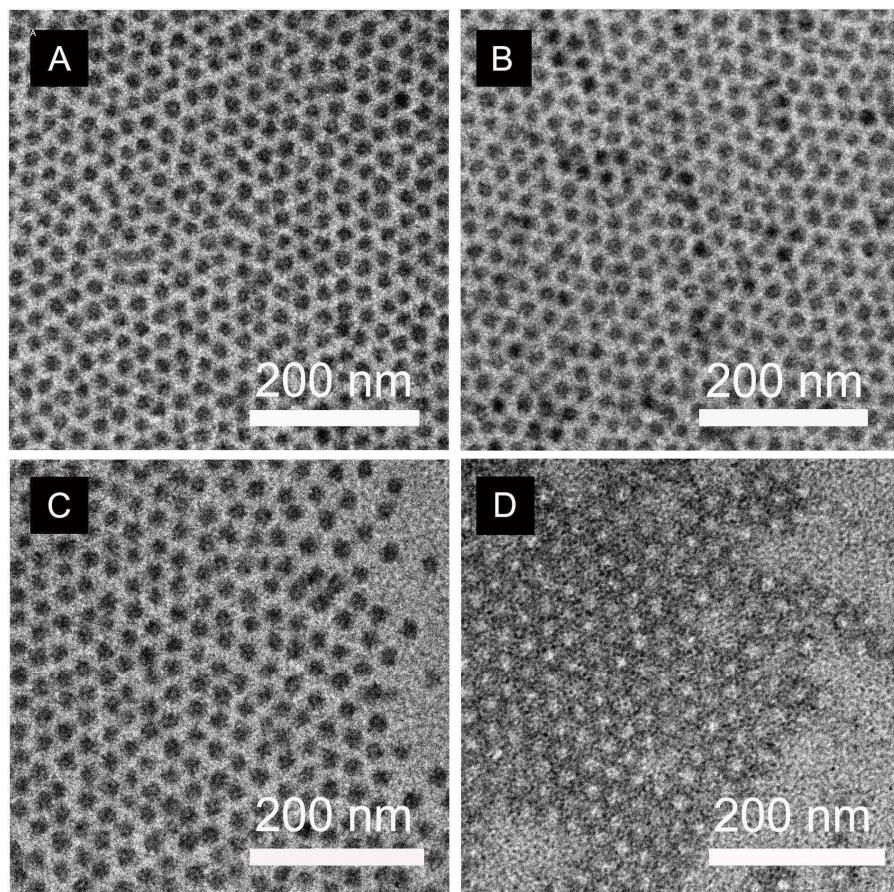


Figure S3. TEM images of hollow polymer nanoparticles with different hollow cavity sizes controlled by HBBA concentration. A, monodisperse hollow nanoparticles prepared using 2wt % PS<sub>19.9k</sub>-PVP<sub>29.4k</sub> and 10mg HBBA before alcohol wash. B, nanoparticle in A after alcohol wash. C, monodisperse hollow nanoparticles prepared using 2wt % PS<sub>19.9k</sub>-PVP<sub>29.4k</sub> and 20mg HBBA. D, nanoparticles in C after alcohol wash. In comparison with the TEM image of nanoparticle prepared with less HBBA (C), TEM image show clearly the hollow cavity when more HBBA added.

