

New Fluorescent Hybrid Materials Comprising Quantum Dots, Organic Fluorophores and Natural Fibre Substrates

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ABSTRACT

The research and nanotechnology presented here is dealing with the development and characterisation of new fluorescent hybrid materials comprising quantum dots and organic fluorophores respectively with wool and paper fibres that exhibit tuneable optical fluorescence and electronic properties. These new hybrid nanomaterials have potential use in textiles and packaging and labelling papers. ZnO has been selected as the quantum dot material, because it can be readily synthesised via a sol-gel method and fluoresces in the visible and UV regions. Zinc oxide quantum dots have been attached to or incorporated into wool and paper fibres respectively either directly or through the use of a linker. 8-Hydroxyquinoline (8-HQ) forms fluorescent chelates with zinc and enhances significantly the photoluminescence intensity of zinc oxide paper and wool fibre composites, if used as a linker molecule. The chemical bonding, optical and electronic properties of these new fluorescent hybrid-fibre materials have been characterised.

Keywords: zinc oxide quantum dots, sol-gel method, 8-hydroxyquinoline, wool and paper fibre, photoluminescence

1 INTRODUCTION

Fluorophores are widely used in different research and industrial areas. They are generally either small molecules or proteins (organic fluorophore) or quantum dots that show remarkable electronic and optical properties. When irradiated with ultraviolet light or excited thermally / electronically, the energy absorbed is released by the emission of light of a definite wavelength. Organic light-emitting diodes (OLED) utilise the electronic and optical properties of organic fluorophores. Some organic fluorophores are also used for dyeing fluorescent 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. 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].

Zinc oxide (ZnO) has been selected here as the quantum dot material for the development of new fluorescent hybrid 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, zinc oxide prepared in nanoscale particles shows anti-bacterial, anti-fungal, 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.

2 EXPERIMENTAL

By choosing wet chemistry methods for the synthesis of ZnO quantum dots, the structure, size and size distribution of the quantum dots can be controlled by changing the reaction concentrations, temperature, time, pH and the stabilizing agent. Stabilizing agents play an important role in the wet chemistry method. Very small particles exhibit 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 area 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.

2.1 Zinc oxide quantum dots

The sol-gel method is often used for the synthesis of metal oxide materials. It makes use of the aqueous chemistry of metal salts (typically metal alkoxides and metal chlorides), which is dominated by hydrolysis and condensation reactions. ZnO nanocrystals have been prepared by a sol-gel method using sodium borohydride (NaBH_4) as an alkali reagent in the presence of polyvinylpyrrolidone (PVP) in a zinc chloride aqueous solution at 70°C reaction temperature. The polymeric dispersant PVP stabilises the zinc ions in solution and controls the nucleation growth by forming a protection layer around the zinc oxide nanocrystals.

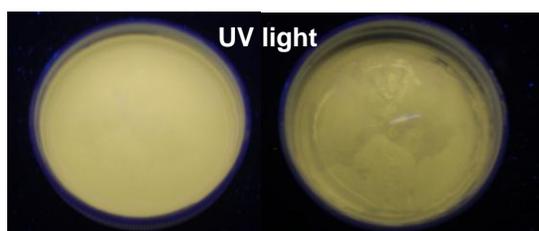


Figure 1: Optical fluorescence of ZnO nanocrystals in water (left) and dried (right) ($\lambda_{\text{exc}} = 254 \text{ nm}$).

The final zinc oxide suspension appears white under ambient light, but shows a yellow-orange fluorescence under UV light (Figure 1) with two emission wave lengths at 380 and 550 nm (Figure 2).

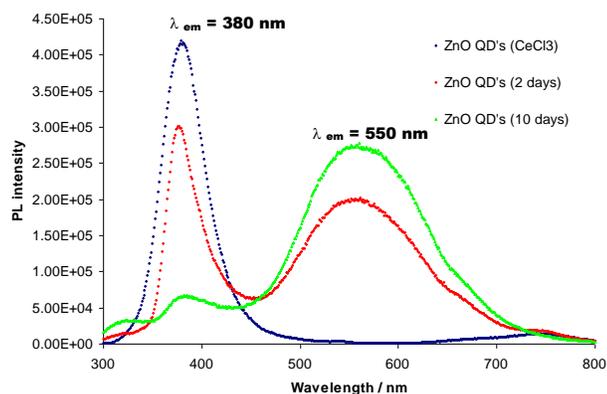


Figure 2: PL scan of ZnO QDs with and without the presence of Ce^{3+} ions ($\lambda_{\text{exc}} = 260 \text{ nm}$).

