COMMUNICATION

The room temperature phosphine-free organometallic synthesis of near-infrared emitting HgSe quantum dots

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Luminescent mercury selenide (HgSe) quantum dots have been synthesised by a phosphine-free method using oleic acid as a capping agent. The modification of experimental conditions such as temperature resulted in particles of various sizes (15 - 100 nm) and morphologies not previously seen in HgSe, with emission tuneable between 1000 nm and 1350 nm.

The popularity of semiconductor quantum dots (QDs) and their association with next-generation opto-electronic devices and biomedical applications has grown rapidly over the last years. Current research focuses on various synthetic routes as a means to modify QD characteristics to satisfy specific optical and magnetic requirements for applications such as biological imaging,[1] telecommunications,[2] photodetection[3] and solar energy.[4] Quantum dots have provided a new source of electromagnetic radiation on the nano-scale. The wavelengths range from near-ultraviolet (NUV),[5] through the visible and even near-infrared (NIR) regions.[2,6] NIR emission have been used widely in the fields of telecommunication[2] and imaging.[1] In the field of telecommunication, semiconductor nanocrystals producing emission within the IR region have the potential to expand the optical-fibre bandwidth, creating high capacity ultra-broadband optical and plasmonic amplifications.[2,7] Due to its long wavelength, IR emission also has the capability of penetrating through human tissue, hence allowing bio-imaging.[1]

The advent of the organometallic synthesis of quantum dots provided access to a wide range of materials that were previously unobtainable using aqueous–based techniques. As a result, new NIR-emitting quantum dots such as lead chalcogenides have emerged, and such materials are now considered well-established and efficient fluorophores. Whilst the majority of semiconductor materials (such as the II-VIs, IV-VIs and III-Vs) have been prepared on the nanoscale using organometallic routes, one family of materials remains relatively unexplored – the mercury chalcogenides, possibly

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due to the lack of obvious and safe precursors (despite the fact that many early routes to nano-dispersed semiconductors were based on mercury chalcogenides). We have focused on mercury chalcogenides due to their low reaction temperatures (which we assigned to the positive redox potential of the mercury precursors) and ease of synthesis resulting in novel IR-emitting and absorbing materials.[6]

Mercury chalcogenide quantum dots are known to have narrow band gaps that satisfy the NIR photoluminescence requirement (>800 nm). For this reason, mercury chalcogenides have already been used in mid-infrared photodetectors.[9,4] The seminal reports on the aqueous growth of high quality mercury telluride (HgTe) quantum described particles which emitted in the range of 800-1550 nm with quantum efficiencies between 55-60%.[10] Our group reported the first metal-organic based synthesis of HgTe using simple Hg salts and trioctylphosphine telluride in the presence of various stabilising ligands.[8] Following this, Piepenbrock *et al.* reported a similar synthesis of organically passivated HgTe nanocrystals.[11] These reports also confirmed the observation of rapidly growing particles with average size from 2 – 6 nm. This was developed further by Li *et al.* who successfully synthesised HgTe quantum dots using the combination of mercury oxide (HgO), tributylphosphine telluride and oleic acid (OA), in octadecene yielding particles capped with dodecanethiol.[12] The report stated, even at room temperature the reaction was rapid and uncontrollable resulting in coagulated HgTe nano-crystals and the precipitation of bulk

materials, due to the combination of HgO and OA, which are known to produce clustered particles.[12] Whilst the synthesis of HgTe has been relatively widely reported, the production of luminescent HgSe quantum dots has yet to be fully investigated.

Mercury selenide, HgSe, is a negative band gap semiconductor with a band gap of -0.24 eV and an exciton diameter of 27.5 nm; smaller than HgTe (*ca.* 80 nm) but substantially larger than the majority of II-VI materials.[8] Using the aqueous route (which was successfully used to prepare thiol-capped HgTe) in an attempt to synthesise HgSe resulted in material with low quantum yields.[3] In recent years Esmaeili-Zare *et al* used a sonochemical technique to synthesise HgSe nanocrystals with a reported band edge of 2.23 eV.[13] The report described the use of $SeCl_4$ and $HgCl_2$ in the presence of hydrazine and capping agents, where ultrasonic waves were used to irradiate the reaction to form the required nano-crystals. The same group have recently developed cubic phase HgSe particles using a similar synthesis method with a band edge of 3.15 eV.[14] In a notable report, Kuno *et al* also reported the use of a reverse micelle approach involving an amphiphilic surfactant, producing stable emissive HgSe clusters with a band edge at 595 nm (2.08 eV) with emission close to 630 nm (1.97 eV). These highly crystalline particles were shown to have a narrow size distribution and a quantum yield of >10%.[15] We have also previously reported the synthesis of HgSe quantum dots with tuneable sizes and morphologies using inorganic precursors, but did not investigate the optical properties in any depth.[6]

