Chemistry in New Zealand April 2010

Colour Tuneable Photoluminescent Quantum Dots for Ink-Jet Printing of Security Documents and Labels

James H. Johnston[*,a] Aaron C. Small[a] and Noel Clark[b]

[a]School of Chemical & Physical Sciences, Victoria University, PO Box 600, Wellington and [b]CSIRO Materials Science and Engineering, Private Bag 10, Clayton South VIC 3169, Australia (e-mail: *jim.johnston@vuw.ac.nz*)

Introduction

Zinc sulfide (ZnS) is a well known semi-conductor material with a band gap, E_g, of about 3.6 eV, which is within the energy range of UV light. When it is in the form of nanocrystalline particles, the particles are referred to as a quantum dots. The ZnS quantum dot lattice can be doped with transition metal ions and, when the doped material is excited by UV light, it exhibits photoluminescence in the visible region with the colour depending on the nature and level of the transition metal ion dopant. When doped with Mn^{2+} ions, UV irradiation gives a red-orange colour at about 600 nm, and when doped with Cu^{2+} ions a green-blue colour is seen at about 530 nm. In ambient light they are invisible. The dopants act as recombination centres for the excited electron-hole pairs, resulting in strong and characteristic photoluminescence.[1] The size of the quantum dots does have an effect on the fluorescence quantum yield Φ of the doped quantum dots, and is given by Eq. 1:[2]

$$\Phi = \frac{1}{1 + \beta D^2} \quad \text{...... Eq. 1}$$

where D is the diameter of the quantum dot and β is the ratio of the non-radiative and radiative decay lifetimes. It shows that the smaller the particle size, the larger the fluorescence or photoluminescence yield. Doped ZnS quantum dots are typically 2 nm in size while the Bohr radius for ZnS is 2.5 nm.

A stable colloid of doped ZnS quantum dots is colourless as the particles are too small to scatter light in the visible region but it exhibits the sharply defined characteristic photoluminescence colour in the visible region when viewed under UV irradiation. This is due to the nature of the particular transition metal ion used as the dopant. Colloid stability is usually achieved by using a capping agent, such as the citrate ion, which coats the individual quantum dot nanocrystals and prevent agglomeration. The ability to form stable colloids of photoluminescent quantum dots opens up the exciting possibility for their use as photoluminescent inks in security documents and labels in both single colour and full colour characters and images, and also in novel flexible photoluminescent displays and advertising.

Preparation of Doped ZnS Quantum Dots

The zinc sulfide quantum dots doped with Mn^{2+} and Cu^{2+} were synthesised using a chemical precipitation method from AR grade reagents and double distilled water for all solutions.[3] In a typical synthesis of Mn^{2+} doped ZnS, 10 mL each of 1.0 M $ZnCl_2$, 0.01 M $MnCl_2$ and 0.5 M sodium citrate solution were mixed and stirred for 10 minutes and then 10 mL of 1 M Na_2S solution was added dropwise from a burette. A white precipitate of ZnS/Mn^{2+} quantum dots formed and the resulting suspension was centrifuged and washed with distilled water and redispersed in 40 mL of distilled water to provide a colloidal suspension. Several experiments were conducted using different concentrations of Mn^{2+} ranging from 1-10 mol % to determine the optimum photoluminescence yield.[3]

In a similar way, the Cu^{2+} doped ZnS quantum dots were prepared from 10 mL each of 1.0 M $ZnCl_2$, 0.01 M $Cu(OAc)_2$, 0.5 M sodium citrate and 0.5 M sodium thiosulfate solution to give the colloidal suspension. The dopant concentrations here were adjusted from 0.2-1.0 mol % to determine the optimum photoluminescence yield.[3] The photoluminescent spectra of the doped quantum dot colloids were measured on a Perkin-Elmer LS-55 Photoluminescence Spectrometer over a range of 300-800 nm using an excitation wavelength of 320 nm and with a filter to remove the excitation line from the emission spectra.

