JNBT
ⓒ2006INBDK

JNBT, Vol 3, No 2, pp. 66-69

Formation and optical characteristics of water dispersible semiconductor nanocrystals

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ABSTRACT

Recent advancesin the synthetic research area on the water dispersible nanosized semiconductors are described. Even though semiconductor nanocrystals have much better optical properties to be introduced in a biological sensor system rather than commercial dyes used for the same purpose, they have been hardly used due to the poor solubility in water solvent. To overcome this problem several polar ligands were introduced to offer a water soluble nature to the hydrophobic nanocrystals by capping their surfaces. In this paper, recently developed polar ligands and their capping methods were summarized.

Key words : nanocrystal, water dispersible, quantum dot, biocompatible nanomaterials, capping ligands

Nano-size semiconductor materials have obtained considerable interest during the past decade (1, 2). These materials are widely used in various applied technological fields such as photoelectronic devices or even for advanced biotechnology due to their size dependant physical and optical properties (3-5). Recently various nanocrystallites such as ZnSe, CdS, ZnS, and CdSeare reported in the literature (6-8). In addition, it has been reported that when the surface of those nanocrystals is passivated by ZnS, a core shell type quantum dot is formed and the quantum yield and PL intensity are greatly improved compared to that for the bare nanocrystals (9). For instance, the ZnSe/ ZnS nanocrystal was prepared from the reaction of diethyl zinc with solvent coordinated selenium in a hot solvent, giving the core ZnSe, and then the reaction of diethyl zinc with hexamethyldisilathiane for the shell ZnS layer. The measured ZnSe/ZnS particle sizes via a TEM image were in the range of 3.5 – 4.6 nm, and the luminescence quantum yield for the ZnSe/ZnS nanocrystal was up to 20 times more than that for the bare ZnSe (9).

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Water dispersible nanocrystal materials were originally developed to be applied for biosensor materials, which directly bond to biomolecules such as DNAs or proteins (10-12). Those materials are not health-hazardous or radioactive like currently used biosensor materials. Semiconductor nanocrystals are also proven to be much more efficient, sensitive, and stable than the organic dyes used for the same purpose. The most common assay method is to prepare water soluble quantum dots by capping their surface with polar solvent molecules such as mercatoacetic acid, aminoacid or dihydrolipoic acid; then the target biomolecules are attached via covalent bonding or self assembly. In this area CdSe/ZnS or CdS/ZnS quantum dots are most commonly used since theiremission wave lengths are in the visible light region (2, 6). The CdS core and ZnS shell have a lattice mismatch of 7%, and their band gaps are 2.58 and 3.83 eV, respectively (13). Recently Eychmuller et. al. reported synthesis of a water-soluble ZnSe (14). The hydrophobic semi-

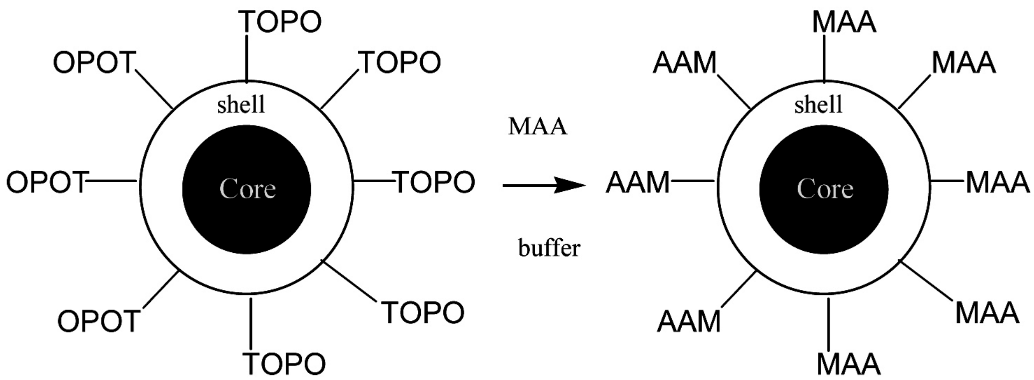

Fig 1. Schematic diagram of the convergence form a hydrophobic nanocrystal to a water soluble nanocrystal