In this report, we extend our synthesis of HgSe quantum dots to a phosphine-free route, yielding near-infra-red emitting materials by utilising a combination of mercury (II) acetate ($Hg(OAc)_2$), oleic acid (OA), selenium (Se) and octadecene (ODE). The process for this synthesis uses OA for the capping agent and ODE as a non-coordinating solvent. This newly developed method seeks to provide materials with improved optical properties and characteristics relative to previously reported HgSe particles.[6]

Experimental

Mercury (II) acetate ($Hg(OAc)_2$), technical grade (90%) oleic acid (OA), selenium powder and octadecene (ODE) were obtained from Sigma-Aldrich and used as received. All reactions were carried out under nitrogen atmosphere using Schlenk line techniques. ODE was degassed under vacuum at 100 °C for one hour. Se-ODE was prepared by adding selenium powder (0.277 g, 3.5×10^{-3} moles) to 35 mL of purified ODE solution under nitrogen (0.1 M solution). The mixture was stirred and heated to 270 °C for approximately 1 hour to fully dissolve the selenium powder, before being cooled to room temperature.

In a typical reaction, mercury (II) acetate (0.44 g, 1.4×10^{-3} moles) was dissolved in 20 ml of oleic acid and heated to approximately 90 °C whilst stirring to affect dissolution, then cooled to room temperature. The Hg precursor was then heated (if required) to the desired synthesis temperature. This was followed by injection of 13 ml of the 0.1 M Se solution

(1.3×10^{-3} moles). The reaction conditions were varied between three protocols; 100 °C injection and growth, room temperature injection and growth, and room temperature injection followed by immediate freezing in liquid nitrogen and gradual warming to room temperature.

With the room temperature reaction, no initial colouration was observed upon precursor injection. However after 2 minutes stirring, the colour started to change, becoming distinctly yellow after 5 minutes, orange after 20 minutes, brown at 35 minutes and eventually turning deep black by 50 minutes. The observed colour change was much faster at 100 °C, becoming black in just 10 minutes, whilst the growth from a frozen matrix required 8 hours. After particle growth, acetone was added to the solution, followed by centrifugation for 10 minutes resulting in the precipitation of a black solid. By adding toluene, followed by centrifuging for a further two minutes and filtration, a transparent black HgSe solution was obtained. It is worth noting that the particles in toluene were stable in solution for *ca.* one month before any precipitation was observed. Experiments were also performed by keeping the mercury (II) acetate and OA mixture under vacuum for an extended period to remove any excess build-up of acetic acid known to cause coagulation of the nanoparticles.[16]

Transmission electron microscope (TEM) images were obtained using a TECNAI 20 microscope at 200 kV at the Centre for Ultrastructural Imaging, Guy's campus, KCL. High resolution images and selected area electron diffraction patterns were collected at the University of Leeds EPSRC Nanoscience and Nanotechnology Research Equipment Facility, using a FEI Tecnai F20 200kv FEGTEM fitted with a Gatan Orius SC600 CCD camera and an Oxford Instruments 80mm2 X-Max SDD EDX detector. The absorption spectroscopy measurements were obtained using a Hitachi U-4100 spectrophotometer. Emission spectra were recorded using an 808 nm excitation laser and a Newport InGaAs 818-IG detector and the same system was used along with an integrating sphere to obtain the quantum yield of the nanoparticles.[17] X-ray diffraction (XRD) measurements were carried out on nanoparticles using a Bruker AXS D8 diffractometer. The XRD samples were prepared by pipetting a highly concentrated HgSe particle solution in toluene drop-wise on a small piece of glass slide with a surface area of 10 mm x 10 mm until an estimated 1mm thick layer was formed.

