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Growth of sphere- and tetrapod-shaped Cd(Cu)Se nanocrystals from $Cu(C_{17}H_{35}COO)_2$ and $Cu_4(PPh_3)_4(\mu_3\text{-}I)_4$

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Spherical cadmium selenide quantum dots doped with copper up to 1 at.% are synthesized with a novel method from cadmium oleate, trioctylphosphine selenide and copper stearate. An alternative precursor, $Cu_4I_4(PPh_3)_4$ cluster, allows the incorporation of a larger number of Cu atoms per nanocrystal to proceed, which leads to the growth of Cd(Cu)Se tetrapods.

Colloidal quantum dots (QDs) are surface-stabilized semiconductor nanocrystals with a sufficiently small size to exhibit quantum size effect. Bright photoluminescence (PL) of the particles is an interesting property allowing one to use them in bioimaging.[1] Synthesis of oleate-capped quantum dots is possible using safe and simple methods.[2,3] Intentional doping of semiconductor nanoparticles with *d* metals is of great interest as it allows one to further modify QDs properties. For example, non-excitonic luminescence from impurity levels can lie in near-IR region and have the lifetime in a microsecond range, which improves contrast in bioimaging. Another example is the control of carrier concentrations in QD films and solids for use in nanoelectronics.[4] From that point of view, copper is an interesting dopant. Bulk cadmium chalcogenides activated with copper are long used as luminophors and in photovoltaics.[5] Copper introduces several levels in the CdSe band gap and can act as acceptor with an energy of 0.5 eV below conduction band minimum when substituting cadmium.[6] Cadmium chalcogenide nanoparticles doped with Cu were investigated in CdS water colloids.[7] Addition of Cu salts leads to quenching of excitonic PL and appearance of new bands in the red region. The first synthesis of monodisperse copper-doped CdSe QDs with long-chain amine was described.[8] Spherical 4 nm nanocrystals with Cu^I contents of up to 15% were obtained. The absence of excitonic PL and intense PL around 800 nm, attributed to both surface defects and copper(I) level was noted.

In this study, Cd(Cu)Se was synthesized by a slightly modified method:[3] 500 μmol of cadmium oleate and trioctylphosphine selenide were mixed at 230 °C in a non-coordinating solvent (diphenyl ether or hexadecane) and QDs are allowed to grow for 5 min. Copper was introduced as 1–50 μmol of copper stearate or with 3–50 μmol of an alternative precursor, $Cu_4(PPh_3)_4(\mu_3\text{-}I)_4$ synthesized according to a published procedure.[9] Detailed procedure and typical properties for the synthesis from copper stearate are given elsewhere.[10] Here, we synthesized Cd(Cu)Se quantum dots with copper up to 1 at.% and mean size of ~3.3 nm. Their size distribution ~10% determined from TEM images [Figure 1(*a*), shot on LEO912 AB OMEGA] is consistent with absorption spectra; their shape is spherical. Poisson distribution adequately describes excitonic PL variations with added copper stearate amount. Distribution coefficient *k*, calculated with the Poisson model, is consistent with experimental one obtained from energy dispersive X-ray fluorescence analysis (EDXRF) on KL2,3 Cu and Se lines. It is found to be ~20, which means most of copper stearate remains unreacted, probably due to formation of Cu complexes with phosphines.[12] The most interesting property of the samples obtained is the intense (QY up to 5–10%) copper-related IR emission at 700–900 nm. Time-resolved measurements[10] showed a 0.5–1 μs lifetime; thus, Cd(Cu)Se are perspective for use in biotags.

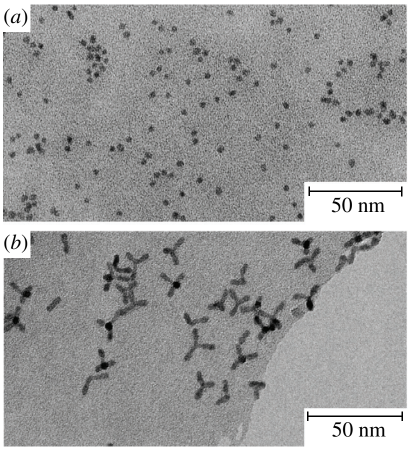

Figure 1 (*a*) TEM image of a Cd(Cu)Se sample synthesized from $Cu(C_{17}H_{35}COO)_2$; (*b*) Cd(Cu)Se sample from $Cu_4I_4(PPh_3)_4$. Average arm length, 9 nm; diameters, 2.4 to 3.5 nm.

Usage of alternative tetranuclear cuprous iodide cluster allows us to achieve higher doping levels. Excitonic PL is visible when small amounts of clusters (1–5 μmol) are used; PL variations similarly follow Poisson statistics. Distribution coefficient *k* for all samples is 1.5–4. Compared to simple stearate synthesis, amount of incorporated copper is 5–15 times higher with the same quantity of copper precursor. This is attributed to a higher number of Cu atoms (4 *vs.* 1) in precursor molecule; PPh_3 ligand weaker coordination also could be the reason. The addition of larger amounts of cluster should lead to higher doping levels.

