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Research Paper

Solid state effective luminescent probe based on CdSe@CdS/amphiphilic *co*-polyarylene ether nitrile core-shell superparticles for Ag^+ detection and optical strain sensing

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ABSTRACT

In this work, a novel amphiphilic copolymer named polyarylene ether nitrile (amPEN) was synthesized and further employed to encapsulate oleic acid (OA) capped CdSe@CdS QD via one-step microemulsion self-assembling, which contributed to the facile fabrication of water dispersible QD/amPEN core-shell superparticles (SP) showing dual emissive feature. It was found that the obtained QD/amPEN core-shell SP can be employed as the sensitive and selective fluorescent probe for determination of trace concentration of Ag^+ down to 1 nM via the photo-induced electron transfer. More interestingly, the obtained QD/amPEN core-shell SP can be integrated with polydimethylsiloxane (PDMS) to fabricate robust luminescent solid state films that still demonstrated sensitive detection of Ag^+ even after placing in water for six days. Furthermore, the QD/amPEN core-shell SP doped PDMS film exhibited the stretching dependent luminescent emission, which implied the composite materials could be also developed as flexible optical strain sensors. Given the facile fabrication and competitive sensing performance both in solution phase and solid state, the present work basically provides a universal strategy for the construction of versatile multifunctional luminescent sensors using QD and polyarylene ethers as building blocks.

1. Introduction

Fluorescence sensor has been widely considered as one of major candidates for the chemo-sensing of various metal cations mainly due to the simplicity, sensitive luminescence signals and availability of tremendous luminescent probes [1]. Generally, the fluorescence properties of sensor probes, including emission intensity and wavelength, can be specifically alternated in the presence of targeted metal ions via several mechanisms such as paramagnetic fluorescence quenching [2], photoinduced electron transfer (PET) [3], photoinduced charge transfer (PCT) [4], fluorescence resonance energy transfer (FRET) [5], excimer or exciplex formation [6], irreversible reaction-based chemodosimeters [7], etc. Thus, the fluorescent probe is one of the most important components for any practical fluorescence chemosensors. Semiconductor quantum dots (QD) have been intensively employed as the promising fluorescent probe in (bio)-chemical analysis and bio-imaging, mainly due to their high fluorescence quantum yield, size dependent emission with narrow bandwidth, wide excitation wavelength range as well as optical stability against photobleaching [8]. In order to act as effective optical transducer for detection of aqueous metal ions, the luminescent QD probe should be water soluble and modified with specific ligand. However, the classical QD with high fluorescence quantum yield are typically synthesized via the solvothermal pyrolysis and surface modified with hydrophobic capping agent, which implies that the phase transfer of hydrophobic QD into aqueous solution and further surface modification are indispensable steps for their practical application of metal ions determination [9]. Although various covalently chemical modification strategies have been used for preparation of water soluble QD-ligand nanoconjugates, the tedious experimental steps and additional chemical reactions would result to obvious declining of QD fluorescence quantum yields. Therefore, the facile modifications of QD via non-covalent or physical manipulation protocols are still strongly required.

Microemulsion is a thermodynamically stable system that can be explored to obtain organic nanostructures with different

