

Zinc Oxide Based Hydrogel for Bio-Applications

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ABSTRACT

This paper presents a novel fluorescent ZnO-Hydrogel colloidal semiconductor nanomaterials system for potential bio-medical applications like bio-imaging. High quality ZnO nanoparticles with UV band edge emission are prepared using gas evaporation method. Since biological applications require water soluble materials, ZnO nanoparticles are first dispersed in water, and their aqueous stability and fluorescence properties are enhanced by incorporating them in bio-compatible Poly N-isopropylacrylamide (PNIPAM) based hydrogel polymer matrix. Photoluminescence Spectroscopy indicates approximately 10 times enhancement in fluorescence in ZnO-Hydrogel colloidal system compared to ZnO-Water system. Ultra fast time resolved experiment demonstrates dominant exciton recombination process in ZnO-Hydrogel system compared to ZnO-Water system, confirming the surface modification of ZnO nanoparticles by hydrogel polymer matrix.

Keywords: Fluorescent semiconductor, Zinc Oxide, Hydrogel, Surface modification, Bio-applications

1 INTRODUCTION

Cell imaging generally uses conventional fluorescent dyes or organic fluorophores. The drawbacks for these routine tags are: a) poor photo stability b) narrow absorption band and c) broad emission spectra. Researchers have recently demonstrated the use of colloidal semiconductor nanocrystals known as quantum dots (QDs) such as Cadmium-Selenide (Cd-Se) and Cadmium-Telluride (Cd-Te) as high efficient fluorophores [1]. Cd-Se and Cd-Te nanocompounds are highly luminescent materials with improved efficiency and high photo stability; however, the toxic nature of Cd element poses a major problem in bio-applications especially in in-vivo imaging [2, 3] and hence requires complicated surface treatments. ZnO nanoparticles are wide band gap fluorescent semiconductors with band edge emission at 3.3 eV and large exciton binding energy of 60 meV [4]. Also, they are low toxic with high photo stability [3]. Therefore, ZnO can be elected as a potential replacement for conventional dyes and toxic quantum dots in bio-medical applications.

Biological applications require water soluble materials. Successful dispersion of ZnO nanoparticles in water using ball milling method has been reported [5], but the reproducibility and stability of this method is unpredictable. Also, luminescence of ZnO particles is subject to aging because of the formation of hydroxides at their surface, leading to quenched luminescence [6]. Therefore, appropriate surface modifications of ZnO particles are necessary. Tailoring the optical properties of ZnO particles capped with various polymers (PMMA, PEG etc) have been investigated [7, 8].

Hydrogel are randomly cross linked hydrophilic polymer networks with 97% (weight %) of water filling interstitial spaces. Hydrogel absorb water or aqueous solvents to become colloidal dispersions and undergo large volume changes in response to external stimuli such as temperature, pH, ion concentration, electric field, magnetic field, solvent composition and light [9, 10]. Hydrogel made of Poly N-isopropylacrylamide (PNIPAM) due to their aqueous inner environment, bio-compatibility and feasibility for conjugating with bio-molecules have been used for applications such as drug delivery, artificial muscles, sensors and actuators, and micro valves for lab-on-a chip[11,12,13]. As PNIPAM hydrogel is not fluorescent, incorporation of ZnO nanoparticles in hydrogel offers a new hybrid material system for developing a biological marker with high sensitivity.

In this paper, synthesis of ZnO nanoparticles and their surface modification using PNIPAM hydrogel to make an aqueous stable and biocompatible material with enhanced optical properties is investigated. The optical properties of ZnO-Hydrogel colloidal dispersion versus ZnO-Water dispersion were analyzed.

2 EXPERIMENTAL DETAILS

2.1 Material Synthesis

Synthesis of ZnO: The ZnO nanoparticles are synthesized using gas evaporation method as reported in reference 5. This process does not use any catalyst or precursors. Metallic Zinc and air are used as source materials. In this method, carbon tip is used as cathode and Zinc ingot is used as anode. The production chamber is vacuumed initially and then filled with air, which is used as Oxygen source. When current is applied between carbon cathode and Zinc

ingot, an arc is generated resulting in high temperature, which evaporates Zinc. This vaporized zinc in turn reacts with the incoming oxygen to produce ZnO nanoparticles and settles on the inner walls of the chamber. Since ZnO is insoluble in water, Ball Milling method is employed to disperse the ZnO nanoparticles in water. The smaller sized particles disperse well into the solvent and the denser particles are deposited at the bottom. Pure dispersion of ZnO in water is separated from the precipitate and is centrifuged at lower speed to remove large particles. Compared to chemical route, organic contaminants on the surface of ZnO nanoparticles can be avoided in this synthesis process as the material is physically evaporated in the absence of any precursors [14].