Results and discussions

In a standard room temperature reaction, multishaped, predominantly pyramidal-shaped HgSe particles (Figure 1A) were produced with an average size of 24 nm ± 4.1 nm, which were clearly larger than the analogous HgSe particles previously obtained.[6] The particles were relatively monodispersed with a range of shapes, including spherical, pyramidal and cubic, and appeared in some cases to aggregate. Aggregation was reduced by removing the acetic acid formed from the reaction between the mercury salt and oleic acid by vacuum evacuation (Figure 1B).[16] This changed the mean particle size to 22 nm ± 2.6 nm, indicating a slight

increase in monodispersity. As the technique of acetic acid removal was effective, it was used for all further synthesis of HgSe samples. The growth of mercury chalcogenides at low (room) temperatures has previously been observed, and suggested to be due to the positive redox potential of the mercury

precursor, (E^0 Hg_2^{2+} + $2e^-$ → $2Hg$ is 0.79 eV, unlike the analogous Cd, Zn and Pb precursors which are all negative), which resulted in the room temperature reduction of the mercury precursor by the phosphine yielding Hg^0 monomers which then reacted with the chalcogen source.[6]

Whilst HgSe and HgTe were reported to form at low temperatures, HgS prepared by the use of mercury salts and TOPS was found to require a preheating step for the TOPS, attributed to the stronger phosphine-sulphur bond and low conversion rate.[18] In this report, the source of mercury salt reduction is unclear, and whilst a recent publication has suggested that octadecene is a reducing agent,[19] this is far from proven. The mercury nuclei, once generated were then available to react with the selenium monomer provided by octadecene/selenium.[20] As the reaction proceeded smoothly at room temperature without the need for external heating, this presented the opportunity to measure the emergence of an optical band edge *in situ* by carrying out a reaction in an absorption cuvette and monitoring the band edge in real time. Figure 2 shows the emergence of the absorption features of HgSe particles prepared at room temperature from 2 min to 100 min. The emergence of an excitonic feature can clearly be seen at 55 minutes. Taking the emergence of the excitonic feature at 55 minutes at *ca.* 760 nm, and the excitonic feature at 90 minutes at *ca.* 820 nm, we estimate using the effective mass approximation described earlier[6] that the particles grew just 0.17 nm in 45 minutes at room temperature, which is much less than a unit cell of HgSe (6.085 Å).[21] This highlights how small structural changes can drastically affect the optical properties of nanomaterials with a large excitonic diameter.

