JOURNAL OF
Materials
CHEMISTRY
Communication

Investigation of factors affecting the photoluminescence of colloidally-prepared HgTe nanocrystals

Mike T. Harrison,*[a] Steve V. Kershaw,[a] Mike G. Burt,[a] Andrey Rogach,[b] Alex Eychmüller[c] and Horst Weller[c]

[a]Advanced Communications Engineering, BT Adastral Park, Martlesham Heath, Ipswich, UK IP5 3RE. E-mail: mike.2.harrison@bt.com
[b]Physico-Chemical Research Institute, Belarussian State University, 220050 Minsk, Belarus
[c]Institute of Physical Chemistry, University of Hamburg, 20146 Hamburg, Germany

Received 30th July 1999, Accepted 7th September 1999

We report the effect of varying the experimental conditions on the synthesis of colloidal HgTe nanocrystals in aqueous solution, and by using deuterated water (D_2O) as a solvent, demonstrate strong luminescence over the full range of the strategic 1.3 and 1.5 μm telecoms windows.

The synthesis and optical properties of colloidal HgTe nanocrystals in aqueous solution using 1-thioglycerol (1-mercaptopropane-2,3-diol) as the size-regulating capping agent has been reported recently.[1,2] A material was produced with a very broad photoluminescence (PL) ranging from 900 to 1300 nm at half-maximum intensity, with an extremely high quantum efficiency (QE) of *ca.* 50%. The sample then underwent an 'ageing' process with the PL shifting to longer wavelengths and the QE apparently dropping, until it was obscured by the strong water absorptions at 1450 and 1900 nm after a period of about two weeks.

Semiconductor nanocrystals, or quantum dots, are currently generating a huge amount of interest for application in novel electrical and optoelectronic devices owing to their unique physical and chemical properties.[3–5] Nanocrystalline HgTe is one of the few examples of colloidal quantum dots that emit in the near-IR, and as such has possible applications in 1.3 and 1.5 μm optical telecommunications systems. However, the issue of the long term spectral stability has to be addressed, and the spectroscopic properties in the near-IR need to be studied. Here, we present the effect of varying the synthetic conditions on the optical properties in an attempt to improve the stability of HgTe quantum dots and to understand the factors affecting the nanoparticle formation. As well as varying the pH, 1-thioglycerol concentration and telluride content, the effect of gently heating the sample was also studied. In order to record meaningful spectra at the longer PL wavelengths obtained by such heating, a complete synthesis was performed using deuterated water (D_2O) as the solvent. This has the effect of shifting the hydoxy O–H absorption bands to longer wavelengths away from the regions of interest, whilst retaining the same chemical properties of the 'aqueous' medium. In addition, we would also be able to ascertain unambiguously whether the intensity of the PL drops as it shifts to longer wavelengths, or if that observation was connected to the increase in solvent re-absorption.

The basic synthesis of colloidal HgTe nanocrystals was described previously[1,2] and is an extension of the aqueous route used for other II–VI systems such as CdS,[6] CdSe[7] and CdTe.[8] In all cases, 40 mL portions of a de-oxygenated, 0.017 M, aqueous solution of $Hg(ClO_4)_2\cdot 3H_2O$ (Alfa, 99.9%) were used. To this was added various amounts of 1-thioglycerol stabiliser (Fluka, >99%) and 1 M NaOH solution to adjust the pH in the region of 8–12. H_2Te was generated by the reaction of dilute sulfuric acid with Al_2Te_3 (Alfa, 99.9%), and then bubbled through the vigorously stirred mercury/thioglycerol solution in a buffering nitrogen stream. Note that it is necessary to use an inert atmosphere and nitrogen-saturated solutions because of the high susceptibility of tellurium anions to oxidation.[9] The mercury-to-telluride ratio was varied by using different weights of Al_2Te_3, with the nitrogen flow kept constant in all cases at around 170 sccm ($cm^3\ s^{-1}$). The D_2O synthesis was performed in exactly the same way as above, except that 40 mL of deuterium oxide (Aldrich, 90 atom %) was used as the solvent, with the Hg^{2+} : thioglycerol : Te^{2-} ratio equal to 1 : 3.04 : 0.27. Heating was then performed in a flask fitted with a reflux condenser and thermometer, again under a flow of nitrogen and with stirring. All of the PL measurements were performed using an Ar-ion laser running on all lines (predominantly 514.5 nm) as the excitation source and the samples were in the form of dilute aqueous solutions in standard quartz fluorescence cells. The spectra have all been normalised against their absorption, and corrected for spectrometer response.

