



Fluorescent nanoparticles from starch: Facile preparation, tunable luminescence and bioimaging

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ABSTRACT

Fluorescent organic nanoparticles (FONs) based on carbohydrate polymers were prepared through one-pot hydrothermal treatment of starch in the presence of polyethyleneimine. These FONs (named as PEI-Starch FONs) were characterized by a series of techniques including UV–Vis absorption spectroscopy, fluorescent spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. Results showed that the size of PEI-Starch FONs is 10–30 nm. The PEI-Starch FONs exhibited high water dispersibility because of the existence of hydrophilic functional groups on their surface. After excited with different wavelength, PEI-Starch FONs emitted strong and excitation-dependent fluorescence. To evaluate their potential for biomedical applications, biocompatibility and cell uptake behavior of PEI-Starch FONs were further investigated. We demonstrated that PEI-Starch FONs are biocompatible with cells and can be easily internalized by cells within 3 h. Taken together, novel FONs have been prepared via a simple and scalable hydrothermal method using starch and polyethyleneimine as precursors. These PEI-Starch FONs showed excellent fluorescence properties, high water dispersibility and good biocompatibility, making them highly potential for various biomedical applications.

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1. Introduction

With the rapid development of nanoscience and nanotechnology, searching of novel fluorescent nanomaterials for biomedical applications has attracted increasing research interest (Bhirde, Xie, Swierczewska, & Chen, 2011; Kim, Piao, & Hyeon, 2009; Rosi & Mirkin, 2005; Weissleder, 2006). Great effort has been devoted toward these areas and a number of bioprobes based on nanomaterials, which composed with inorganic and organic components have been developed (Ding, Li, Liu, & Tang, 2013; Michalet et al., 2005; Zhang, Zhang, tao, et al., 2014; Zhang, Zhang, Yang, Zhang, & Wei, 2014). As compared with small organic dyes, fluorescent nanomaterials are normally exhibited better optical properties and can

be easily integrated with other functional components including targeting agents and drugs, etc. (Boisselier & Astruc, 2009; Breul, Hager, & Schubert, 2013; Feng et al., 2013). Since the first report of using semiconduct quantum dots for bioimaging applications (Bruchez, Moronne, Gin, Weiss, & Alivisatos, 1998; Chan & Nie, 1998), many fluorescent inorganic nanoparticles (FINs) including silicon quantum dots, lanthanide ions doped nanomaterials, carbon quantum dots and fluorescent metal clusters have been developed for biomedical applications (Boisselier & Astruc, 2009; Chandra, Das, Bag, Laha, & Pramanik, 2011; Díez & Ras, 2011; Hui et al., 2012; Liu, Zhang, Qiao, & Su, 2012; Luo et al., 2014; Mitra et al., 2012; Sena & Gao, 2010; Zhang, Hui, Yang, et al., 2013; Zhang, Wang, Liu, et al., 2013; Zhang, Wang, Zhu, et al., 2013; Zhang, Zhang, Yang, et al., 2014). Although great advance has been achieved in biomedical applications of FINs, the accumulation of FINs in reticuloendothelial system (RES), non-biodegradability and potential toxicity have significantly limited their practical biomedical applications (Choi et al., 2007; Gao, Cui, Levenson, Chung, & Nie, 2004). It is therefore development of novel fluorescent nanoprobes which could overcome these obvious disadvantages of FINs should be of great importance.

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As compared with FINs, fluorescent organic nanoparticles (FONs) have recently received increasing attention for biomedical applications because of their flexible synthesis strategies, designability of small organic molecules, ease of surface functionalization, biodegradable potential and good biocompatibility (Feng et al., 2013; Li & Liu, 2014; Qin, Lam, & Tang, 2012). To date, a series of FONs based on small organic dyes, conjugated polymers, aggregation induced emission (AIE) dyes or aggregation induced enhancement of emission (AIEE) dyes have been emerging as fluorescent probes for biomedical applications (Ding et al., 2013; Kim, Ohulchanskyy, Pudavar, Pandey, & Prasad, 2007; Liu, Zhang, Yang, Deng, et al., 2014; Liu, Zhang, Yang, Liu, et al., 2014; Thomas, Joly, & Swager, 2007; Wang, Yuan, et al., 2014; Yu et al., 2013; Zhang, Zhang, Yang, et al., 2014; Zhang, Zhang, Yang, Zhang, et al., 2014; Zhao et al., 2008, 2010). Different strategies including encapsulation of hydrophobic dyes using commercial and synthetic amphiphilic polymers, covalently conjugation of dyes with hydrophobic molecules via Schiff-base or ring-opening reaction, and incorporation of polymerizable dyes with other monomers through polymerization reaction have been utilized to fabricate various FONs (Qin et al., 2012b; Zhang, Zhang, Yang, et al., 2013; Zhang, Zhang, Yang, Hui, et al., 2014; Zhang, Zhang, Yang, Liu, et al., 2014; Zhang, Zhang, Yang, Liu, Liu, et al., 2014). The basic principle for fabrication of FONs is to prepare dye contained amphiphilic polymers, which can be further self-assembled into fluorescent core-shell nanoparticles in aqueous solution (Breul et al., 2013). However, there still have a number of problems for fabrication of FONs for biomedical applications. For example, fluorescence intensity of FONs based on conventional organic dyes will be significantly decreased because of the notorious aggregation caused quenching (ACQ) effect (Leung et al., 2013). Dyes with AIE or AIEE properties could overcome the ACQ effect of conventional organic dyes, however, the synthesis of small organic dyes is rather complex and tedious. On the other hand, high cost small organic precursors and hazardous organic solvents are generally required to synthesis these dyes. Therefore, the development of a simple method for preparation of novel FONs, which showed excellent fluorescent properties, high water dispersibility and good biocompatibility using low cost precursors is highly desirable.