The emission peak at 380 nm 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 drastic influence on the optical properties. The photoluminescence (PL) intensity at 380 nm of the ZnO suspension was reduced after 8 days ageing, whereby the broad peak at 550 nm increased (red and green scan in Figure 2). 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 emission peak at 375 nm. The visible emission of zinc oxide is presumably suppressed by the presence of Ce^{3+} ions. With ageing (2 years), the peak shifts to the higher wavelength around 385 nm (blue scan in Figure 2). This indicates a further crystal growth according to Ostwald ripening process.

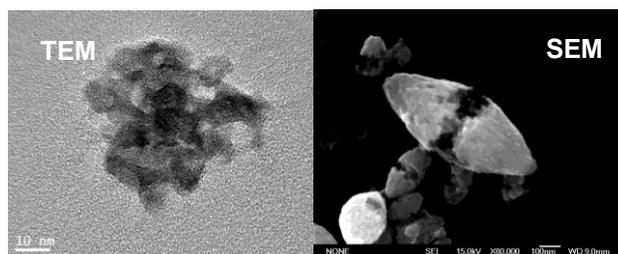


Figure 3: TEM (left) and SEM (right) image of zinc oxide nanocrystals.

TEM image in Figure 3 shows an agglomeration of individual ZnO nanocrystals with wide size distributions. These colloidal ZnO nanocrystals vary in size (5-10 nm) and adhere loosely together forming nanoclusters. The presence of Hydroxyl ligands (OH^-) on the surface of the nanocrystals may have a destabilisation effect of the particles due to the high ionic strength. Zinc oxide nanocrystals undergo a further particle growth via coalescence. They form agglomerates in a self-assembled stabilizing mechanism taking the shape of round rice grains of different sizes (25 nm to $1 \mu\text{m}$, SEM image in Figure 3). Controlling the morphology and size of zinc oxide at nanoscale is difficult. SEM observations (Figure 3) reveal that the self-assembled polycrystalline particles are not stable and split in halves. Furthermore, ZnO nanocrystals prepared according to the sol-gel method agglomerate and precipitate. The precipitate, however, can be easily re-dispersed and it shows a long fluorescence life-time.

2.2 Fluorescent – Fibre composites

The combinations of ZnO QDs with paper and merino wool create new hybrid nanomaterials with photoluminescent functionality. ZnO QDs synthesized according to the sol-gel methods mentioned in 2.1 have been attached to or incorporated into wool and paper fibres respectively either directly or by using linkers. L-cysteine, Mercaptosuccinic acid (MSA) and 8-HQ have been used as linker molecules for wool and paper fibres.

2.2.1. Fluorescent wool fibres

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 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 quantum dot can react with the nitrogen, oxygen and sulphur atoms on the surface proteins of the wool fibres.

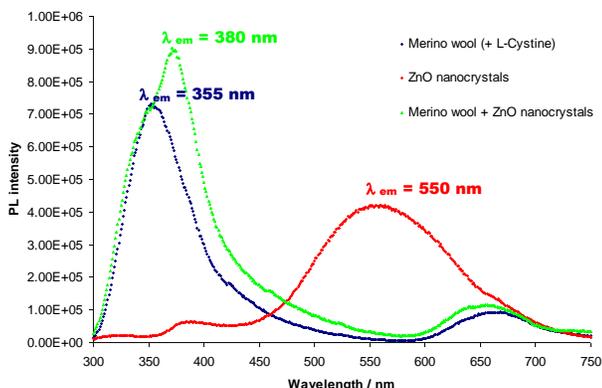


Figure 4: PL scan of ZnO QDs attached onto wool fibre using L-Cysteine as linker molecule ($\lambda_{exc} = 260\text{nm}$).