Synthesis of PNIPAM Hydrogel: PNIPAM hydrogel is synthesized chemically by precipitation polymerization method, in which N-Isopropylacrylamide (NIPAM) is used as the main monomer. Appropriate quantities of NIPA monomer, co-monomer (allylamine) and cross linker (N, N'-Methylene bisacrylamide) were mixed in water, and purged with nitrogen gas to remove oxygen produced by the reflux action. The mixture was heated to approximately 60°C and the initiator was added to initiate the reaction. After crosslinking for 5 hours, the colloidal suspension was dialyzed for 7 days to remove any non-reacted reagents followed by centrifugation and washing with water to remove any impurities. The precipitate was then re-dispersed in water to obtain hydrogel colloidal solution. The synthesis process of PNIPAM hydrogel is shown in figure 1. Co-monomers are chosen according to the requirement of the gel functional group for specific applications. PNIPAM-co-allylamine (PNIPAM-aa) hydrogel with positively charged amine ($-\text{NH}_2^+$) functional group is used in this study.

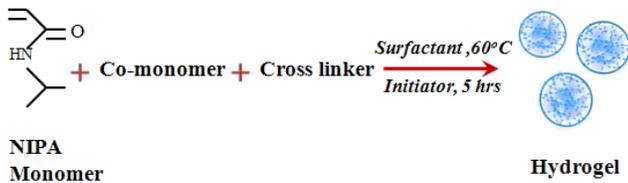


Figure 1 Synthesis process of PNIPAM hydrogel

Surface Modification of ZnO: For surface modification process, ZnO dispersed in water was used as reagent, because ZnO-water dispersion is assumed to have smaller size particles compared to ZnO in powder form. 2ml of 1.26wt% ZnO-water solution was first homogenized by stirring at room temperature for few minutes. 2ml of 2wt% PNIPAM-aa hydrogel was added to 10 ml of water and stirred for 5 minutes to mono disperse the gel particles to form colloidal hydrogel solution. The homogenized ZnO-water solution was added to this hydrogel solution and the mixture was stirred at room temperature for about 24 hours, which was then centrifuged at 1000rpm for about 3 hours

and then re-dispersed in hydrogel. It is observed that ZnO dispersion stability is high in hydrogel medium compared to water. It is presumed that the hydrogel with positive charged NH_2^+ ions is adsorbed on the surface of negatively charged ZnO nanoparticles.

2.2 Characterization

The optical properties of ZnO-Hydrogel colloidal dispersion versus ZnO-Water dispersion were analyzed. For comparison purposes, concentration of ZnO in both the samples was maintained constant. The sizes of the ZnO and hydrogel particles were measured optically using Dynamic Light Scattering (DLS) using ALV/DLS/SLS – 5000 equipped with an ALV – 5000 digital time correlator. The excitation source was a He-Ne at a wavelength of 632 nm. Photoluminescence (PL) spectroscopy was used to measure the fluorescence from the samples. PL spectrum was measured using a He-Cd laser with an excitation wavelength of 325 nm. Fluorescence decay mechanisms and life times of the samples were measured using Time Resolved PL (TRPL) spectroscopy. A Ti: Sapphire mode-locked laser was used as excitation source with an excitation wavelength of 350 nm, which was obtained by doubling 700nm output laser line using a non-linear BBO (β -Barium Borate) crystal. The pulses have a repetition rate of 80 MHz and pulse duration of 30 ps with a power output of 0.8 mW. Exposure time used was 2 ns. A Hamamatsu synchroscan streak camera with a resolution of 30ps was used to acquire the fluorescence signal.

3 RESULTS

Figure 2 shows the fluorescence spectra of ZnO in hydrogel compared to ZnO in water at room temperature. The emission peak maximum of both the samples is at 376 nm, which corresponds to the band-edge emission of ZnO.

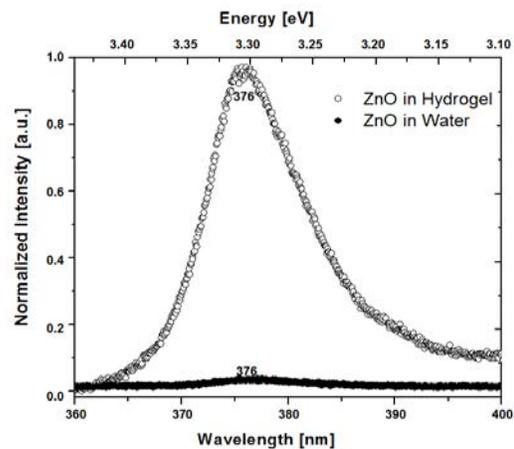


Figure 2 Photoluminescence spectra of ZnO in hydrogel (open circle) and ZnO in water (solid circle) at room temperature; both samples have same concentration of ZnO.