It was found that both the pH (in the range 8–12) and the 1-thioglycerol concentration (above a certain critical value) did not have very much effect on the optical properties and stability of the nanocrystals, see the selection of PL spectra in Fig. 1. Note that these are all spectra from two-week old samples, and represent a significant improvement from the original synthesis (which used a higher pH and telluride content) where the PL had virtually disappeared after the ageing period.[2] There are some differences, but these can be accounted for by uncertainties in the other experimental parameters, particularly the variation in the weight of Al_2Te_3 (molar ratio of Hg : Te was *ca.* 1 : 0.2), and which does have a significant effect, as is discussed later. Below a thioglycerol-to-mercury ratio of 2.5 : 1, the colloidal solution is unstable and the nanocrystals tend to flocculate owing to insufficient stabiliser.

Fig. 2 shows the effect of varying the amount of Al_2Te_3 on the PL, which gives a much more pronounced effect. The greater the amount of telluride, the longer the PL wavelength after two weeks ageing, and the more the luminescence is obscured by the water absorptions. All of the samples demonstrated a red-shift in their PL during this ageing period, with the shift increasing with increasing H_2Te volume. This shift appears to continue indefinitely, albeit at a progressively slower rate. The width of the PL, and hence the size distribution, also appears to increase with increasing telluride content, although again this is ambiguous due to the water absorption. There is also a general lowering of the stability of the colloidal solutions at the very highest telluride contents, with precipitation occurring not too long after the two week ageing period. This is perhaps due to the decrease in the concentration of excess polynuclear mercury–thiolate complexes which surround the nanocrystals and aid in stabilising the colloidal solution.[10] So, it is possible to control the PL wavelength of the quantum dots, and perhaps therefore

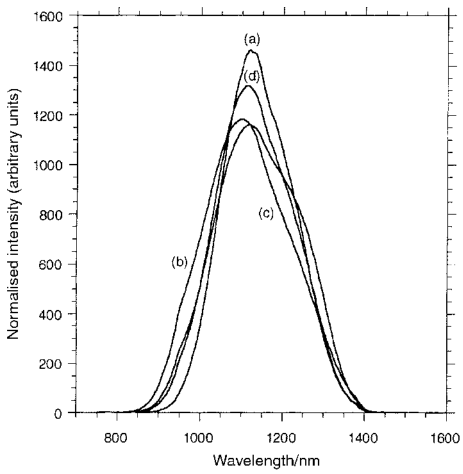

Fig. 1 Room temperature PL spectra of nanocrystalline HgTe in aqueous solution comparing the effect of varying pH: (a) pH = 8, (b) pH = 12, and 1-thioglycerol concentration (relative to mercury): (c) 2.6, (d) 4.3.

their size, by controlling the amount of telluride added to the system, however, it is an extremely complex system and the spectra in Fig. 1 do not necessarily tell the full story. For example, the fact that the optical density of the solution also increases with increasing telluride quantity is an indication that the concentration of dots is higher, and that in itself may affect the equilibria governing growth and ageing.

Fig. 3 shows the effect of heating the one-day old D_2O preparation. Note that some of the asymmetry in the spectra at shorter and longer wavelengths is caused by the detector response which is quite low at both ends of the measurement range. A relatively low temperature of 70 °C had to be used in order to make the process controllable, as refluxing the solution immediately put the PL too far into the IR and out of our region of interest. Heating has very much the same effect as both the ageing process and increasing the telluride quantity, with the PL shifting from 1020 out to 1500 nm. This time however, the evolution of the spectra is visible as well as the significant, strong PL signal in the strategic telecoms windows of 1.3 and 1.5 µm. There is a drop in intensity coupled with the red-shift of the emission, but it is much smaller than it appears in the standard H_2O synthesis, and the quantum yields are still around the 10% mark. This is remarkable for an organically capped nanocrystalline material at these important wavelengths using far from optimal excitation at *ca.* 500 nm. The luminescence is also extremely stable, after the initial ageing stage, for a period of several months after the heating, with only a few nm red-shift observable.