The quantum dot colloids were incorporated into an ink-jet formulation and ink-jet printed onto paper and textile substrates using a 2811 Dimatix Materials digital printer. The requirements for the quantum dot ink-jet formulation needed to be matched as closely as possible to those of commercial inks and these are shown in Table 1. In order to approximately match these requirements and to ensure stability of the ink formulation, mercaptosuccinic acid [HO_2C-CH(SH)-CH_2-CO_2H – MSA] in a mole ratio of MSA:Zn = 8:1 for Mn^{2+} doped ZnS and MSA:Zn = 4:1 for Cu^{2+} doped ZnS was used.

Table 1. Property match for ink for ink-jet printing.

Property	Value
Viscosity	10-12 centipoise at 60 °C
Surface tension	28-33 dynes at 60 °C
Low volatility	bp < 100 °C
Density	Specific gravity > 1 g/mL
Filtration	Filtered to 0.2 μm

Results and Discussion

The photoluminescence spectrum of Mn^{2+} doped ZnS is shown in Fig. 1. A peak is observed in the visible range at *ca.* 600 nm that gives rise to the fluorescent red-orange colour. This is due to the presence of Mn^{2+} in the host ZnS lattice, which produces localized energy levels ($^4T_1$ – $^6A_1$). Incident UV light, with energy greater than the band gap, promotes an electron from the valence band to the conduction band. This then decays back to the valance band via a pathway involving a transition from the intermediate $^4T_1$ to the $^6A_1$ energy levels, giving rise to the emission of light in the visible region red-orange colour.[2] The emission at about 400 nm (Fig. 1) is due to S^{2-} vacancies in the ZnS lattice.[4] A similar mechanism takes place for Cu^{2+} doped ZnS where the transition is between the ^2E and $^2T_2$ energy levels. The emission occurs at about 530 nm and gives rise to the blue-green colour (Fig. 2).[5] The emission from the S^{2-} vacancies is not observed in this case as there are fewer S^{2-} ions available due to the use of $S_2O_3^{2-}$ in the reaction.

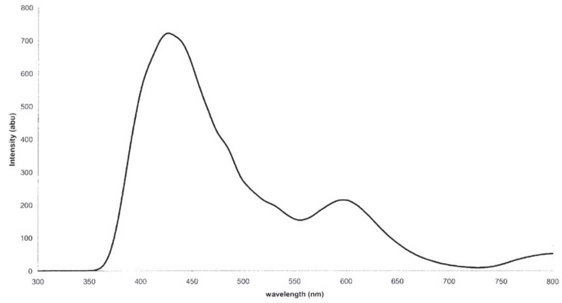

Fig. 1. The photoluminescent emission spectrum of Mn^{2+} doped ZnS quantum dots under UV light –see ref. 3.

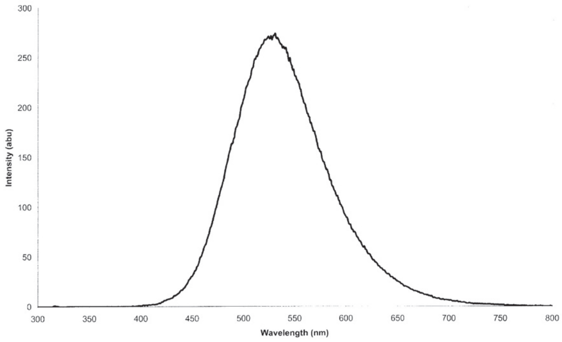

Fig. 2. The photoluminescent emission spectrum of Cu^{2+} doped ZnS quantum dots under UV light – see ref. 3

The Mn^{2+} doped ZnS quantum dots (using MSA as the colloid stabiliser) were ink-jet printed onto photocopy paper and photo quality ink-jet paper. The drop spacing was adjusted to give the highest ink loading without smearing in order to achieve the brightest image. A 15 micron drop spacing proved to be ideal. Furthermore, the image brightness could be enhanced by printing a number of passes. Similar print conditions were used for Cu^{2+} doped ZnS quantum dots.[3]