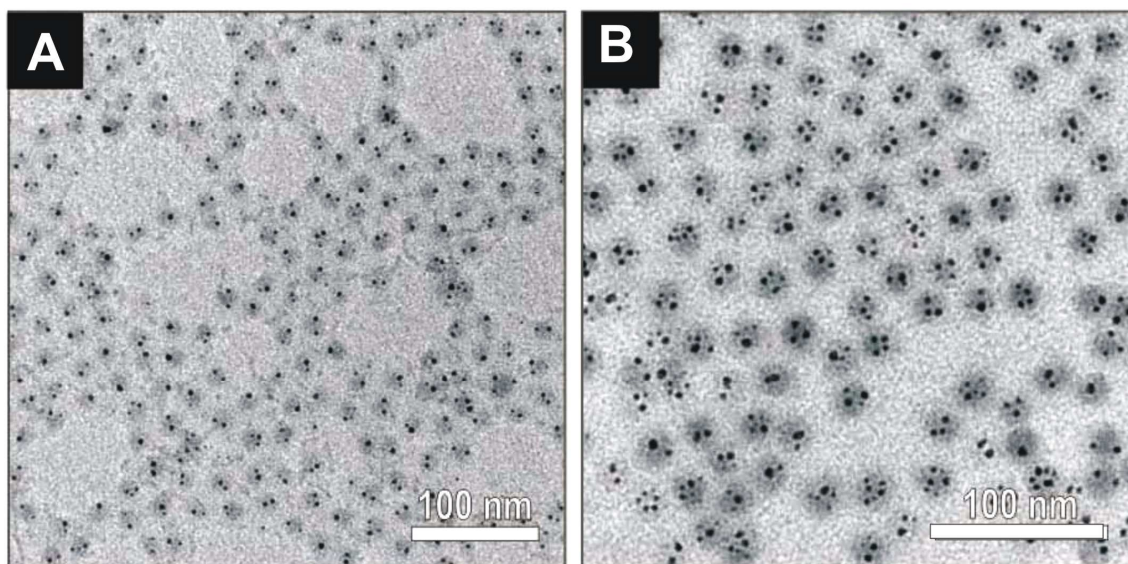


Figure S4. A, representative TEM image of hybrid nanoparticles that were prepared using PS<sub>21k</sub>-PVP<sub>8k</sub> and titanium (IV) tert-butoxide (TBO). B, representative TEM image of hybrid nanoparticles that were prepared using PS<sub>23k</sub>-PVP<sub>16k</sub> and TBO. TEM images show the hybrid nanoparticles with an average diameter of 20-nm. The hybrid nanoparticles were prepared using larger PVP chain show more TiO<sub>2</sub> nanoparticles loading than those prepared using smaller PVP chain. This is because a larger PVP chain provides more reactive sites (-N=) for nucleation and growth than a smaller PVP chain.