One method of preparing monodispersed particles is to separate the nucleation and growth phases, usually achieved by utilising a high temperature precursor injection and a slow, lower temperature growth step. This was attempted with the room temperature growth route by freezing the reaction to liquid nitrogen temperatures immediately after precursor injection. The reaction solution was then allowed to warm slowly to room temperature over a period of 8 hours followed by isolation of the particles as described above. The resulting particles were observed to be monodispersed, approximately spherical in morphology (figure 1C) with some hexagonal and cubic particles observed. The average size of these particles was 14 nm ± 2 nm. The close-packing formation of these particles was observed, unlike particles prepared without acetic acid removal, which had a tendency to agglomerate. The high resolution electron microscopy
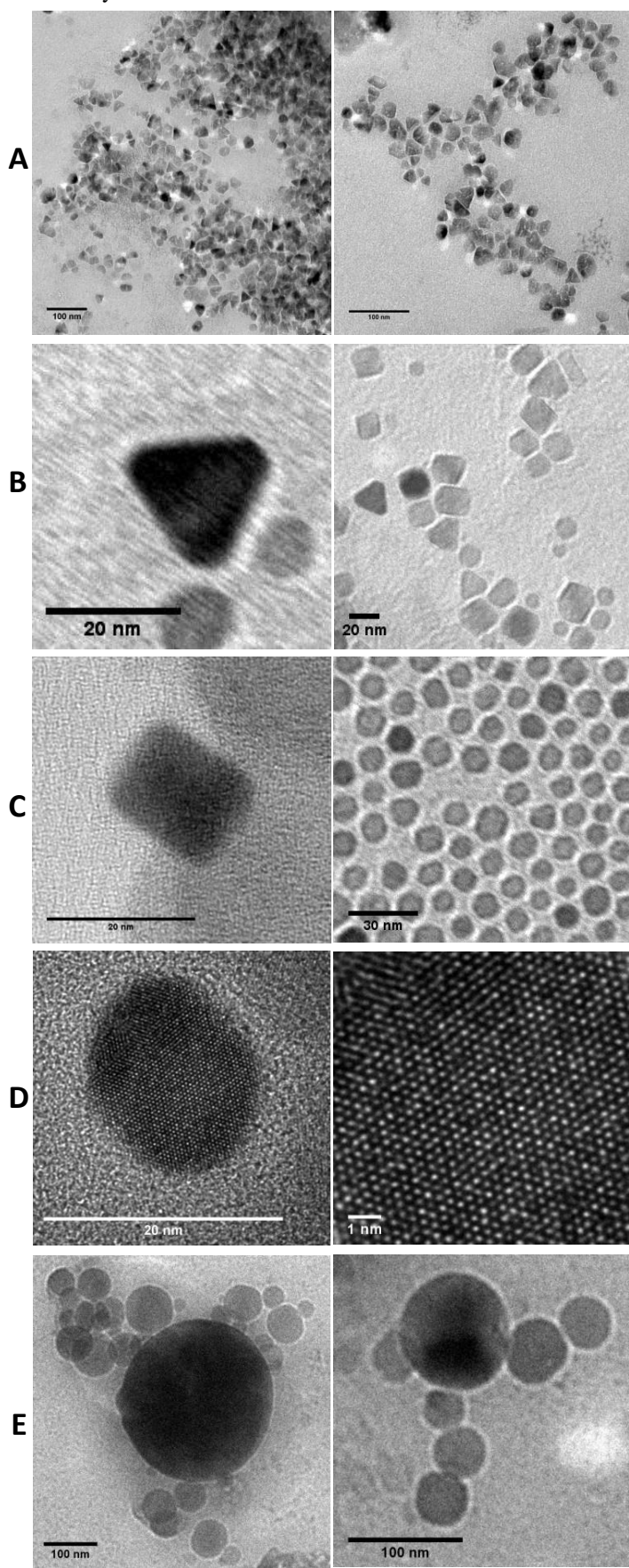
Figure 1 - TEM images of HgSe nanoparticles synthesised at various temperatures - A) Room temperature (aggregated due to acetic acid effects). Scale bars = 100 nm; B) Room temperature synthesis with reduced acetic acid. Scale bars = 20 nm; C) Room temperature injection followed by freezing. Scale bars = 20 nm (left) and 30 nm (right); D) High-resolution electron micrographs after room temperature injection/freezing. The internal crystal structure is clearly visible. Scale bars = 20 nm (left) and 1 nm (right); E) Particles synthesised at 100 ºC. Scale bars = 100 nm.
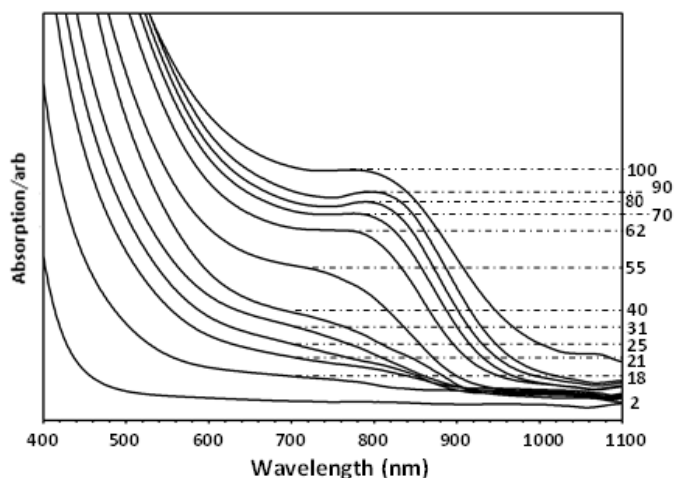
Figure 2 – *In situ* Real-time monitoring of absorption features for room temperature growth.
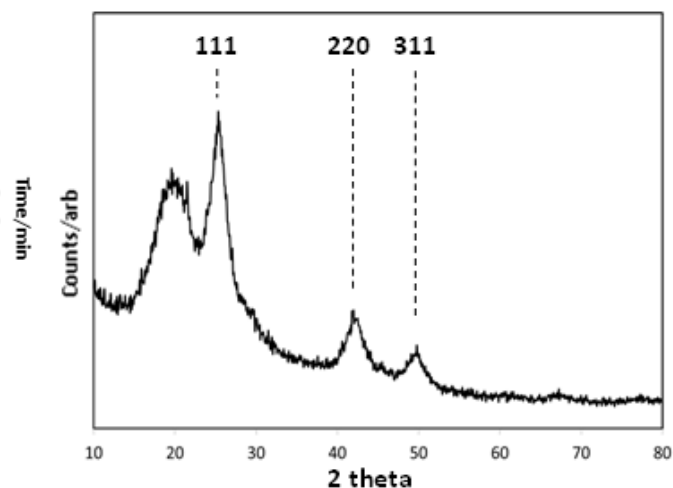

Figure 3 – X-Ray diffraction pattern (XRD) of zinc blende HgSe particles prepared at room temperature and associated Miller indices.

