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The Room-Temperature Synthesis of Anisotropic CdHgTe Quantum Dot Alloys: A "Molecular Welding" Effect

Shohei Taniguchi,[†] Mark Green,[*,†] and Teck Lim[‡]

[†]Department of Physics, King's College London, The Strand, London WC2R 2LS, U.K.

[‡]Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.

Supporting Information

ABSTRACT: The room-temperature chemical transformation of spherical CdTe nanoparticles into anisotropic alloyed CdHgTe particles using mercury bromide in a toluene/methanol system at room temperature has been investigated. The resulting materials readily dissolved in toluene and exhibited a significant red-shift in the optical properties toward the infrared region. Structural transformations were observed, with electron microscopy showing that the CdTe nanoparticles were chemically attached ('welded') to other CdTe nanoparticles, creating highly complex anisotropic heterostructures which also incorporated mercury.

The synthesis of anisotropic quantum dot structures demonstrates the high level of control now available using solution-based chemical precursors.[1] Usually, the correct choice of materials (allowing growth down a specific crystal axis) and conditions (high reaction temperatures resulting in 'kinetic overdrive') yields highly desirable structures with a wide range of novel optoelectronic properties that can be exploited in applications such as solar energy conversion.[2] Other notable synthetic procedures also exist, such as the oriented attachment of PbSe particles to produce a variety of highly structured engineered nanowires.[3,4]

Similarly, postsynthetic chemical modifications of nanocrystals are becoming increasingly important as such reactions provide routes to materials exhibiting various photo/electronic characteristics in addition to opening new chemical strategies to complex morphologies which are inaccessible by conventional single-step colloidal procedures.[5] There have been several seminal reports in this field: the oriented attachment of TiO_2 nanocrystals under hydrothermal conditions,[6] the reaction of cobalt nanoparticles with chalcogens yielding hollow nanocrystals through the nanoscale Kirkendall effect,[7] and the single-step cation-exchange reaction which showed reversible transformation between CdSe and Ag_2Se nanoparticles.[8] Depending on nanoparticle morphology and optical properties, potential applications include catalysis,[9] sensors,[10] photovoltaics,[11] electronics, and photonics devices,[12,13] while the theoretical understanding of the nanoscale chemistry underlying these intriguing phenomena is essential.

In this communication, we report a room-temperature, rapid chemical transformation using CdTe quantum dots in toluene with mercury bromide to form wirelike CdHgTe nanostructures that exhibit a significantly red-shifted absorption profile not accessible by the simple growth of CdTe rods. We suggest that Hg^{2+} reacts with the CdTe nanoparticles, linking the preformed spherical particles in an analogous fashion to macroscale welding, which simultaneously incorporates the mercury, resulting in an alloyed structure. This differs from existing techniques described above as the formation of the anisotropic material occurs at room temperature, and the resulting structure appears to be a collection of individual CdTe quantum dots linked together, not through ligand attachment, but through a chemical reaction which formed a new solid-state material (CdHgTe) which retained the approximate width of the initial quantum dots and, hence, the term 'molecular welding'.

The desirable properties of postreaction-modified nanomaterials are clearly partly dependent on the characteristics of the parent material. For our study we have chosen CdTe nanocrystals, which are routinely prepared with a highly monodispersed size distribution and have tunable emission with high efficiencies and solubility in various solvents. Importantly, numerous examples of shape-controlled nanocrystal synthesis have been reported, and CdTe quantum dots are regarded as a standard tool for many wishing to explore novel structures[14,15] in part due to the small energy difference between polytypes.[16,17] Therefore, CdTe is an ideal candidate for studies into the postsynthetic chemical transformation of nanocrystals. There are several recent reports which describe the use of CdTe nanocrystals to create functional nanomaterials. Postsynthetic modification of thioglycolic acid-capped CdTe nanoparticles caused an aggregation of particles and produced wirelike structures.[18,19] Notably, the resulting one-dimensional (1D) semiconductor structure retained the original optical characteristics of the parent CdTe nanoparticles.