The photoluminescence spectrum in Figure 4 shows that quantum dots attached to wool fibre with L-Cysteine do not decrease the fluorescence properties of the wool fibre. Wool fibre contains fluorescent amino acids, phenylalanine, tyrosine and tryptophan and gives an overall emission peak at 355 nm ($\lambda_{exc} = 260\text{ nm}$).

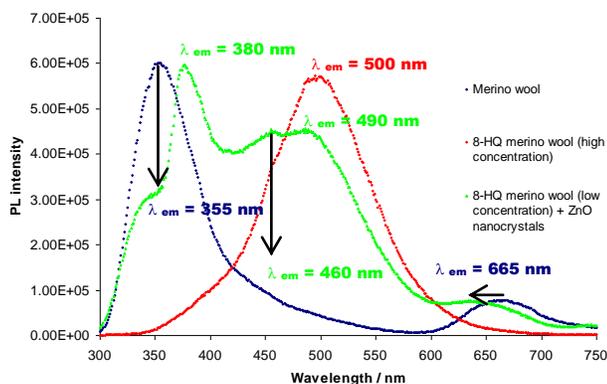


Figure 5: PL spectra of ZnO nanocrystals attached onto wool fibre using 8-HQ as linker molecule ($\lambda_{exc} = 260\text{nm}$).

In the presence of 8-Hydroxyquinoline as linker and fluorescent complex binder, the natural fluorescence of wool fibre decreases (Figure 5 & 6). 8-HQ acts as a quencher molecule for the natural fluorescence of the wool

fibre. The adsorption of high concentrated 8-HQ ethanol solution onto wool fibre results in total quenching of the emission wavelength at 355 nm and the formation of a new broad emission peak located around 490 to 500 nm depending on the amount of 8-HQ adsorption (Figure 5). Further, all scans of 8-HQ wool fibre composites show a small peak at 460 nm. This position is independent of the 8-HQ concentration.

The addition of zinc ions to 8-Hydroxyquinoline-wool composites has a marked effect on the optical properties of the composite materials. Figure 6 shows broad emission peaks of Zinc – (8-HQ wool) composites with increase in emission intensity until the shoulder peak at 460 nm which is shown after the 355 nm quenching peak. The intensity then increases to the main emission peak at 480 – 490 nm where the PL intensity increases with the concentration of 8-HQ onto the wool fibre. Also, a shift of the wavelength maxima to the red end of the spectra is observed when a higher content of 8-HQ was adsorbed onto the wool fibre.

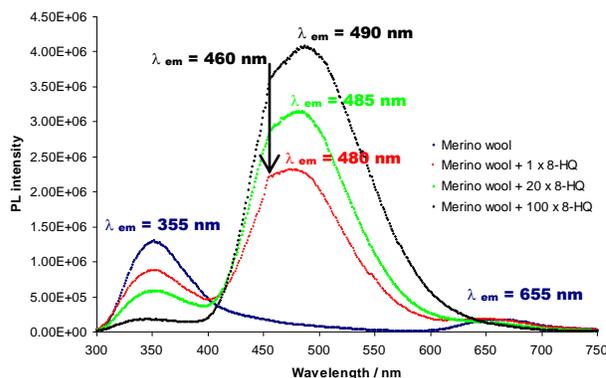


Figure 6: Emission spectra of Zinc – (8-HQ wool) composites with different contents of 8-HQ ($\lambda_{exc} = 260\text{nm}$).

The wool fibre composite prepared according this method appears white under ambient light. By applying higher concentration of 8-HQ onto the wool fibre, the wool takes on a slightly different appearance. The wool fibre composite looks shiny, which however turns into a greyish colour at higher concentration of 8-HQ. This probably indicates a polymerisation reaction of 8-HQ monomers.

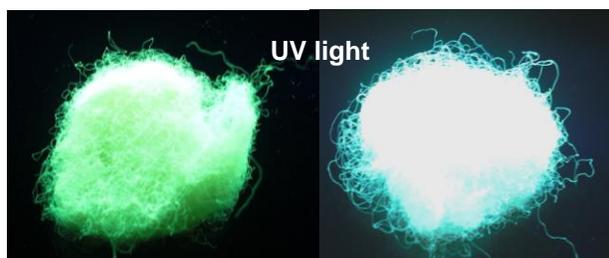


Figure 7: 8-Hydroxyquinoline-Zinc-wool fibre under UV-light (left, $\lambda_{exc} = 254\text{ nm}$ / right, $\lambda_{exc} = 366\text{ nm}$).