Starch is a type of natural, renewable and biodegradable polymers. Due to its biocompatibility, non-immunogenicity, stability in the air, abundant and low cost, starch has been an attractive substitute for preparation of starch based nanoparticles for various applications (Ma, Jian, Chang, & Yu, 2008; Moreira, Pedro, Glenn, Marconcini, & Mattoso, 2013; Shi, Wang, Li, & Adhikari, 2013; Tay, Pang, & Chin, 2012; Xie, Pollet, Halley, & Averous, 2013). A numerous of previous reports have demonstrated that starch based nanoparticles could be prepared through cold acid hydrolysis, high power ultrasonication, high-pressure homogenization, gamma irradiation and miniemulsion cross-linking, and nanoprecipitation (Bel Haaj, Magnin, Pétrier, & Boufi, 2013; Chin, Pang, & Tay, 2011; Kim, Han, Kweon, Park, & Lim, 2013; Lamanna, Morales, García, & Goyanes, 2013; Shi, Li, Wang, Li, & Adhikari, 2011). Recently, the preparation of luminescent starch nanoparticles has also demonstrated via self-assembly of fluorescein-labeled starch acetate in water (Li et al., 2011). The utilization of fluorescein-labeled starch maleate nanoparticles for metal ions sensing has also been reported by Chin, Azman, Pang, and Ng (2014). However, to the best of our knowledge, limited effort has been focused on the preparation of fluorescent starch based nanoparticles without linkage starch with small organic dyes. In the present study, we reported a method for preparation of starch based FONs via one-step hydrothermal treatment of starch in the presence of polyethyleneimine (PEI). This method is rather simple, cost effective and scalable. Thus obtained FONs (named as PEI-Starch FONs) were characterized by a

series of characterization techniques including UV-Vis absorption spectroscopy, fluorescent spectroscopy, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). To explore their biomedical applications, biocompatibility as well as cell uptake behavior of PEI-Starch FONs were further evaluated.

2. Experimental

2.1. Materials and measurements

Polyethyleneimine (PEI, Mw = 600, Alading Reagent Inc.), water soluble starch (Alading Reagent Inc.) were used as received. All the other solvents and chemicals were purchased from commercial sources and used directly without further purification.

UV-Vis absorption spectra were recorded on UV/Vis/NIR Perkin-Elmer lambda750 spectrometer (Waltham, MA, USA) using quartz cuvettes of 1 cm path length. Fluorescence spectra were measured on a PE LS-55 spectrometer with a slit width of 3 nm for both excitation and emission to obtain suitable fluorescent intensity. The FT-IR spectra were obtained in a transmission mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA). Typically, 8 scans at a resolution of 1 cm^{-1} were accumulated to obtain one spectrum. The XPS spectra were performed on a VGESCALAB 220-IXL spectrometer using an Al K α X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy (E_b) of the C1s peak of a carbon contaminant at 284.6 eV. Transmission electron microscopy (TEM) images were recorded on a JEM-1200EX microscope operated at 100 kV, the TEM specimens were made by placing a drop of the nanoparticles suspension on a carbon-coated copper grid. The size distribution of PEI-Starch FONs in water was determined using a zeta Plus apparatus (ZetaPlus, Brookhaven Instruments, Holtsville, NY).

Fluorescence quantum yield was measured according to established procedure in our previous reports (Zhang, Wang, Liu, et al., 2013). The optical densities were measured on UV-Vis spectra were obtained on a UV/Vis/NIR Perkin-Elmer lambda750 Spectrophotometer. Quinine sulfate in 0.1 M H₂SO₄ (literature quantum yield 0.54 at 360 nm) was chose as a standard (Shen, Yao & Lu, 2013). Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

$$\varphi_x = \varphi_{std} \frac{I_x A_{std} \eta_x^2}{A_x I_{std} \eta_{std}^2}$$

where φ is the quantum yield, I is the measured integrated emission intensity, and A is the optical density, and η is the refractive index. The subscript "std" refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (360 nm).

2.2. Preparation of PEI-Starch FONs

PEI-Starch FONs were prepared by hydrothermal treatment of starch and PEI. Briefly, starch (300 mg) and PEI (150 mg) were dissolved in 20 mL deionized water with magnetic stirring. And then the mixture was heated to 100 °C for 2 h. Thus obtained FONs were purified by dialysis through porous cellulose dialysis bag (molecular weight cut off 7000 Da) using ethanol to remove the unreacted PEI. Finally the product inside the dialysis bag was collected and dried by vacuum oven at 40 °C.

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