# Synthesis and Characterization of Copper (I) Oxide and Zinc Oxide Quantum Dot Materials and the Development of New Fluorescent Fibre Composites

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## ABSTRACT

New fluorescent composites of Cu<sub>2</sub>O and ZnO quantum dots with wool and paper fibres for potential use in tuneable photoluminescent coloured textiles and packaging and labelling papers, have been developed. Cu<sub>2</sub>O quantum dots were synthesised by a wet chemical method to produce nanocubes of about 100 nm in size comprising an assemblage of small spherical nanocrystals (5 nm) with a super lattice structure. A sol-gel method was developed to synthesise ZnO quantum dots as polycrystalline particles 50 - 300 nm in size, similarly comprising agglomerations of small 10-12 nm spherical and ellipsoidal nanocrystals. ZnO quantum dot composites with wool and paper fibres were prepared by forming the quantum dots in the chemical medium surrounding the fibres and utilising cross linking reactions to bind them to the wool fibres. When 8-Hydroxyquinoline was used as a linker, it influenced and enhanced the photoluminescence properties of the ZnO wool and paper fibre composites significantly.

*Keywords*: zinc oxide quantum dots, copper (I) oxide quantum dots, 8-hydroxyquinoline, wool fibre, paper fibre, photoluminescence

# **INTRODUCTION**

Quantum dots are inorganic semiconductor materials of 1-10 nm in diameter and show electroluminescent and photoluminescent properties due to their very small dimension ("Quantum confinement effect") [1].

When these quantum dots are combined with wool and paper fibres, new photoluminescent textiles and paper products can be produced. Here we present the development of new photoluminescent composites made of  $Cu_2O$  and ZnO quantum dots with wool and paper fibres for potential use in tuneable photoluminescent textiles, and packaging and labelling papers. The photoluminescent colours of these quantum dots can be tuned by varying the particle size of the quantum dot which is controlled by the reaction conditions, and by functionalising the quantum dot surface.

Some organic fluorophores are also used for producing photoluminescent textiles or as optical brighteners. The life

time of these organic fluorophores, however, is often limited due to their sensitivity towards moisture and degradation upon long exposure to light. Quantum dots, in contrast to organic fluorophores, may show higher stabilities to external environments and a longer life time. This study therefore focussed on the use of  $Cu_2O$  and ZnO quantum dots to prepare the photoluminescent quantum dot wool and paper fibre composites. The size and shape of the quantum dot nanocrystals and their photoluminescence spectra together with the spectra of the composites have been characterised accordingly.

# COPPER (I) OXIDE AND ZINC OXIDE QUANTUM DOT MATERIALS AND THEIR WOOL AND PAPER FIBRE PLOTOLUMINESCENT COMPOSITES

Cubic Cu<sub>2</sub>O quantum dots were synthesised by a wet chemical reduction method using sodium borohydride. TEM images revealed that these nanocubes of about 100 nm in size were formed by an assemblage of small spherical nanocrystals (5 nm) with a super lattice structure (Figure 1).



**Figure 1**: Transmission electronmicroscope image of cubic  $Cu_2O$  quantum dots showing the nanocubes which comprise an assemblage of small spherical nanocrystals.

This arrangement has a strong effect on the light absorption and scattering properties of the  $Cu_2O$  suspension. Colloidal suspensions containing mainly large polycrystalline nanocubes show a dichroic effect The suspension was yellow-green in reflected light and red-

purple in transmitted light. This same effect was observed when the  $Cu_2O$  quantum dots were incorporated into a cellulose film (Figure 2). It is comparable to that shown by the Lycurgus cup which looks green in reflected light and red in transmitted light. This effect opens up interesting possibilities for applications in novel packaging and for security papers which cannot be reproduced by colour photocopying.



**Figure 2:** Cu<sub>2</sub>O quantum dots incorporated into a cellulose film appear yellow in reflected light and purple-blue in transmitted light.