The basic procedure was inspired from the report describing the cation exchange reactions of quantum dots.[20] First, tetradecylphosphonic acid/hexadecylamine capped CdTe nanoparticles (4.5 ± 0.9 nm) in toluene were used as a starting material (Supporting Information and Figure 1a).[21] To a vigorously stirred $HgBr_2$ toluene/methanol solution, the CdTe nanoparticles solution was injected, causing an immediate precipitation with a change in color from yellow to brown. The resulting precipitate was collected by centrifugation and readily redispersed in toluene. From the transmission electron microscope (TEM) images, randomly directed 2D structures can be seen (Figure 1b). Most of the anisotropic particles were elongated or

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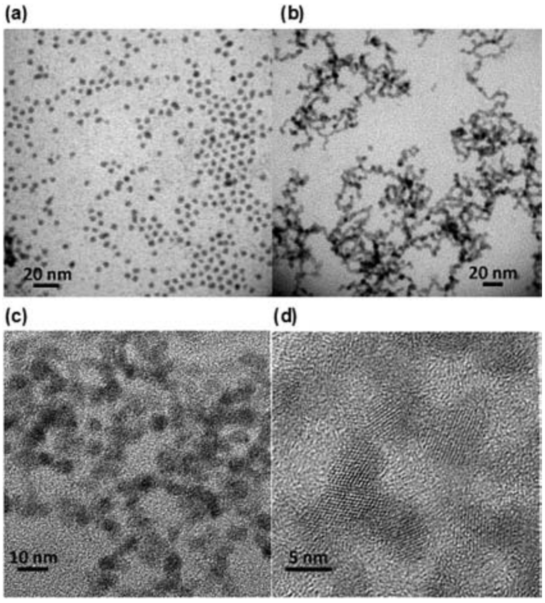

Figure 1. TEM image of (a) CdTe nanoparticles (diameter is 4.5 ± 0.9 nm). (b) CdHgTe nanoparticles after the reaction with mercury bromide. (c,d) High-resolution TEM images of CdHgTe nanorods. Scale bars are shown inside the micrographs.

connected to a neighboring structure to form a complex material over the micrograph, while few original CdTe nanoparticles (in terms of size and shape) were observed with the heterostructures. High-resolution TEM (Figure 1c,d) confirmed each crystalline entity was completely linked with another, while the overall anisotropic particles show several crystalline orientations with different directions in lattice fringes, consistent with the attachment of several particles. X-ray diffraction (XRD) analysis (Supporting Information, Figure S1) of the particles before and after the reaction showed a shift in reflections at ~20° (2θ) to a smaller angle, consistent with an increase in lattice parameter and in agreement with Vergard's law confirming an alloyed composition.[22] This demonstrates a change in the solid-state material while maintaining the overall cubic crystal structure. Similar effects have been observed in ZnCdS alloyed nanoparticles.[23]

Mass spectroscopy showed significant mercury content after the reaction (Cd 63.3%, Hg 19.8%, Te 16.9%), equivalent to $Cd_{3.7}Hg_{1.2}Te_{1.0}$.

The average width of the elongated structure in Figure 1b was 3.9 ± 0.8 nm, which was consistent with our hypothesis that the resulted structures were predominantly based on CdTe nanoparticles. To elucidate the mechanism of the heterostructure formation from CdTe nanoparticles, we have focused on the reactive nature of the mercury cation, the relatively soft acidic nature, and strong oxidizing characteristics of Hg^{2+}. We suggest a cation-exchange reaction from CdTe to HgTe proceeded under the hard—soft acid—base theory, in which harder acids preferentially bind with harder bases and vice versa. In the CdTe solution, Cd^{2+} is regarded as a relatively hard acid when compared to monovalent metal ions or ions with larger ionic radii (Ag^+, Hg^{2+}, Pb^{2+}, etc.). Therefore, the Cd^{2+} would be preferably exchanged with Hg^{2+} using MeOH, a hard base, which binds strongly with Cd^{2+} instead of Hg^{2+}, leading the cation-exchange reaction from CdTe to HgTe. Indeed, notable reports on the synthesis of Ag_2Se, Cu_2Se, Cu_2S, and PbS nanocrystals and relevant core—shell particles were based on this theory.[8,20,24,25] It is probable, therefore, that in our case displaced Cd^{2+} was dissolved into the MeOH, while Hg^{2+} was incorporated into the particle to form CdHgTe.

