Fluorescent Semiconductor Nanocrystals, A Promising Fluorescent Anti-Counterfeiting Material for Specialty Paper

Qijie Chen,^{a,b,*} Fushan Chen,^c and Yongxiang Yan^a

Fluorescent semiconductor nanocrystals, also called quantum dots (QDs), have unique electronic and optical properties. One of the most useful features of QDs is that whereas their absorption spectra are broad, their emission spectra are very narrow. Different QDs can emit different wavelengths of visible light under UV excitation. QDs as a fluorescent anti-counterfeiting material have been attracting great interest in the application of specialty papers, such as security paper, banknote paper, packaging paper, *etc.* An anti-counterfeiting technique using QDs is one of the newest achievements in the anti-counterfeiting field. In the long run, research and development in the area of QDs anti-counterfeiting will surely create many fruitful results.

Keywords: Fluorescent semiconductor nanocrystals; Quantum dots (QDs); Fluorescent properties; Anti-counterfeiting properties; Special paper

Contact information: a: Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha, Hunan Province, 410004, People's Republic of China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong Province, 510640, People's Republic of China; c: College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, Shandong Province, 266042, People's Republic of China; * Corresponding author: chenqijie@126.com

Introduction

Fluorescent semiconductor nanocrystals, also called quantum dots (QDs), are nanometer-sized polyhedra. Quantum dots possess unique size-dependent properties because of their very small size (generally 1 to 10 nm). Representative semiconductor metal chalcogenide-based (compounds consisting of at least one element of S, Se, or Te) QDs are: ZnS, ZnSe, CdS, CdSe, CdTe, PbS, and PbSe. Compared with traditional organic dye molecules and the other fluorescent molecules, inorganic QDs are much more stable under relatively harsh conditions. QDs have unique optical properties such as high quantum yield and broad absorption with narrow, symmetric photoluminescence spectra. The photoluminescence properties of QDs can be characterized by three parameters: emission wavelength, full width at half maximum (FWHM), and quantum efficiency (or quantum yield). One of the most useful features of QDs is that their emissions spectra are very narrow (typically 20 to 30 nm for the FWHM of the emission spectrum peak). The emission wavelength of QDs is strongly dependent on particle size, and the FWHM is dependent on the size distribution of the nanoparticles. For example, CdSe QDs can emit different wavelengths of visible light under UV excitation depending on their size. The surface of the ODs affects the quantum efficiency greatly because of the extremely high surface-to-volume ratio of such small nanoparticles.

QDs are usually used as core-shell structures, as the wider band-gap semiconductor shell material improves fluorescent properties, passivates the core, and prevents leaching. High-quality QDs are most commonly synthesized in organic solution at high temperatures using pyrophoric precursors, and they are surface-stabilized with hydrophobic organic ligands that lack aqueous solubility.

Application and Challenges

With the development of economic systems, anti-counterfeiting technology has developed rapidly, and specialty paper for anti-counterfeiting is widely used in many fields. Because of their unique electronic and optical properties resulting from the quantum size effect, QDs have been attracting a great interest for anti-counterfeiting applications.

A novel fluorescent ink including QDs has been studied. By adjusting the particle size and the concentration of QDs, the QDs ink can form a special fluorescent code. When the QDs ink is coated or printed on the matter surface, a unique anti-counterfeiting code is incorporated into the paper. Based on calculation, a set of QDs having six different particle sizes and ten different QDs concentrations can form one million unique fluorescent codes. The special fluorescent QDs ink can perform an anti-counterfeiting function when used in passports, ID cards, *etc.* Also, QDs as the fluorescent anti-counterfeiting material have great promise for applications in specialty papers, such as security paper, banknote paper, packaging paper, *etc.*

QDs can be used as anti-counterfeiting fluorescent materials:

- The different QDs can emit different wavelengths of visible light under UV excitation. The different spectra of emitted light can function as the anti-counterfeiting codes.
- Mixtures of the same QDs with different particle size can emit different wavelengths of visible light under UV excitation. The QDs anti-counterfeiting code can be specified according to the mixture proportion.
- Mixtures of different QDs can emit different wavelengths of visible light under UV excitation. In recent work, the proportion of different QDs has been controlled and the anti-counterfeiting code has been confirmed.
- Different QDs concentration and proportion can build up many anticounterfeiting codes and incorporate specific anti-counterfeiting information.

Also, for all anti-counterfeiting applications in the specialty paper, QDs carriers are very important. The QDs carriers should not influence the characteristics of QDs, and especially they must not quench the QDs fluorescence. Starch derivatives, cellulose derivatives, and nanocrystalline cellulose are promising carriers for the QDs.

The world is usually full of challenges and opportunities. This is also true for anticounterfeiting paper production. Future research and development in the area of QDs anti-counterfeiting technique can be expected to provide fruitful revolutions, including new insights, new possibilities, and new products.

Acknowledgements

The authors would like to acknowledge support from the Foundation (No.201001) of State Key Laboratory of Pulp and Paper Engineering (South China University of Technology) and the Foundation (No.2012CL02) of Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation (Changsha University of Science & Technology), P. R. China.