A simple rectangle printed with Mn^{2+} doped ZnS quantum dots is shown in Fig. 3. Under visible light (Fig. 3, left) the paper appears characteristically off-white and no image is discernible. However, when viewed under UV light (Fig. 3, right), the rectangle is clearly visible due to the light emission from the $^4T_1 - {}^6A_1$ transition. The paper itself appears blue due to photoluminescence under the UV light. Fig. 4 shows a more complex image of the VUW logo printed with Mn^{2+} doped quantum dots. It gives an orange image under UV light (Fig. 4, left) whereas the Cu^{2+} doped quantum dots give a green image under the same conditions (Fig. 4, right). Two passes of printing were used for the Mn^{2+} doped ZnS quantum dots and one pass for the Cu^{2+} doped ZnS quantum dots. Fig. 5 shows a printed circuit pattern printed with orange Mn^{2+} doped quantum dots.[3]

These images show that a good level of print quality and print resolution can be achieved with the quantum dot ink formulations developed here. Thus, there is excellent potential for the use of such photoluminescent quantum dots for printing images of different colours that are only visible under UV light.

Conclusion

The research has shown that photoluminescent doped zinc sulfide quantum dots have been successfully prepared and formulated into a stable ink-jet formulation. It has been used successfully to print digital characters and images that are invisible in ambient light, but are visible in different colours when viewed under UV light. The colour depends on the nature and level of dopant metal ion contained in the host ZnS lattice. Mn^{2+} doped ZnS (red-orange) and Cu^{2+} doped ZnS (green-blue) have been used here. This new technology opens up significant potential applications in the ink-jet printing of security documents and labels in single colour and full colour characters and images, and also in novel flexible photoluminescent displays and advertising.

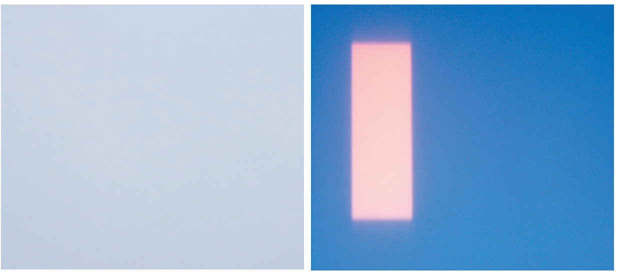

Fig.3. Photo quality ink-jet paper printed with a rectangle on Mn^{2+} doped quantum dots and viewed under ambient light (left) and UV light (right) – see ref. 3.

Fig. 4. Ink-jet paper printed logo with two passes of Mn^{2+} doped quantum dots (left) and with one pass of Cu^{2+} doped quantum dots (right) viewed under UV light – see ref. 3.

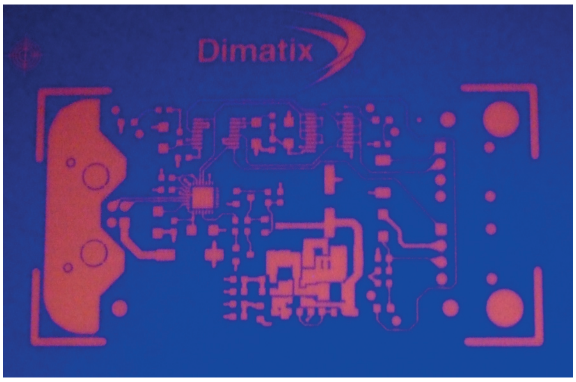

Fig. 5. A detailed ink-jet printed image of a printed circuit board template on photo quality ink-jet paper using Mn^{2+} doped ZnS quantum dots, viewed under UV light – see ref. 3.

Acknowledgement

We acknowledge the financial support received from the MacDiarmid Institute for Advanced Materials and Nanotechnology.

References

1. Vij, D.R. *Luminescence of Solids*, Plenum Press: New York, 1998.
2. Bhargava, R.N.; Gallagher, D. *Phys. Rev. Lett.* **1994***, 72,* 416-419..
3. Small, A.C. *Novel Hybrid Materials and Their Applications*. PhD Thesis, Victoria University of Wellington, **2008***,* 1-248.
4. Sooklal, K.; Cullum, B.S.; Angel, S.M.; Murphy, C.J. *J. Phys. Chem.***1996**, *100*, 4551-4555.
5. Sun, L.; Liu, C.; Liao, C.; Yan, C. *Solid State Commun,* **1999**, *111*, 483-488.