Surprisingly, it also leads to tetrapod formation. An example is given in Figure 1(*b*). The sample is synthesized from $Cu_4I_4(PPh_3)_4$ (50 μmol) and shows near-IR PL at 820 nm. The sample has absorption features similar to undoped samples. No excitonic PL is observable; thus, we assume that all particles are doped. The copper content is 1 at.%, but when the shape of the particles is considered, we can estimate the number of copper atoms at ~80 per particle (assuming

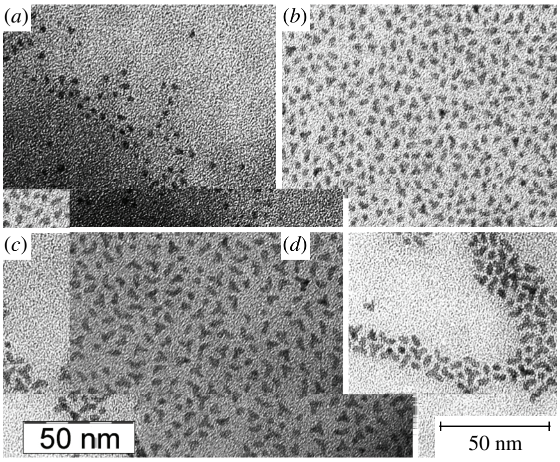

Figure 2 TEM images of the samples taken during growth at (*a*) 5 s, (*b*) 20 s, (*c*) 1 min and (*d*) 5 min.

that all particles are tetrapod-shaped and each arm has ~2000 atoms, given its average length and diameter). When smaller amounts of copper cluster are used, the arm length of particles decreases until particles could be considered spheres: the addition of 10 μmol leads to 4.5 at.% and about 20 atoms per particle, but their form is still tetrapods with shorter arms; 1–5 μmol of cluster lead to particles with shape undistinguishable from spheres.

Why the change in copper precursor leads to tetrapod formation? We have excluded possible change in growing conditions due to another ligand (PPh_3) presence by conducting synthesis with it and copper stearate. It showed no difference with our previous stearate experiments in shape, optical properties and copper doping levels. EDXRF shows iodine absence from tetrapod samples. To investigate the growth, we have taken samples at various time intervals in the synthesis with 25 μmol. TEM images and spectra are presented in Figures 2 and 3.

Copper is present in all growing particles from the beginning, as seen in Figure 3. However, their shape is near spherical even at 20 s, only then the arm growth starts. The first explanation for tetrapod growth would be presence of growing zinc-blende particles and availability of 111 faces, forming a good starting point for wurtzitic arms;[13] copper can stabilize zinc-blende structure of particles.[8] XRD clearly shows <111>, <220>, <311> zinc-blende reflexes and absence of wurtzite ones in all our pure CdSe and low-doped samples. Nevertheless, these samples are spherical. The second explanation is the influence of saturation and decreased number of nuclei during growth in the presence of copper precursor.[14] Indeed, in CdSe growth experiments at low temperature (120–150 °C) we observe formation of lower number of particles and growth of tetrapods. At 160 °C and higher, the particles grow into spheres in all cases. If the copper addition decreases number of particles at the nucleation phase, thus increasing supersaturation, this would explain the tetrapod growth.[14] We measured the concentrations of nuclei in the reaction media. We assume that incorporated Cu does not significantly change extinction coefficients or at least lower them. We also do not calculate number of particles at 1 and 5 min, since the extinction coefficients should differ for tetrapods (see Figure 2). At 5 s for CdSe and Cd(Cu)Se synthesis the numbers of particles are $(1.6\pm0.25)\times10^{17}$ and $(1.35\pm0.2)\times10^{17}$, respectively; at 20 s, $(1.9\pm0.3)\times10^{17}$ and $(1.8\pm0.25)\times10^{17}$.[11] The numbers are nearly equal, so the model[14] is not applicable to our case.

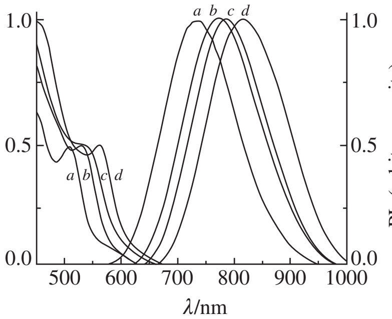

Figure 3 Normalized absorption and photoluminescence spectra corresponding to samples from Figure 2.

We propose that increased doping levels lead to change of CdSe growth rate on several faces, whether this is so by adsorption of Cu on the surface or by other means when Cu is inside growing particle. We have performed a few experiments to test this hypothesis. For example, it is possible, though hard, to obtain tetrapods under conditions with a large excess of copper stearate. Another example would be anomalous growth of CdSe layers over Cd(Cu)Se dots that leads to multipods, not spheres.

In summary, we synthesized spherical Cd(Cu)Se quantum dots from cadmium oleate and copper stearate with doping levels up to 1 at.%. When the copper precursor is replaced with tetranuclear cuprous iodide cluster, larger doping levels are easily achieved and the nanoparticles grow into tetrapod shape. We attribute this to the increased copper content of the growing particles, which can change the growth conditions of several facets. Other tetrapod growth models are shown inapplicable.

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