

# Quantum Dot – Fibre Composites

Andreas Zeller\* and James H. Johnston\*

\*School of Chemical and Physical Sciences, Victoria University of Wellington,  
PO Box 600, Wellington 6140, New Zealand, email: a.j.zeller@gmx.de, jim.johnston@vuw.ac.nz

## ABSTRACT

The nanotechnology research presented here is concerned with the development and characterisation of selected quantum dot materials which can be used to produce new hybrid materials comprising such quantum dots and wool and paper fibres that exhibit tuneable optical fluorescence and electronic properties, for potential use in textiles and packaging and labelling papers. ZnS, ZnO and Cu<sub>2</sub>O have been selected as they can be readily synthesised and fluoresce in the visible and UV regions. Wet chemical methods have been used to synthesise these quantum dots. The quantum dots have been attached to or incorporated into wool and paper fibre substrates either directly or by using linkers. The chemical bonding, optical and electronic properties of the new quantum dot – fibre composites have been characterised. The applications are being progressed.

**Keywords:** quantum dots, ZnS, ZnO, Cu<sub>2</sub>O, wool, paper, photoluminescence.

## 1 INTRODUCTION

Quantum dots are nano-scale inorganic semiconductor materials typically 1-10 nm in size, which exhibit interesting electroluminescent, photoluminescent, electronic, magnetic and catalytic properties. Their unique properties have attracted widespread interest and have resulted in applications ranging from optoelectronic devices such as light-emitting diodes, laser diodes and solar cells, to stable inorganic fluorophores [1], fluorescent labelling in biotechnology (e.g. biochips) and medical imaging (optical detection of certain cancerous tumours) [2]. Quantum dots offer advantages in comparison to organic fluorophores as they can be less toxic, relatively resistant to photobleaching and possess a longer lifetime/stability.

The electroluminescent and photoluminescent properties are related to the very small dimension of the nanostructure of the semiconductor crystal. An inorganic semiconductor is characterised by a band gap ( $E_g$ ) between its valence and its conduction band. By decreasing the size of the semiconductor crystal, the conduction and valence band become a continuum of individual orbital energy levels. The smaller the crystal, the more discrete are the energy levels. Hence the mobility of the electrons is limited within discrete (quantized) energy states of the nanocrystals. This is known as the “quantum confinement effect”. Due to the quantum confinement effect, quantum dots exhibit optical

fluorescence when excited thermally, electrically or by UV light. For example, when irradiated with UV light, an electron gains sufficient energy to cross the band gap from the valence band to the conduction band and leave a hole in the valence band. After a series of heat-emitting steps, the excited electron falls back from the lower edge of the conduction band (LUMO) to the hole in the top of the valence band (HOMO), by emitting light. The emitted light is the excess energy of the radiative recombination of the electron-hole pair or exciton, which corresponds to the energy value of the band gap ( $E_g = E_{LUMO} - E_{HOMO}$ ). Hence the wavelength of the emitted light is directly related to the energy of the band gap. Changes in the band gap energy have significant effects on the optical and electrical properties of the quantum dots. A decrease in the size of the quantum dot results in an increase in the band gap energy. From this, it follows that quantum dots of the same semiconductor material but with different sizes emit light in different colours. However, light emission and absorption is not only dependent on the physical dimension of the nanostructure, other factors also determine the optical properties. For example, the presence of impurity ions (dopants) in the quantum dot crystal structure can also affect the radiative recombination of the electron-hole pair. Hence an electron or hole is trapped in the energy level within the band gap introduced by a dopant. A controlled addition of small quantities of dopants into the crystal lattice can therefore be used to change the fluorescent wavelength to within the visible range.

We have applied both methods, varying the size and incorporation of metal ion impurities, for selected quantum dot materials in order to obtain tuneable fluorescent colours in the visible range and have developed new hybrid nano-materials comprising quantum dots and paper or wool fibres. Potential applications for these include security packaging and labels for the paper industry and new photoluminescent wool fibres for product authentication in the textiles and fashion industry [3-5]. The quantum dots have been attached to wool and paper fibre substrates either directly or by using linkers which provide chemical bonding between the quantum dots and the respective fibre substrates.