The spectra indicates approximately 10 times enhancement of fluorescence in ZnO-Hydrogel colloidal system compared to ZnO-Water system. This enhancement is attributed to the surface modification of ZnO nanoparticles by hydrogel polymer networks. We postulate that the surfaces of ZnO particles are modified by the adsorption of microgel particles on the ZnO surface. Since, hydrogel consists of microspheres of polymeric networks filled with water; it introduces scattering centers in ZnO-Hydrogel hybrid system. These scattering centers increase the area of absorption cross-section of ZnO-hydrogel hybrid system, and hence increase the luminescence.

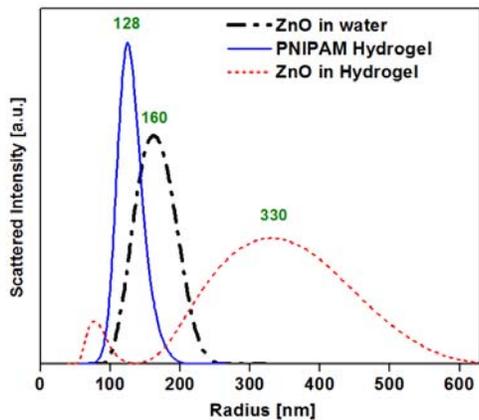


Figure 3 Particle size change before and after addition of ZnO nanoparticles to PNIPAM-aa hydrogel solution

Size distributions of the samples before and after the surface modification process are shown in figure 3. PNIPAM hydrogel particles are narrowly distributed with hydrodynamic radius (R_h) around 128 nm, whereas ZnO in water show an average hydrodynamic radius (R_h) around 160 nm. The ZnO-hydrogel hybrid nanomaterials system shows an average hydrodynamic radius around 330nm with a wide distribution confirming the dispersion of ZnO nanoparticles within the PNIPAM-aa hydrogel colloidal solution. The increase in particle size of ZnO-hydrogel is attributed to the surface capping of ZnO particles by hydrogel polymer chains.

Figure 4 shows the room temperature time resolved PL of ZnO-Hydrogel and ZnO in water dispersions. The decay constants are fitted using a bi-exponential model over a spectral window of 5 nm around the PL peak maximum. Table 1 shows the decay constants and amplitude ratios of both the samples. TRPL studies at room temperature showed that there is no significant change in the recombination dynamics involved in the fluorescence emission between both the samples.

Sample	τ_1 [ps]	τ_2 [ps]	A_2/A_1
ZnO in Water	53.73±2.7	367.16±18.5	0.046
ZnO in Hydrogel	75.74±2.4	496.87±19.2	11.12

Table 1 Fluorescence decay parameters from bi-exponential fits of the TRPL data

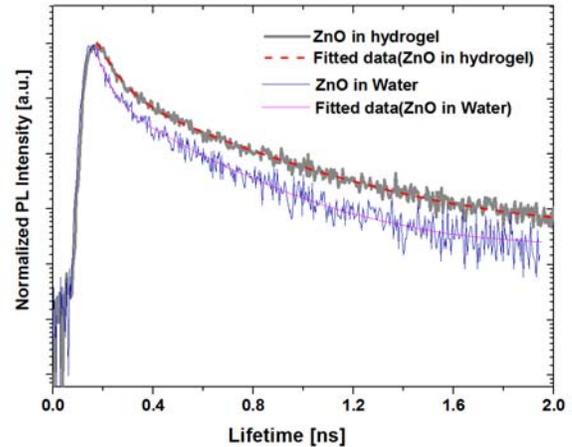


Figure 4 Time Resolved Photoluminescence of ZnO in hydrogel and ZnO in water at room temperature

The faster decay constants τ_1 is assigned to the non radiative process induced by surface states and slower decay constant τ_2 is assigned to the radiative recombination process by excitons. The relative magnitude of slow decaying component to the fast one (A_2/A_1) indicates dominant non radiative processes in ZnO in water sample, whereas ZnO in hydrogel shows dominant radiative process. Dominant non radiative processes in ZnO in water is believed to be due to the surface defects caused by the ball milling procedure, and also due to the formation of hydroxides on the ZnO surface. Dominant radiative process in ZnO-Hydrogel hybrid system confirms passivation of ZnO particle surfaces ensuring stable exciton emission.

4 CONCLUSIONS

We have developed a novel nontoxic fluorescent ZnO-Hydrogel colloidal semiconductor nanomaterials system via surface capping fluorescent ZnO nanoparticles using PNIPAM-aa hydrogel. It is observed that the surface of nanoparticles can be modified to enhance the optical properties. A significant enhancement of the emission from ZnO nanoparticles are observed when these nanoparticles are functionalized with PNIPAM hydrogel. The amplitudes of fluorescence decay curves confirm that the enhancement

in emission is due to the increase in effective radiative recombination process.

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