2.2.2. Fluorescent paper fibres

Paper fibres consist mainly of cellulose which makes them an excellent choice of substrate for the formation of quantum dot – hybrid material. 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 after a sol-gel method described in 2.1 can be attached to *Kraft* paper fibres. The new paper composite material shows red orange fluorescence under UV light, whereby under ambient light it has a white colour (Figure 8).

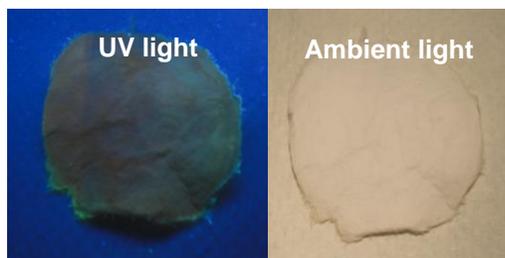


Figure 8: ZnO-paper composite under UV light (right, $\lambda_{exc} = 254$ nm) and ambient light (left).

It has been found that the fluorescence properties of the ZnO – paper fibre composites can be enhanced significantly by applying 8-Hydroxyquinoline as a fluorescent complex binder. Thereby the maxima emission wavelength of ZnO-paper shifts from 445 nm to longer wavelength in the visible spectrum (Figure 9).

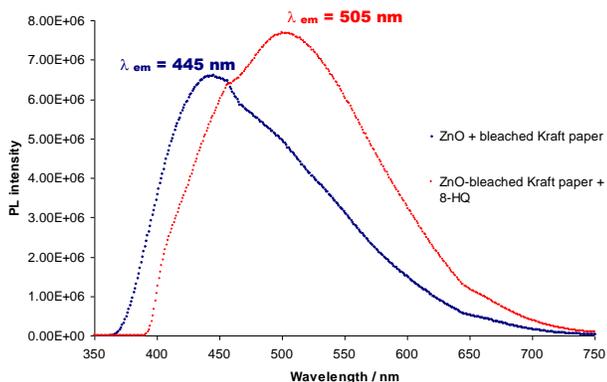


Figure 9: PL scan of ZnO-paper fibre with (red scan) and without 8-HQ (blue scan) ($\lambda_{exc} = 350$ nm).

Depending on the concentration of 8-Hydroxyquinoline and other parameter conditions (e.g. solvent, precursor, temperature and ageing time) it is possible to tune the fluorescence colour of the paper composites from white, light green, yellow-green to dark yellow (Figure 10).

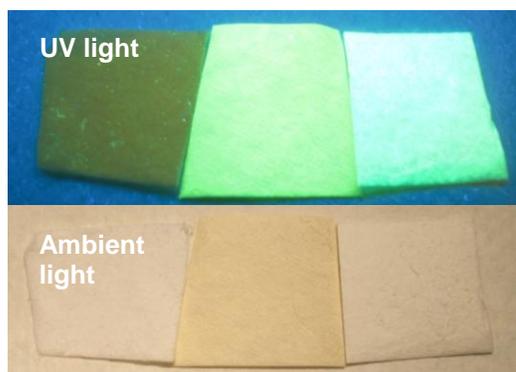


Figure 10: The fluorescence colours of ZnO-8-Hydroxyquinoline-paper composites under UV light (above, $\lambda_{exc} = 254$ nm) and ambient light (below).

3 CONCLUSIONS

The fluorescence colour of zinc oxide – wool and paper fibre composites can be tuned by the use of 8-Hydroxyquinoline as a fluorescent complex binder. Extended light exposure (photo-bleaching) results in a darkening of Zinc – (8-HQ wool) composites with a high content of 8-HQ. Light exposure also causes the progressive reduction of the fluorescence activity of these wool fibre composites. This may indicate a degradation process of the 8-HQ with UV light and that the degradation products are acting as quencher molecules. In contrast, Zinc – (8-HQ paper) composites show stable colours and the PL intensity remains nearly unchanged after extended light exposure. 8-HQ has inherent anti-microbial properties. These properties are also exhibited by the Zn-8-Hydroxyquinoline wool and paper fibre composites.

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