## 2 QUANTUM DOT SYNTHESIS

By choosing solution and sol-gel chemistry methods, the structure, size and size distribution of the quantum dots

can be controlled by changing the reaction concentrations, temperature, time, pH and the stabilizer agent. Stabilizing agents play an important role in the wet chemistry method. Very small particles exhibit a strong affinity to undergo agglomeration and oxidation processes due to the attractive van der Waals forces. This can be inhibited by shielding the semiconductor surface with an ionic capping agent (electrostatic stabilization) or by tailoring the particle surface with a polymeric dispersant (steric stabilization). The stability of the particle dispersion is not only dependent on stabilizer agents, but also on the temperature and solvent used in the wet chemistry method. If the interaction between the surfactant and the solvent is favourable, the nano-crystals remain isolated and do not agglomerate.

## 2.1 Chemical reduction method

Copper (I) oxide ( $\text{Cu}_2\text{O}$ ) quantum dots with interesting optical properties have been synthesised by a chemical reduction method in the presence of an ionic and polymeric stabilizer in aqueous solution.

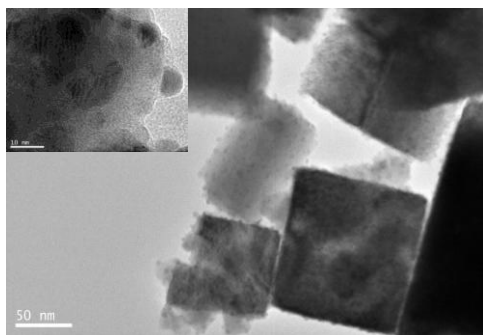


Figure 1: TEM image of regular shaped nanocubes consisting of small  $\text{Cu}_2\text{O}$  nanocrystals.

Initially, 5 nm spherical  $\text{Cu}_2\text{O}$  nanocrystals are formed by reducing aqueous copper nitrate with sodium borohydride ( $\text{NaBH}_4$ ) at  $100^\circ\text{C}$  in the presence of sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) as a capping agent and poly(methacrylic acid sodium salt) (PMAA-Na) as a polymeric dispersant. These small spherical nanocrystals successively transform over time to larger cube-shaped  $\text{Cu}_2\text{O}$  nanocrystals (Figure 1).

Sodium borohydride reduces the  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  ions which then combine with oxygen due to their high surface energy to form the small 2-5 nm  $\text{Cu}_2\text{O}$  nanocrystals. In the second step, these small  $\text{Cu}_2\text{O}$  nanocrystals aggregate to form larger cubic  $\text{Cu}_2\text{O}$  particles which range in size from about 25-250 nm depending upon the synthesis conditions (Figure 1). By changing the process parameters, it has been established that the particle size distribution is dependent principally on the stirring time and sodium borohydride concentration. These  $\text{Cu}_2\text{O}$  nanocrystals exhibit strong yellow-green colour in visible light. When excited with UV light, fluorescent peaks occur at 380, 422, 486 and 530 nm,

with the latter two being responsible for the yellow-green colour.  $\text{Cu}_2\text{O}$  nanocrystals prepared in the cubic shaped form are resistant to oxidation in air and in solution. They also exhibit an interesting dual colour effect. In suspension or coated on the inner side of glass tubes, the crystals show a red colour in transmitted light and a yellow green colour in reflected light (Figure 2). This is similar to the well known Lycurgus Cup which has nanogold and nanosilver particles in the glass matrix.



Figure 2: Colour effect of  $\text{Cu}_2\text{O}$  nanocrystals in transmitted light (left) and reflected light (right).

## 2.2 Sol-gel method

The sol-gel method is often used for the synthesis of metal oxide materials. It make use of the aqueous chemistry of metal salts (typically metal alkoxides and metal chlorides), which is dominated by the complexation with water molecules and their subsequent deprotonation (hydrolysis).  $\text{ZnO}$  nanocrystals have been prepared by a sol-gel method using a reducing agent,  $\text{NaBH}_4$ , in the presence of polyvinylpyrrolidone (PVP) with a zinc chloride solution, at a reaction temperature of  $70^\circ\text{C}$ . The addition of sodium borohydride (alkali) to the acidic zinc salt solution results in a rapid reaction whereby hydroxyl groups coordinate to the zinc ions forming reactive hydrolysed monomers or oligomers. These reactive intermediates are more likely to be involved in condensation reaction due to the higher nucleophilic properties of the  $\text{OH}^-$  ligand. The polymeric dispersant PVP stabilises the zinc ions in solution and controls the nucleation growth via the condensation reaction by the formation of a protective layer around the  $\text{ZnO}$  nanocrystals.