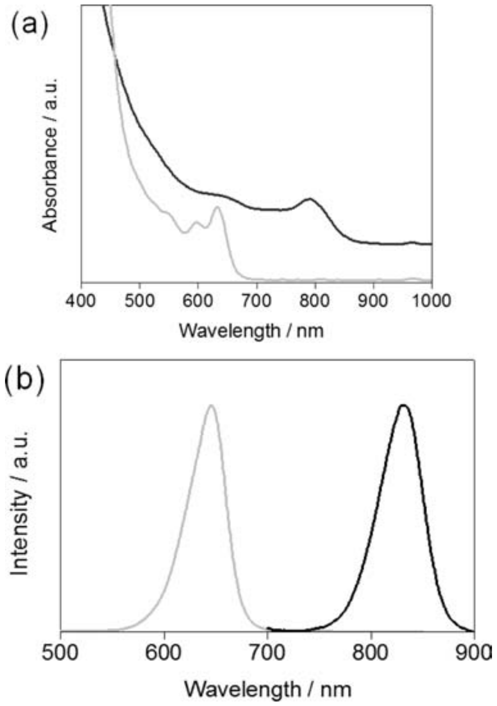

Figure 2. (a) Absorption spectra of CdTe nanoparticles (gray) and CdHgTe nanoparticles (black). (b) Normalized emission spectra of CdTe nanoparticles and CdHgTe nanoparticles (excitation wavelength for emission: 500 nm).

We also need to explore the strong oxidizing nature of the Hg^{2+} ion, which has a positive redox potential, and the effect such a species could have on the surface chemistry of CdTe nanocrystals, unlike other metal species commonly used in quantum dot synthesis (such as cadmium, lead, and zinc) which have negative redox potentials. Our previous report into the remarkable rapid growth of HgSe quantum dots[26] and the difficulty in shape control proposed that the difference was possibly explained by redox potential of Hg^{2+}, where E^0 for $Hg^+ + e^- \rightarrow Hg$ is +0.79 V, while E^0 for $Cd^{2+} + 2e^- \rightarrow Cd$ is −0.40 V, $Pb^{2+} + e^- \rightarrow Pb$ is −0.13 V, and $Zn^{2+} + 2e^- \rightarrow Zn$ is −0.76 V.[26] We also suggested that a surfactant molecule reduced the mercury ion from Hg^{2+} to Hg^0, a key step in the reaction mechanism which led to the rapid growth.

Given the similarity in the environment surrounding the nanoparticles, surfactant molecules (tetradecylphosphonic acid, trioctylphosphine, hexadecylamine) could reduce Hg^{2+} to provide elemental Hg on the CdTe surface or provide Hg—Te bonds through a dangling bond on the CdTe surface, which might lead the subsequent attachment with the next nanoparticles. As the parent CdTe particles are well-known to be labile, we suggest the surface tellurium/surfactant molecules react with the mercury in solution giving HgTe-type species in a manner similar to that of the mechanism suggested previously for HgSe quantum dot formation.[26] As there is clearly cadmium still present in the final anisotropic nanomaterial, it is proposed that this is a surface phenomenon, which corresponds with the TEM observation that the final anisotropic CdHgTe structures are slightly narrower than the diameter of the parent CdTe particles which act as a donor material in the reactions with mercury. The resulting HgTe then acts to 'weld' CdTe particles together, resulting in a CdHgTe alloy. Figure 2a shows the absorption spectra of CdTe nanoparticles and CdHgTe alloyed particles after $HgBr_2$ addition. An excitonic peak at 620 nm is clearly observed in the starting CdTe nanoparticles, while the CdHgTe product exhibited a significant excitonic peak at 780 nm. While referring to the red-shift in the absorption peak, one might need to take into account the effect of particles aggregation or rod formation. Chen et al. reported a 3D nanostructure where water-soluble CdTe nanoparticles were located in close proximity to each other.[19] According to the report, the optical characteristics of the original CdTe and the CdTe assembly showed similar optical features with a slight broadening of the peak shape in the case of the assembly. Highly anisotropic CdTe nanorods also show a red-shift in the optical profile, although not as significant as the shift we report here.[27] It is likely, therefore, that the large red-shift in the absorption peak in our heterostructure is caused by mercury incorporation and hence alloy formation rather than by simple aggregation of CdTe nanoparticles. Indeed, alloyed CdHgTe nanocrystals synthesized via an aqueous route using 10% Hg were reported to have an absorption peak around 800 nm, depending on reaction conditions,[28] which is in good agreement with our CdHgTe particles. The emission spectra of each sample are shown in Figure 2b. The original CdTe nanoparticles exhibited strong narrow band edge emission, whereas the CdHgTe nanostructures displayed weak (less than 1% quantum yield) red-shifted band edge emission whose shape was slightly broadened. Additionally, it should be mentioned that the emission profile from CdHgTe alloys differs from the trap emission of CdTe nanoparticles, which is typically much broader and generally located approximately 100 nm red-shifted from the band edge emission.[29] Again, the emission profile is consistent with previously reported CdHgTe nanoparticles.[28]