Zinc oxide (ZnO) has been selected here as the quantum dot material for the development of new photoluminescent composite materials. It can be readily synthesized via a wet chemistry method and fluoresces in the visible and UV regions. Bulk ZnO is a well known II-IV semiconductor material with a wide direct band gap of 3.37 eV at room temperature and high exciton binding energy (~60 meV) [2]. It is used as an environmentally friendly, non-toxic inorganic component in various personal care products such as baby powder and sun screen lotion. In addition, ZnO prepared in nanoscale particles shows anti-bacterial, antifungal, anti-corrosion, catalytic, and UV filtering properties. The bacteriostatic and fungistatic behaviour of zinc oxide nanoparticles is well studied and because of the compatibility with skin, it makes a suitable additive for textiles and surfaces that come in contact with human skin.

Zinc oxide quantum dots (ZnO QDs) can be attached to or incorporated into wool and paper fibres respectively, either directly or through the use of linker molecules. The attachment of quantum dots with linker molecules can be achieved by the formation of disulfide -, peptide- and hydrogen bonds of the linker with the quantum dots and respective functional groups of the fibre substrates. These new fluorescent hybrid materials have potential applications in the paper industry for security packaging and labels and in the fashion industry for product authentication in textiles.

A sol-gel method was developed to prepare ZnO quantum dots as polycrystalline particles a few 100 nm in the size. A scanning electronmicroscope image shows an

agglomeration of individual ZnO nanocrystals of about 5-10 nm in size in the form of rice grain type shapes of different sizes from about 50 - 300 nm. Furthermore, ZnO nanocrystals prepared according to the sol-gel method agglomerate and precipitate as larger particles of about 1 micron in size. The precipitate can be easily re-dispersed and it shows a long photoluminescent life-time.



**Figure 3:** TEM image of ZnO quantum dots showing the polycrystalline nature of the particles.

The ZnO suspension was white under ambient light and a photoluminescent yellow-orange colour under UV light (Figure 4). When excited with UV light of  $\lambda \sim 280$  nm, an intense photoluminescent peak at 380 nm is observed in the photoluminescence spectrum (Figure 5). If the ZnO quantum dots are doped with Ce during the preparation, the photoluminescence spectrum shows a broad peak at 550 nm which increases considerably in intensity with ageing. There is a corresponding decrease in the intensity of the 380 nm peak (Figure 5).



**Figure 4:** The ZnO quantum dot suspension showing a white colour under ambient light (left) and a photoluminescent yellow colour under UV light (right).



**Figure 5:** Photoluminescence spectra of ZnO quantum dots doped with Ce measured at different times after preparation showing the change in fluorescent intensity.

The emission peak at 380nm is directly related to the radiative recombination of the electron-hole pair (exciton) in spherical zinc oxide quantum dots. The broad peak around 550 nm refers to a defect emission caused by defects on the nanocrystal surface. It is assumed that an oxygen vacancy is generated by trapping a hole in a surface state and then tunnelling it into the bulk of the ZnO nanocrystals. A shallowly trapped electron close to the band edge of the conduction band recombines with the oxygen vacancy within the band gap and causes the "trap emission" [3]. In this case, the surface state of the nanocrystals has a significant influence on the optical properties. The photoluminescent intensity at 380 nm of the ZnO suspension reduced after 10 days ageing, whereby the broad peak at 550 nm increased accordingly. This indicates that the number of surface defects increases with ageing. The synthesis of zinc oxide nanocrystals in the presence of  $Ce^{3+}$ ions reveals only one photoluminescent peak at 375 nm. The visible photoluminescence of zinc oxide is presumably suppressed by the presence of Ce<sup>3+</sup> ions. With ageing the peak shifts to the higher wavelength around 385 nm. This indicates a further crystal growth according to Ostwald ripening process.

The photoluminescent colour can also be changed by functionalising the ZnO surface with 18-methyleicosanoic acid (18-MEA), 8-Hydroxyquinoline (8-HQ) or polypyrrolidone (PVP) (Figure 6).