(HRTEM) images of particles prepared by low temperature growth (figure 1D) showed the highly crystalline structure of these particles despite the absence of thermal annealing normally afforded by high temperature growth.

When the reaction was carried out at 100°C, the particles were observed to be significantly larger than those prepared at room temperature, approximately spherical and polydispersed due to rapid uncontrolled growth (Figure 1E). The average size obtained was 78 nm ± 58 nm. X-ray diffraction (on particles prepared at room temperature) confirmed the cubic zinc blende structure of the HgSe quantum dots (Figure 3) [22] similar to those shown in a recent report on the synthesis of HgSe and HgCdSe [23] quantum dots prepared by an aqueous route. In this case, the particles were used as near-infrared photodetectors.

Optical spectroscopy of the synthesised materials showed size-dependent absorption and emission in the near-infrared region (figure 4). Material prepared at 100°C displayed an onset of absorption at approximately 1300 nm (0.95 eV) and an excitonic shoulder at *ca.* 1050 nm, a substantial widening of the band gap of *ca.* 1.2 eV. Emission was found to be slightly Stokes shifted with a maximum at *ca.* 1250 nm (0.99 eV) with a full width at half maximum (FWHM) of 184 nm.

Room temperature injection and growth resulted in smaller materials with an absorption band edge onset at *ca.* 1100 nm (1.12 eV) and a less well-defined excitonic feature, possibly attributable to the less well-defined separation of nucleation and growth. The blue shifted onset of absorption relative to the materials prepared at 100 °C is expected from smaller particles exhibiting a larger widening of the band gap. Emission was found to be Stokes shifted, with a maximum at *ca.* 1070 nm (1.15 eV) with a FWHM of 135 nm.

Particles prepared by room-temperature injection followed by immediate freezing displayed an onset of absorption at *ca.* 1000 nm (1.24 eV), with an excitonic feature

at *ca.* 875 nm. Emission was again Stokes shifted from the band-edge with a maximum at *ca.* 1000 nm (1.24 eV) with a FWHM of 170 nm. This increase in the band gap confirmed that particles prepared by the slow growth method were smaller than the particles grown entirely at room temperature. All particles displayed similar emission quantum yields (approximately 4 %, with a maximum of 7 %) irrespective of the method used to manufacture them, and whilst lower than HgTe quantum dots prepared by analogous synthetic techniques, is the highest recorded for HgSe.
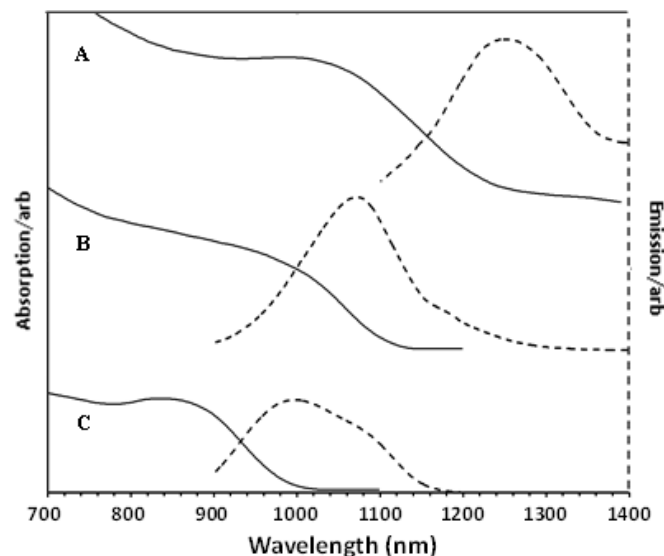

Figure 4 – Absorption and emission spectra of HgSe nanoparticles synthesised at various growth temperatures. A) 100 °C; B) Room Temperature; C) Room temperature injection/freezing.

In conclusion, we have amended our previous synthetic pathway to prepare crystalline HgSe quantum dots at low temperatures using a simple phosphine-free method. The particles, with a range of different morphologies were approximately 15 nm to 200 nm in diameter and exhibited tuneable band-edge emission between 1000 and 1350 nm with quantum yields of approximately 4-7 %.

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