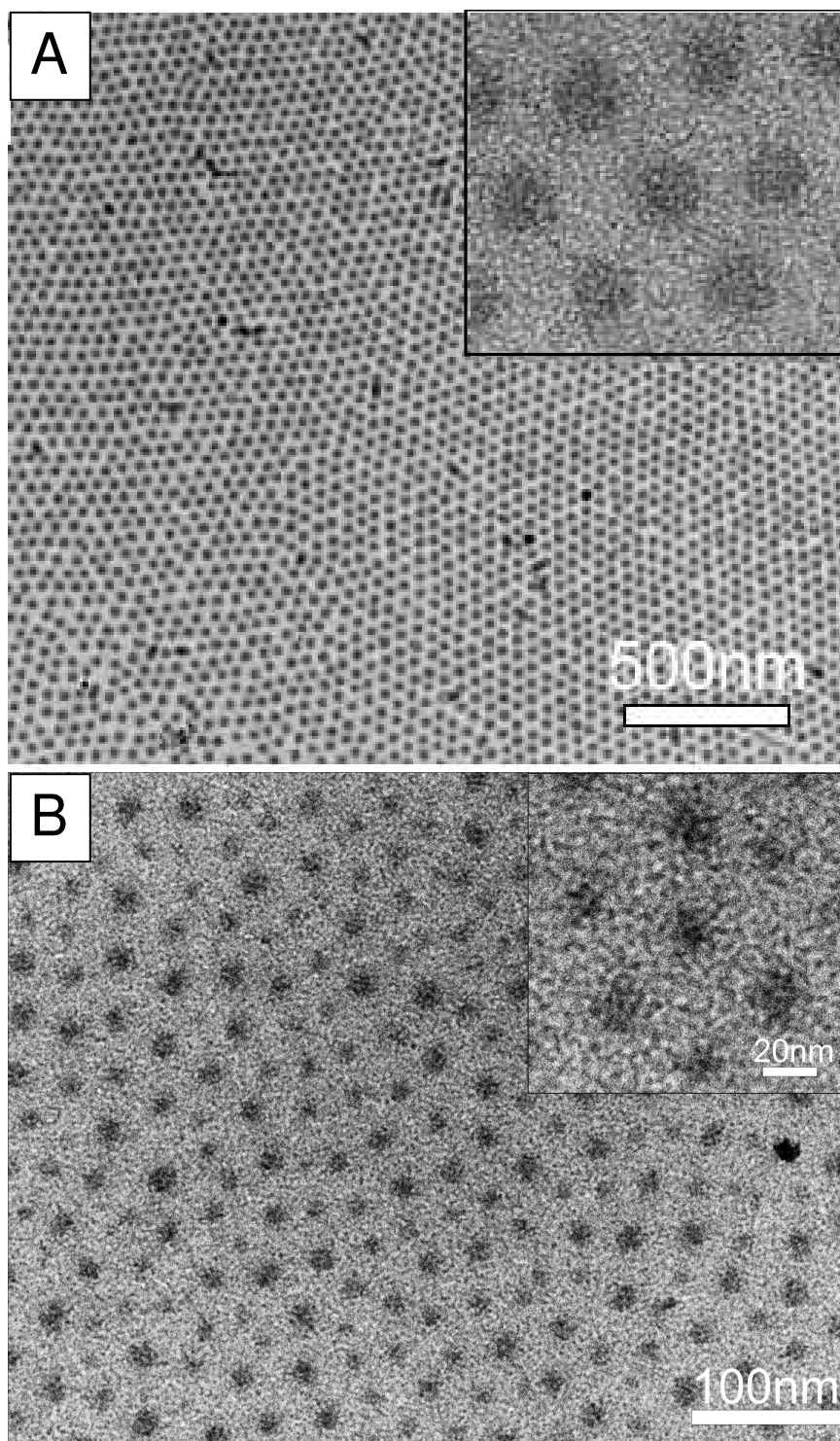


Figure S5. TEM images of spherical polymer nanoparticle containing SiO<sub>2</sub> nanoparticles (A) prepared using PS<sub>19.9k</sub>-PVP<sub>29.4k</sub> and tetraethyl orthosilicate and WO<sub>3</sub> (B) prepared using PS<sub>122k</sub>-PVP<sub>22k</sub> and tungsten isopropoxide. The average polymer particle size is 30-nm. Inset TEM images highlight one silica/polymer and WO<sub>3</sub>/polymer composite nanoparticles.

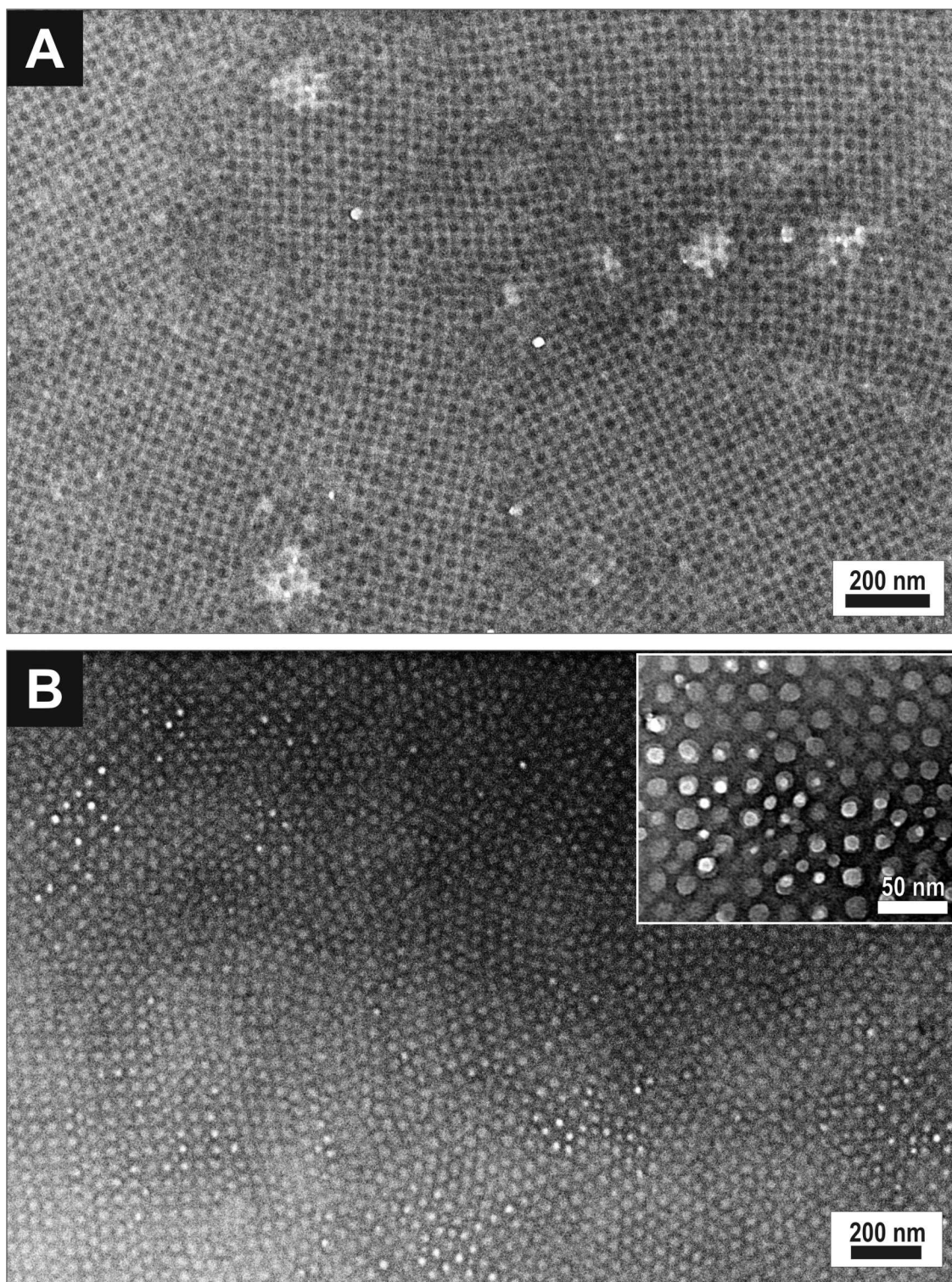


Figure S6. TEM images of 3-dimensionally ordered arrays of polymer nanoparticles before (A) and after removal of HBBA (B). Inset, TEM image highlights part of the image in B to show the hollow nature of the nanoparticle within the 3D arrays.