We suggest this mechanism as "Molecular Welding" and we can state that the molecular welding effect is at least partly driven by the positive redox potential of the mercury species. Carrying out the same experiments substituting the Hg^{2+} salt with Pb^{2+}, Cd^{2+}, and Zn^{2+} salts enhanced the emission spectra but did not change the position of emission, unlike addition of Hg^{2+} (Figure 3), suggesting a coordination to the particle surface, but no reaction. The welding reaction proceeds rapidly at room temperature due to the significant reactivity of Hg^{2+} toward CdTe nanoparticles, which is notable as most conventional heterostructured/anisotropic growth in nanomaterials required high temperature. However, additional investigation into the reaction mechanism caused by Hg ions is necessary, whereas the strategy for more precise control in both morphology and optical property is essential for practical applications. We do, however, suggest the positive redox potential hypothesis may well explain why gold tips can be grown on other nanomaterials using a simple gold salt (the standard electrode potential of $Au^{3+} + 3e^- \rightarrow Au$ is $+1.52$ V), without the need for heating,[30] whereas growing PbSe tips on semiconductor rods required mild heating.[31]

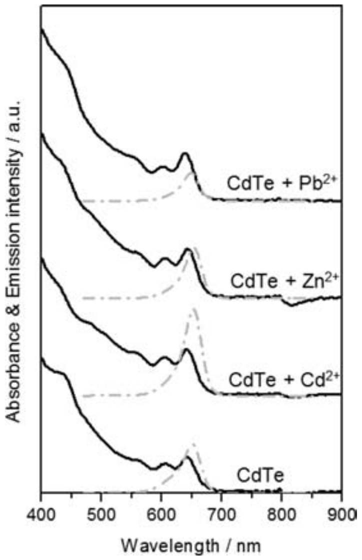

Figure 3. Absorption and emission spectra of CdTe nanoparticles after metal cation addition. Black curves represent absorption spectra, the gray curves represent emission spectra (excitation wavelength: 450 nm). The detailed reaction procedure is described in Supporting Information.

In conclusion, we have synthesized 2D CdHgTe anisotropic alloy nanostructures at room temperature by the simple addition of a mercury salt to a CdTe quantum dot solution. The TEM studies revealed anisotropic nanoparticle structures with random directions in the lattice fringes, and optical measurements suggested CdHgTe alloys, similar to aqueous CdHgTe nanoparticles previously reported. We have focused on two intrinsic properties of the mercury ions, relative softness in hard−soft-acid−base theory and, significantly, the positive redox potential, to suggest the possible explanation for the room temperature molecular welding effect and associated changes in optical properties. We believe these observations may contribute to the synthesis of nanostructures where particles are attached to each other in the pursuit of highly organized designer structures with very specific optoelectronic functions.[32] When combined with intelligent synthesis,[33] a wide range of materials may become accessible.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental procedures and XRD analysis. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

mark.a.green@kcl.ac.uk

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