In conclusion, the synthesis of stable nanocrystalline colloidal HgTe in aqueous solution has been demonstrated. It was found that the most significant experimental parameter in determining both the final PL wavelength and the long term sample stability was the relative quantity of H_2Te gas bubbled through the mercury–thiolate solution. In the alkaline pH range, and above a critical stabiliser concentration, there was very little variation. In order to practically demonstrate strong, broad PL around the strategic telecommunications wavelength of 1.5 µm, a sample was prepared using D_2O as the solvent and gently heated. A similar progression into the IR was observed as for increasing the telluride content, showing that there are several methods of tuning the PL to the desired wavelength in the range of 1000–1700 nm and beyond. By removing the problem of luminescence re-absorption by the solvent, the potential of this novel material in future optical telecommunication systems has been confirmed.

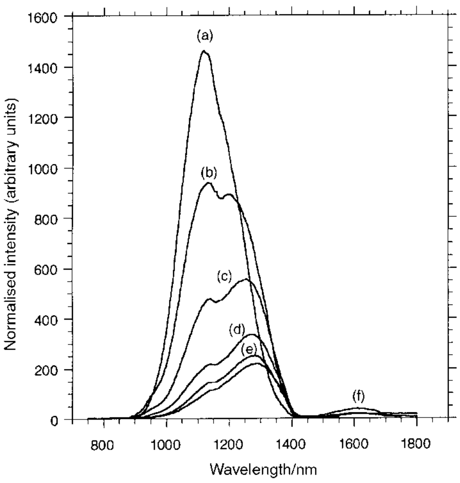

Fig. 2 Effect of varying the telluride quantity on the room temperature PL from two-week old nanocrystalline HgTe in aqueous solution. The Hg^{2+} : thiol : Te^{2-} ratio used was 1 : 2.6 : x where x = (a) 0.17, (b) 0.24, (c) 0.44, (d) 0.55, (e) 0.71 and (f) 1.24.

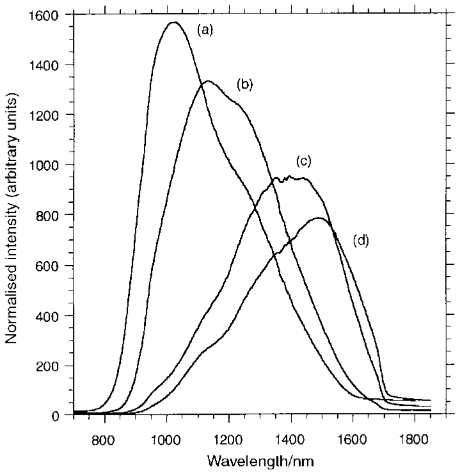

Fig. 3 Room-temperature PL spectra of HgTe preparation in D_2O following different amounts of heating under nitrogen at 70 °C after one day ageing. (a) Unheated. (b) 30 min, (c) 60 min, (d) 90 min.

Notes and references

1 A. L. Rogach, S. V. Kershaw, M. G. Burt, M. T. Harrison, A. Kornowski, A. Eychmüller and H. Weller, *Adv. Mater.*, 1999, **11**, 552.
2 M. T. Harrison, S. V. Kershaw, M. G. Burt, A. L. Rogach, A. Kornowski, A. Eychmüller and H. Weller, *MRS Symp. Proc.*, 1999, **536**, 217.
3 R. Rossetti, S. Nakahara and L. E. Brus, *J. Phys. Chem.*, 1983, **79**, 1086.
4 D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos and P. L. McEuen, *Nature*, 1997, **389**, 699.
5 B. O. Dabbousi, M. G. Bawendi, O. Onitsuka and M. F. Rubner, *Appl. Phys. Lett.*, 1995, **66**, 1316.
6 T. Vossmeyer, L. Katsikas, M. Giersig, I. G. Popovic, K. Diesner, A. Chemseddine, A. Eychmüller and H. Weller, *J. Phys. Chem.*, 1994, **98**, 7665.
7 A. L. Rogach, A. Kornowski, M. Gao, A. Eychmüller and H. Weller, *J. Phys. Chem. B*, 1999, **103**, 3065.
8 A. L. Rogach, L. Katsikas, A. Kornowski, D. Su, A. Eychmüller and H. Weller, *Ber. Bunsen-Ges. Phys. Chem.*, 1996, **100**, 1772.
9 M. L. Steigerwald and L. E. Brus, *Annu. Rev. Mater. Sci.*, 1989, **19**, 471.
10 M. Gao, S. Kirstein, H. Möhwald, A. L. Rogach, A. Kornowski, A. Eychmüller and H. Weller, *J. Phys. Chem. B*, 1998, **102**, 8360.

Communication 9I07224A