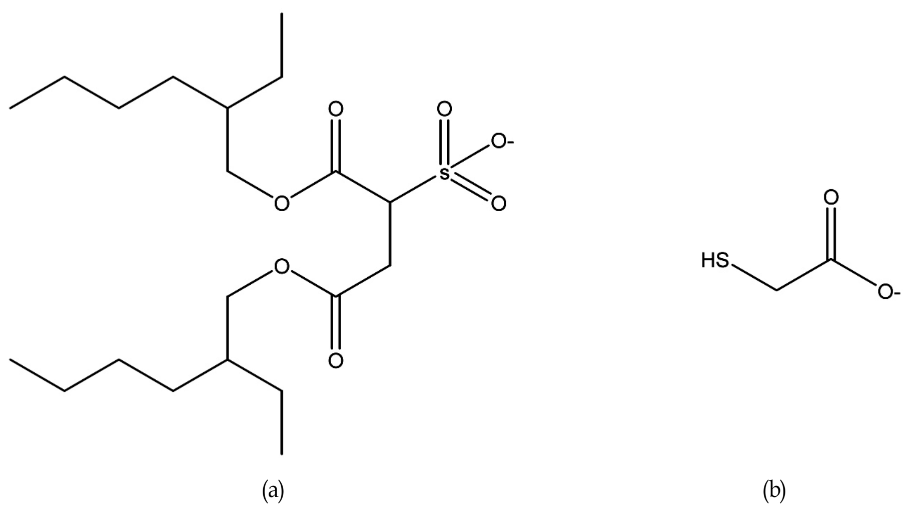

Fig 2. Typical hydrophilic capping ligands; (a) bis(2-ethylhexyl) sulfosuccinate (AOT) (b) mercaptoacetate (MAA)

conductor was passivated with thiol stabilizers and further photochemical treatment caused significant enhancement in PL intensity. The water soluble nanocrystal ZnSe was used for the fabrication of UV-blue emitting film, which can be applied in various areas, including biotechnology. The most common synthetic scheme for the ZnSe nanocrystal is from thermal decomposition reactions of air-sensitiveorganometallic precursors: diethylzinc (15) or organoselenium (16, 17) compounds in coordinating hot solvents. Optical properties of the ZnSe nanocrystals have been shown to be strongly depending on the mixing temperature of the zinc and selenium precursors in the coordinating solvent (18). **Fig 1** shows a representative preparation scheme for a water dispersible quantum dot from a hydrophobic nanocrystal.

Selecting the capping material depends on the band gap difference and lattice mismatch rate. One of the best matches; for instance, for the ZnSe nanocrystal should be ZnS nanocrystal shell, where the band gaps for ZnSe is 2.72 eV and 3.80 eV for ZnS. In addition, the lattice mismatch for the ZnS with the core ZnSe is about 4.6% (19). The shell layer was also prepared via a thermal decomposition reaction of organometallic zinc precursor with $(TMS)_2S$ in a hot coordinating solvent. Capping the surface of a nanosize material has been shown to cause a remarkable increase in Photo Luminescence intensity (9, 17). The passivation of the core does not change absorption or emission features but greatly increases the quantum yield of the core material (20). Water-soluble semiconductor nanocrystals were developed for fluorescent labeling technologies especially to be applied in biology (11, 18). Unfortunately, most highly luminescent

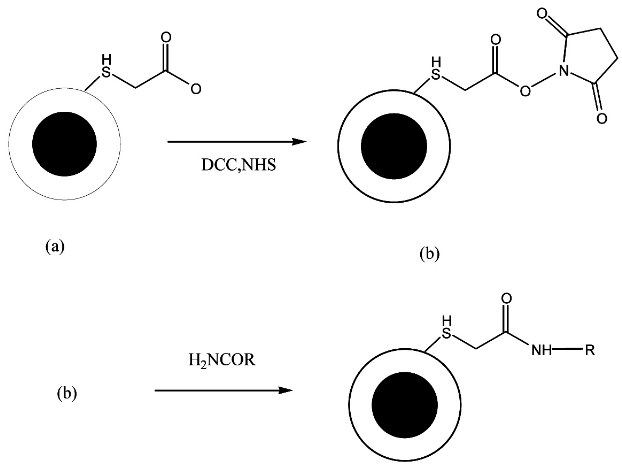

Fig 3. Schematic diagram of a typical bioconjugation process of MAA capped QD to a biomolecule: (a) MAA capped QD, (b) NHS-carboxylate intermediate

semiconductor nanocrystals are grown in hydrophobic media so that they are hardly compatible with biological systems. There are several reports of solubilizedhydrophobic nanocrystals in water (21-23). For instance, the surface of CdSe/ZnS semiconductor nanocrystal were coated with silica, mercaptoacetic acid, or dihydolipoic acid in buffer solution and they were claimed to be water soluble semiconductor nanocrystals.

Fig 2 shows most commonly used polar capping agents for the preparation of water dispersible nanocrystals. The polar Mercaptoacatate (MAA) and AOT coated nanocrystals are water dispersible and readily conjugated various biomolecules such as protein or DNA. Recently Bharali *et. al* (24). reported synthesis of InP/ZnS core-shell quantum dot and its bioconjugation with folic acid. They demonstrated that the receptor mediated delivery of folic acid conjugated QD into folate-receptor-positive cell line such as KB cells. Those QDs were cofirmed by using two-photon excitation and imaging by fluorescence. **Fig 3** presents a general scheme of bioconjugation process for a water soluble nanocrystallite. The potentialfor multiphoton imaging provides the possibility for longer term imaging of cellular processes, with less damage than UV-excited imaging. In addition, quantum dots are a key probe for multicolor fluorescence microscopy and multiphoton microscopy since they are fairly photostable and their fluorescence lights are bright enough for various imaging tasks.

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(Received June 20, 2006; Accepted July 28, 2006)