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In Situ Characterization of ZnO Quantum Dots in Solution: Aggregation and Brownian Motion

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Innovation in novel devices based upon semiconductor "quantum dot" (QD) nanotechnology have benefitted from fairly simple and cost-effective means of QD production. These are the wet chemical approaches collectively referred to as the sol-gel process. With an ample and relatively inexpensive supply of QD's, and the ability to tailor the size of the quantum dots in the manufacturing, advances in device design have been achieved. In particular, ZnO nanomaterials have become increasingly prominent in three main areas: (*i*) the energy sector, (*ii*) information and communication technology applications and (*iii*) life sciences as attractive candidates for future medical sciences nanotechnology markets [1].

Electron microscopy characterization of ZnO QD's has traditionally been performed by examining dried samples supported on some form of film, typically carbon or in some cases thin silicon nitride windows. In this study we report on both, the dried *ex situ* imaging in the SEM as well as the *in-situ* STEM examination of the particles while still dispersed in the ethanolic growth media. The ZnO QD's were prepared according to the well-known procedure [2]. For the SEM study, a drop of an ethanolic 0.1 M solution was placed on a Si chip and allowed to dry before inserting into a Zeiss Merlin FEG-SEM for examination. To study their behavior in the liquid growth media, a few drops of the same nanocolloid were loaded into the Protochips Poseidon P210 liquid cell holder and examined in STEM mode using the high angle annular dark-field (HAADF) detector in an FEI Talos F200X analytical TEM at 200 kV.

Typical results from the dried ZnO *ex situ* SEM images are shown in Figure 1. The images indicate an average particle diameter of approximately 5 nm, with different levels of aggregation. Near the periphery of the dried spot, single particles can be observed along with aggregates composed of a few to up to 100 particles forming chain-like assemblies. Within the interior of the dried droplet, extensive agglomeration is observed (not shown). However, when examined *in situ* in the liquid cell holder, such large aggregates were not as prominent, and thus it is likely that they form as a result of the drying process. This is also supported by the fact that the nanocolloids are optically transparent with negligible scattering, thus without significant aggregation. Taking the average particle size of 5 nm and the colloid molarity of 0.1 M, one can calculate the mean interparticle distance to be approximately 30-40 nm. Figure 2 shows a typical example of how these particles behave in solution. Figures 2a and 2b are HAADF STEM images taken approximately 32 seconds apart, and Figure 3c is a composite image displaying Figure 2a as the red channel, and Figure 2b as the green channel. The ZnO particles that remained stationary during this time period are thus depicted by yellow. The larger aggregates, in this case up to about 10 particles, tend to remain more stationary whereas we observe very rapid movement of some, but not all, of the single particles.

The results of the liquid *in situ* TEM study are extremely promising, and will be extended to further explore the effects of small amounts of water and other surface capping agents on aggregation and

Brownian motion of the QD's.

References:

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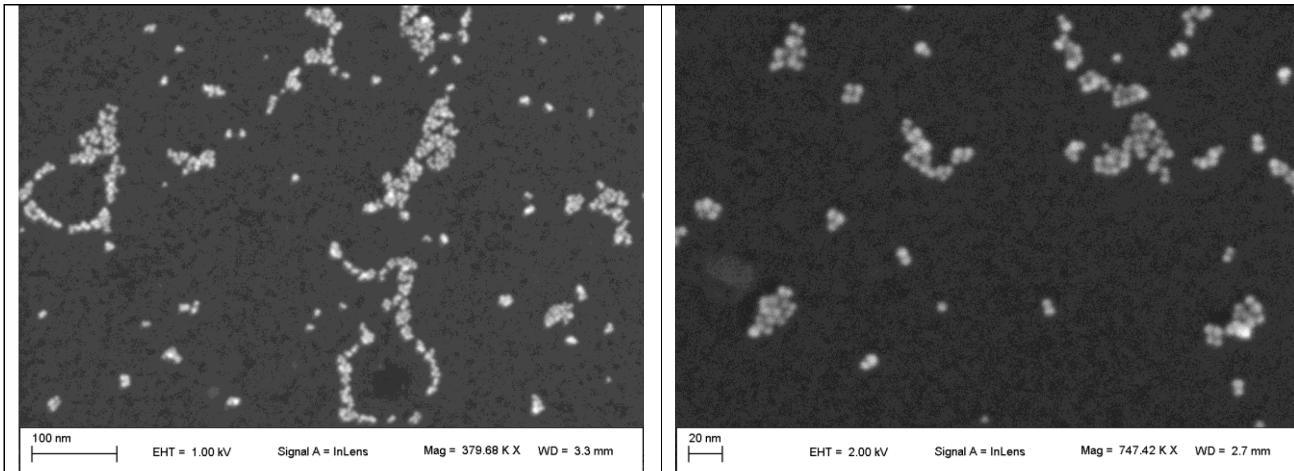
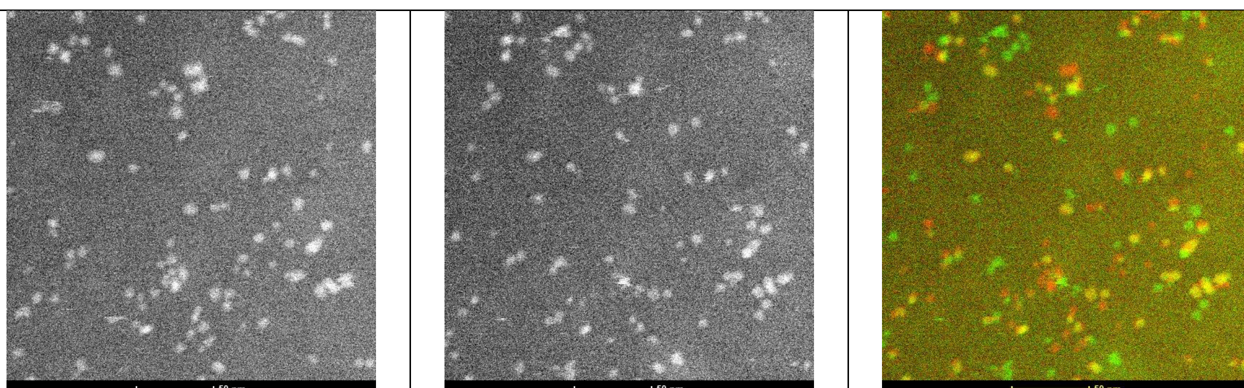


(a) (b)

Figure 1. (a) Secondary electron (SE) image of dried ZnO particles. Accelerating voltage is 1 kV. (b) SE image of dried ZnO particles. Accelerating voltage is 2 kV.



(a) **(b)** **(c)**

Figure 2. HAADF STEM images of ZnO quantum dots in ethanolic growth solution. Figures 2a and 2b were acquired as part of a video whose frames are approximately 8 seconds apart. Figure 2c is a composite image of 2a and 2b, where 2a is shown as red, 2b shown as green and hence any particles that have not moved are displayed as yellow. Note that many of the yellow particles are larger clusters, but this is not always the case. Some single particles have not moved, while others have moved in and out of the field of view.

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