doi:10.1017/S1431927618001976
Microsc. Microanal. 24 (Suppl 1), 2018

Observation of PbTe Nanorod Formation Using *in situ* Liquid Cell TEM

Nabraj Bhattarai[1,2], Danielle L. Woodall [1,2], Janice E. Boercker[2] and Todd H. Brintlinger[2]

[1.] NRC Postdoctoral Associate, U.S. Naval Research Laboratory, Washington, DC.
[2.] U.S. Naval Research Laboratory, Washington, DC.

PbTe nanoparticles (NPs) are candidates for photovoltaic applications because of high quantum efficiencies, and their capacity for multiple exciton generation (MEG) [1]. Furthermore, the MEG efficiency can be enhanced even further using high aspect ratio particles such as nanorods (NRs) [2]. The challenge in fully exploiting these properties is in controlling the colloidal synthesis of large quantities of NPs/NRs with the desired composition and morphology, which requires a clear understanding of growth mechanisms. For PbTe NR formation, it is not clearly understood whether rods form from a seeded growth, axial growth, or oriented attachments. The driving factors, such as particle size, ligand effects, dipole interactions, solvent, *etc.*, for NR growth thus need to be thoroughly investigated [3].

The use of *in situ* liquid cell transmission electron microscopy (LCTEM) provides direct visualization during the nucleation and growth of particles, as it happens, in their native state [4]. In this report, we employ *in situ* LCTEM to investigate the formation and growth of PbTe NRs. The LCTEM was carried out using a commercial electrochemical single-port liquid cell system (Protochips Inc, Poseidon P500) in a JEOL JEM2200FS equipped with Gatan One View camera. Previously synthesized PbTe single crystal NPs were deposited onto a 'microwell chip' (with regions of silicon nitride that are especially, thin, 5-10 nm, to reduce background signal) by drop casting a 0.5 µL suspension of NP-loaded toluene.

Figure 1 shows the bright field (BF) TEM images for oleic acid (OA) capped PbTe NPs obtained from 'static' LCTEM (in which there is no flow) using electron dose rates of 100 $e^-/Å^2/sec$. The particles are monodispersed, approximately 7 nm in diameter and separated by 4 nm (Figure 1a). The particles start to come closer and then form structures, typically by fusing two particles, which we deem nanorods due to their increased aspect ratio, as shown by colored circles in figures 1b-d. For longer exposure of the particles, the radiolysis affects the particles dynamics, so both electron dose rates and cumulative electron dose need to be taken into consideration. In another experiment, OA capped PbTe NPs are dispersed in toluene mixed with diethylamines and the resulting structures are presented in Figure 2. Figure 2a and b show low magnification TEM images showing the presence of both isolated NPs and rod-like structures. The higher aspect ratio structures' lengths vary from 12 nm to 22 nm with diameters from 4 to 5 nm. Figure 2c shows the presence of the high aspect ratio structures or NRs absent the co-location of the original NPs. Here, the NRs are likely individual PbTe crystals, albeit with a smaller diameter than the original NPs. Also, these structures form *previous* to electron beam exposure and only form while in the LCTEM 'sandwich', not when they are simply drop cast onto a single silicon nitride membrane [5].

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[5] The authors acknowledge funding from the Office of Naval Research (Naval Research Laboratory Basic Research Program). This research was performed while N.B. and D.L.W. held National Research Council Research Associate Award at the U.S. Naval Research Laboratory.

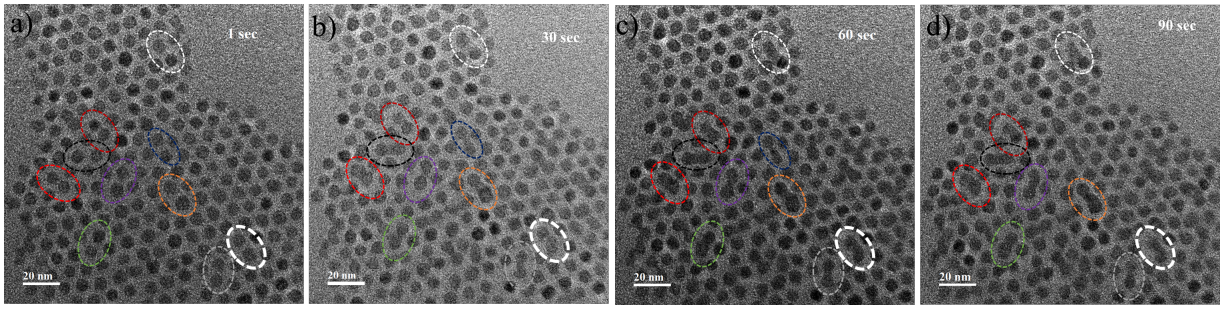

Figure 1. BF TEM images of PbTe NPs capped with oleic acid as seen under electron dose rate of 100 $e^-/Å^2$/sec during in situ liquid cell TEM experiment. The time span during imaging is inserted on each frame. In the beginning, as seen for 1 sec case, the particles are well dispersed with size ~7 nm and separated by ~4 nm. The particles come closer and form longer NR fusing 2 particles as shown by circles with different colors (a-d).

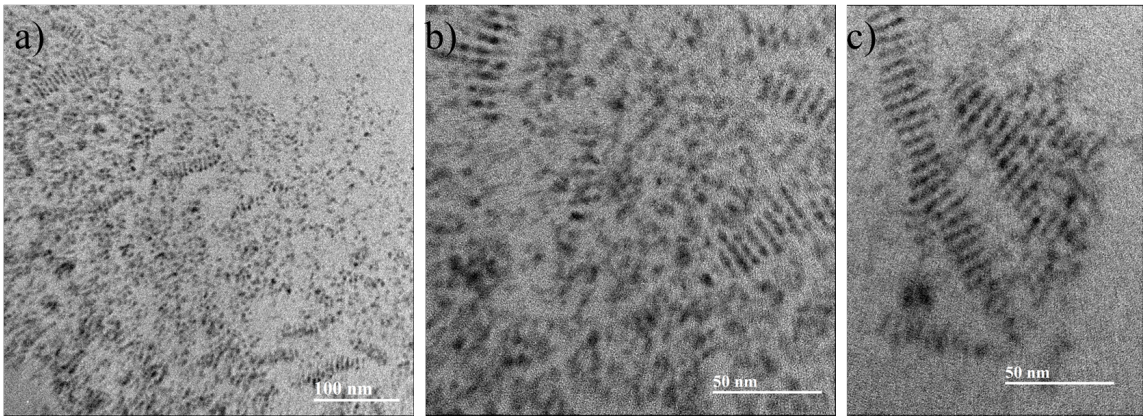

Figure 2. BF TEM images in liquid showing the formation of NRs for diethylamine capped NPs. a) and b) Low mag TEM images showing the presence of both particles and longer chains or NRs. c) TEM image showing the NRs sizes ranging from 12 to 22 nm.

https://doi.org/10.1017/S1431927618001976 Published online by Cambridge University Press