**Figure 6:** Photoluminescent colours of ZnO quantum dots functionalised with (A) 18-MEA; (B) 8-HQ and (C) PVP.

The combinations of ZnO QDs with paper and merino wool fibres enable the development of new composite nanomaterials with photoluminescent properties. ZnO QDs synthesized by the sol-gel method have been attached to or incorporated into wool and paper fibres respectively, either directly or by using the linker molecules L-cysteine, Mercaptosuccinic acid (MSA) and 8-Hydroxy quinolone (8-HQ). 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, 18-Methyleicosanoic acid, which may hinder the adsorption of quantum dots. Alcoholic alkali treatment has been shown to remove this layer and expose the underlying amino acids. Thereby the ZnO quantum dots can react with the nitrogen, oxygen and sulphur atoms on the surface proteins of the wool fibres. Various photoluminescent colours can be produced. When 8-HQ is used as the linker, the 8-HQ itself influences the photoluminescent colour range as shown in Figure 7.



**Figure 7:** Photoluminescent colours of Zn(8-HQ) – wool fibre composites with increasing levels of 8-HQ (left to right).

In addition with 8-HQ the colour changes with the excitation wavelength with the longer wavelength giving a more intense white colour (Figure 8).



**Figure 8:** 8-Hydroxyquinoline-Zinc-wool fibre under UVlight (left,  $\lambda_{exc} = 254$  nm / right,  $\lambda_{exc} = 366$  nm).

Paper fibres consist mainly of cellulose which makes them an excellent choice of substrate for the formation of quantum dot composite materials. The presence of surface hydroxyl groups in the cellulose chains in particular, allows the binding of various materials to it through hydrogen bonding [4]. ZnO quantum dots produced by a sol-gel method can be attached to *Kraft* paper fibres. The new ZnO quantum dot paper fibre composite shows red orange photoluminescence under UV light, whereby under ambient light it has a white colour. As with wool fibres, if 8-HQ is used to attach the ZnO quantum dots to the paper fibres, it has been shown that the photoluminescence properties of the ZnO paper fibre composites can be enhanced and a different range of colours achieved. Depending on the concentration of 8-HQ and other parameter conditions (e.g. solvent, precursor, temperature and ageing time) it is possible to tune the photoluminescent colour of the paper composites from white, light green, yellow-green to dark green, of which some colours are shown in Figure 9.



Figure 9: The photoluminescent colours of ZnO-8-Hydroxyquinoline-paper composites under UV light (above,  $\lambda_{exc} = 254$  nm) and ambient light (below).

### CONCLUSIONS

New fluorescent composites of Cu<sub>2</sub>O and ZnO quantum dots with wool and paper fibres have been developed. The fluorescent colours of these quantum dots can be tuned by varying the particle size of the quantum dot which is controlled by the reaction conditions. Cu<sub>2</sub>O quantum dots were synthesised by a wet chemical method to produce nanocubes of about 100 nm in size comprising an assemblage of small spherical nanocrystals (5 nm) with a super lattice structure. A sol-gel method was developed to synthesise ZnO quantum dots as polycrystalline particles 50 - 300 nm in the size. TEM images showed these comprise agglomerations of small 10-12 nm spherical and ellipsoidal nanocrystals. ZnO quantum dot composites with wool and paper fibres were prepared by forming the quantum dots in the chemical medium surrounding the fibres and utilising cross linking reactions to bind them to the wool fibres. The fluorescence colour of ZnO wool and paper fibre composites can be further tuned by the use of 8-Hydroxyquinoline as a photoluminescent linker. This enhances the range of colours and their photoluminescent intensities. The intensity remains nearly unchanged after long light exposure times.

#### REFERENCES

- A.A. Balandin and K.L. Wang: Handbook of Semiconductor Nanostructures and Nanodevices (5-Volume Set). American Scientific Publishers, (2006).
- [2] D. Harnath, S. Sahai and P. Joshi: Tuning of Emission in Zinc Oxide Quantum Dots. Appl. Physics letters 92, (2008).
- [3] H.S. Nalwa: Handbook of Nanostructured Materials and Technology. Academic Press, London, (2000).
- [4] Aaron C. Small and James H. Johnston: Novel Hybrid Materials of Cellulose and Doped ZnS Nanoparticles. Current Applied Physics 8, (2008).

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