The resulting  $\text{ZnO}$  nanocrystals or quantum dots typically show a yellow-brown fluorescence under UV light with a maximum emission wave length of 550nm (Figure 3).

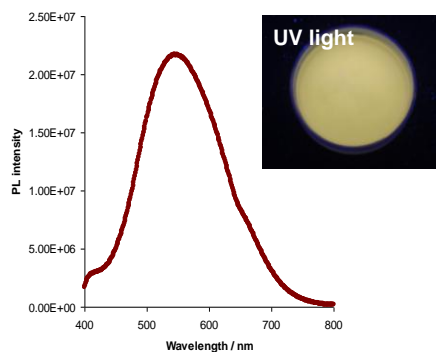


Figure 3: Optical emission spectrum of ellipsoidal shaped ZnO nano-crystals in aqueous solution.

A TEM image shows individual ZnO nanocrystals of about 5 to 10nm in size, loosely adhering to each other to form nanoclusters. (Figure 4).

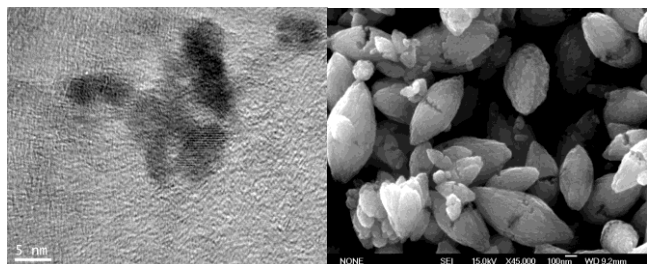


Figure 4: TEM image of ZnO nanocluster (left) and SEM image of the final polycrystalline product (right). Note the different magnifications and marker bar scales.

The presence of hydroxyl ligands (OH<sup>-</sup>) on the surface of the nanocrystals may have a destabilising effect on the particles due to the higher ionic strength of the medium. ZnO nanocrystals undergo further particle growth via coalescence and aggregation to form approximately ellipsoid shaped crystals of about 25 nm to 1µm in size, as shown by SEM (Figure 4).

### 2.3 Wet chemical precipitation method

The principle of the wet chemical method is the precipitation of a solid phase from solution during a chemical reaction by controlling the reaction equilibrium between the solid phase and solvated metal ions. This method is readily used in the synthesis of II-VI quantum dots. Zinc sulfide quantum dots have been formed by the slow addition of a Na<sub>2</sub>S solution into a ZnCl<sub>2</sub> solution in the presence of poly(methyl methacrylate) (PMMA) as a polymeric stabilizer at room temperature. This method also allows the introduction of small quantities of impurities or dopants such as Mn<sup>2+</sup> and Cu<sup>2+</sup> ions into ZnS lattice during the precipitation process. This method of adding controlled impurities into the semiconductor material is known as “doping”. As mentioned above, the nature and level of the

dopant ion(s) can be used to control the fluorescent wavelength(s). ZnS quantum dots synthesised by this method show a strong blue fluorescence under UV light. However, ZnS quantum dots doped with Mn<sup>2+</sup> exhibit a yellow-orange fluorescence and Cu<sup>2+</sup> doped ZnS quantum dots show green-grey fluorescence (Figure 5).

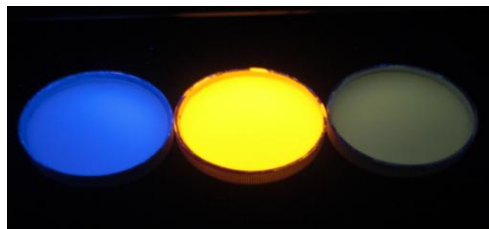


Figure 5: ZnS quantum dots in the undoped form (left), doped with Mn<sup>2+</sup> ions (centre) and Cu<sup>2+</sup> ions (right)

## 3 QUANTUM DOT – FIBRE COMPOSITES

The combination of these quantum dots with paper and wool fibres has enabled the development of new hybrid nanomaterials with photoluminescent functionality.

### 3.1 Quantum dot – paper fibre composites

Paper fibres consist mainly of cellulose which makes them an excellent choice as a substrate for the formation of a quantum dot – hybrid material. This is due to the presence and the ability of the surface hydroxyl groups on the cellulose chains to bind to various materials through hydrogen bonding. ZnS quantum dots doped with manganese ions and copper ions have already been successfully attached to *Kraft* paper fibres by members of our research group [3]. The printing of doped ZnS quantum dots directly onto fibre surfaces using modified ink-jet technology has also been successfully demonstrated [3].