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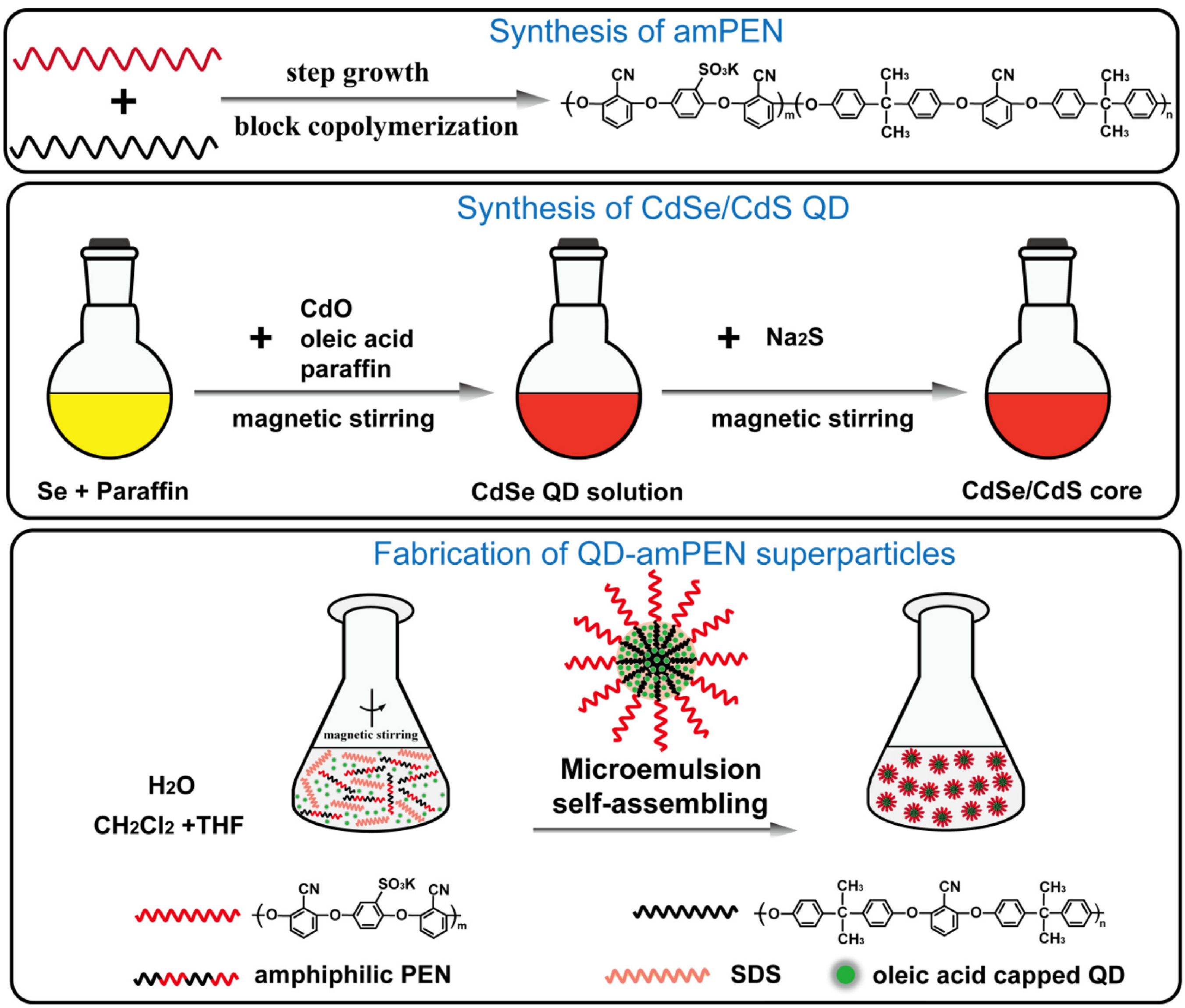
morphology to fulfill diverse functionalities ranging from nanoreactor for chemistry reaction, precise nanoparticle synthesis, vehicles for drug delivery to loading of sensitive functional molecules or probes, etc [10]. Meanwhile, the self-assembling of amphiphilic polymers in immiscible solvents is considered as a powerful and effective tool for the construction of hierarchical nanostructures [11]. For instance, William Yu, et al. has previously reported that the amino terminated polyethylene glycol (PEG) was grafted onto an alternating copolymer named of polymaleic anhydride-alt-1-octadecene (PMAO) to obtain the amphiphilic copolymer of PMAO-PEG, which can effectively transform hydrophobic OA-capped QD into water solution with same fluorescence emission and quantum yield [12]. In addition, other alkylated polymers including polymaleic anhydride-alt-tetradecene (PMAT) [13], PEG grafted triblock polymers [14], polyisoprene block ethylene glycol [15], polystyrene-*co*-maleic anhydride [16], amphiphilic polyethyleneimine (am-PEI) [17], etc., have also been explored to successfully transfer hydrophobic QD into aqueous solution via microemulsion self-assembling technique. Although the water soluble QD-copolymer conjugates with promising fluorescent properties have been fabricated and evaluated in various biosensing or bioimaging applications in the above mentioned reports, the used amphiphilic polymers are basically non-luminescent, meanwhile the obtained QD-copolymer conjugates still need to be modified with specific ligand and are hardly fabricated into solid state films. It should be noted that the solid-state sensors are advantageous in terms of easier regeneration and possible repeated uses when compared to the conventional single-use liquid phase analytical system [18], moreover the flexible solid state films contain fluorophores can be constructed as optical strain sensor as long as stretching dependent luminescence is realized [19]. However, the majority of fluorescent (bio)-chemical sensors demonstrated sharply deteriorated analytical performance in solid state because of strong fluorescence quenching. Therefore, the facile preparation of hybrid nanostructures showing robust multi-band fluorescence emission both in solution phase and solid state still remains a great challenge. In addition, the amphiphilic copolymers involved in majority of published work are aliphatic or chain polymerized macromolecules with poor mechanical properties and thermal stability [20], while the self-assembling of amphiphilic aromatic polymers derived from step-polymerization showing enhanced intermolecular interaction is quite limited.



Scheme 1. The illustration for chemical synthesis of amPEN and OA-capped QD and the fabrication of QD/amPEN core-shell superparticles (SP) via microemulsion self-assembling.