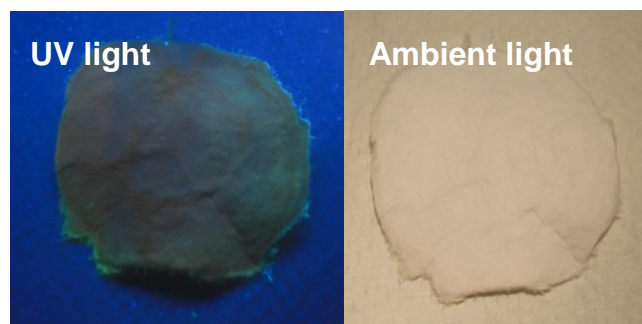


Figure 6: A ZnO paper fibre composite showing a red-orange fluorescence tinge under UV light (left), and the original off white colour under ambient light (right).

ZnO quantum dots produced by the sol-gel method described in section 2.2, can be attached to *Kraft* paper fibres. The new paper composite material shows a red-orange fluorescence tinge under UV light, whereas under ambient light it is an off white colour (Figure 6).

### 3.2 Quantum dot – wool fibre composites

The main component of wool is keratin, a structural protein, which is made up of long chains of various amino acids. The wool fibre surface is coated with an external fatty acid monolayer, which hinders the adsorption of quantum dots. Alcoholic alkali treatment has been shown to remove the lipid fatty acid mono layer and expose the underlying amino acids. This enables the quantum dot or linker molecule to bind to the nitrogen, oxygen and sulfur atoms on the surface proteins of the wool fibres.

The attachment of the quantum dots onto the wool fibre surface can take place by the use of linkers such as mercaptosuccinic acid. This can be realised by the formation of disulfide, peptide and hydrogen bonds between the quantum dot, linker and functional groups of the wool fibre substrates.

Mn<sup>2+</sup> doped and Cu<sup>2+</sup> doped ZnS quantum dots have been attached to wool fibres using mercaptosuccinic acid. Under UV light, the Mn<sup>2+</sup> doped ZnS wool composite fluoresces with a red-orange colour and the Cu<sup>2+</sup> doped ZnS wool composite fluoresces with a green colour (Figure 7). The photoluminescent emission spectrum for the Mn<sup>2+</sup> doped ZnS wool composite shows the typical fluorescent peaks for Mn<sup>2+</sup> doped quantum dots [3] (Figure 8). The peak at 460 nm is due to S<sup>2-</sup> vacancies and the peak at 590-600 nm is due to the <sup>4</sup>T<sub>1</sub>-<sup>6</sup>A<sub>1</sub> transition. The incorporation of the quantum dots onto the wool fibres essentially does not change the wavelengths of these photoluminescent emissions.



Figure 7: Photoluminescent Mn<sup>2+</sup> doped ZnS quantum dot wool fibre composite (left) and Cu<sup>2+</sup> doped ZnS quantum dot wool fibre composite (right), viewed under UV light.

It has been observed that the intensity of the photoluminescence emission decreases with time due to quenching effects. Wool fibre itself contains fluorescent amino acids, notably phenylalanine, tyrosine and tryptophan. The excitation energy of the quantum dots is transferred to the fluorescent amino acids via resonance

energy transfer, thereby decreasing the photoluminescent intensity with time.

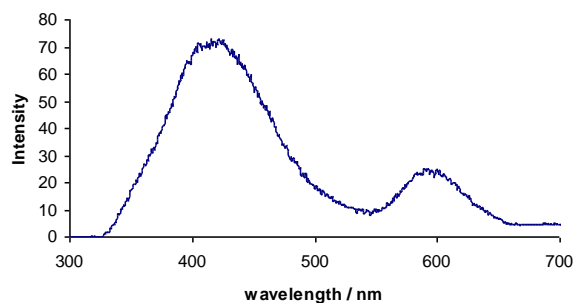


Figure 8: Photoluminescent spectrum of Mn<sup>2+</sup> doped ZnS quantum dots attached to wool fibres using mercaptosuccinic acid as the linker.

## 4 CONCLUSION

Photoluminescent quantum dots of Cu<sub>2</sub>O, ZnO, and Mn<sup>2+</sup> and Cu<sup>2+</sup> doped ZnS materials have been successfully synthesised by wet chemical methods and characterised. These have been incorporated into paper and wool fibres to produce new photoluminescent composite materials for possible security labelling and tracer applications.

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