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Photoluminescence modulation of silicon nanoparticles via highly ordered arrangement with phospholipid membranes

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ABSTRACT

Highly ordered self-assembly of nanoparticles (NPs) in a large scale promises attractive potential in optical modulation of the NPs for illuminating, imaging and sensing applications. In this work, a type of multi-lamellar nanocomposite membranes composed of phospholipid multilayers and Si NPs sandwiched between each adjacent lipid layers was fabricated via a facile co-assembly method. X-ray reflectivity (XRR), grazing incident X-ray diffraction (GIXRD) and TEM measurements verified the highly ordered arrangement of NPs within the multilayers with a controlled in-plane inter-particle separation from ~7 nm to ~14 nm. Due to such an arrangement, the photoluminescence (PL) properties of the Si NPs were effectively modulated. Compared to the NPs in suspension or its pure film, the PL of the NPs in the membranes blue-shifted and remarkably narrowed, with the full-width-at-half-maximum (FWHM) value reduced from > 110 nm of the pure Si NP film to below 43 nm. The radiative lifetime of the NPs was also significantly reduced from ~16.7 ns to ~3.3 ns depending on the inter-particle distance in the membrane. Meanwhile, the Si NPs within membranes maintained robust photostability under UV irradiation.

1. Introduction

The strongly size-, shape- and surface-dependent optical properties of semiconductor nanoparticles (NPs) promise them as tunable emitters in applications such as illumination, imaging, and single-photon sources [1–5]. However, modulation of the NP photoluminescence (PL), including emission wavelength, monochromaticity, radiative lifetime, and photostability, etc., is still challenging to date [6–8]. Much efforts have been made to regulate the PL property of NPs via, for example, shell coating with a foreign material and ligand decoration by means of physical adsorption or covalent binding [9–11]. For example, the quantum yield and radiative lifetime of the colloidal CdSe NPs can be significantly modulated via surface reconstruction during synthesis or by introducing photooxidation with laser irradiation [12]. The stability of CdSe NPs was also found to be significantly influenced by the phase of the surrounding phospholipid molecules (i.e. liquid or gel phase) [13]. Through ion doping, the excitation intensity of BCNO (stands for the elements of B, C, N and O) nanocrystals can be improved and the emission spectra of them can be red shifted by up to 45 nm [14]. Moreover, the PL of Si nanocrystals has been successfully tuned across the entire visible spectral region via surficial functionalization without changing particle size [8]. However, the practical applications of the engineered NPs are somewhat impeded due to the complicated manipulation procedures, difficulties in purification after ligand functionalization, and/or easy aggregation of NPs. In this regard, self- or directed-assembly of NPs into well-ordered structures provides a promising solution to these problems [15–17]. Controllability in the structures, *e.g.* the inter-NP distance and the spatial organization of NPs, gives the NP assembling a unique advantage for PL modulation due to the coupling effect between adjacent particles and/or between particles and surrounding medium [7,11]. Specifically, plasmonic Au/Ag nanoparticles have been co-assembled with CdSe NPs. A precise control over the separation between the NPs and the plasmonic surface has been observed to exert an obvious influence on the emission spectra

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and lifetime of the NPs due to the exciton-plasmon coupling effect [18–20]. This method would bring in heterogeneous particles to the system. On the other hand, the introduction of a flexible and biocompatible scaffold for NP dispersion broadens the use of the NP-based composites in the field of bionanotechnology [21,22]. Many strategies including substrate-directed NP deposition and polymer- (as well as ligand, DNA and protein) modulated NP organization (in one-dimensional chains, two-dimensional layers or three-dimensional scaffold), have been intensively investigated [23,24]. However, challenges still lie in assembling NPs into a defect free, ordered and controllable structure, especially on a large scale. Moreover, all the works mentioned above focused on the modulation of PL properties of NPs including their quantum yields, emission wavelengths and radiative lifetimes. However, to the best of our knowledge, little work has been done to improve the PL monochromaticity of NPs.

In recent years, successful synthesis of small (2–5 nm) and water-dispersible silicon NPs (Si NPs), which have strong fluorescence, robust photostability and favorable biocompatibility, promises the fabrication of such composites for applications, especially those PL-related, in biosensing, long-term bioimaging, disease diagnosis and monitoring, to name a few [25–28]. On the other hand, phospholipids have unique properties such as favorable biocompatibility, modifiable structure for biofunctionalization, and the ability to self-assemble into various phases including micelles, vesicles, liposomes, hexagons and mono-/multi-layers. Functionalization of nanostructures, e.g. nanoparticles, colloidal crystals, and even nanoporous (gold or alumina) surfaces, with phospholipids, further broadens their applications for biosensors and/or drug delivery, etc [29,30]. Therefore, phospholipids have been regarded as one of the most representative biological molecules and promised attractive advantages for biocomposite fabrications [13,31–33].

In this work, three types of water-dispersed Si NPs with different PL properties were synthesized. Phospholipids were used to organize the Si NPs into composite membranes with controlled arrangement. Based on a facile co-assembling method, a type of multi-lamellar composite lipid membranes was fabricated, in which NPs were sandwiched between adjacent layers with high in-plane ordering. On the basis of this, the PL properties of the NPs were efficiently modulated with a significantly improved monochromaticity, blue-shifted emission and shorter radiative lifetime; meanwhile, the Si NPs within membranes maintained robust photostability under UV irradiation.

2. Materials and methods

2.1. Materials and machines

1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-dioleoyl-sn-glycero-3-phospho-(1′-rac-glycerol) (DOPG), 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP) and 1,2-di-(10Z,12Z-tricosadiynoyl)-sn-glycero-3-phosphocholine (Diyne-PC) were purchased from Avanti Polar Lipids. The molecular structures of the lipids are shown in Fig. S1 (Supplementary information). (3-Aminopropyl)-trimethoxysilane (APS, 97%) and 1,8-naphthalimide were purchased from Sigma-Aldrich. Trisodium citrate dehydrate (≥99.0%), chloroform (99.7%), and other chemicals (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were used without additional purification.

The microwave system NOVA used for NP synthesis was manufactured by Preekem of Shanghai (China). The system operates at a frequency of 2450 MHz and works in the power range of 0–500 W. UV irradiation in the experiments was performed with a xenon lamp at a wavelength of 365 nm and a power of 450 W.

2.2. Synthesis of Si NPs

Three types of Si NPs with different PL properties were synthesized following our previous reports [34–36]. Briefly, a NP precursor solution was prepared by adding 100 mL of APS to 400 mL N_2-saturated aqueous solution containing 18.6 *g* of trisodium citrate dehydrate. The mixture was stirred for 10 min and its pH was adjusted to 8.0 or 12.0 for the synthesis of Si-Blue or Si-Turquoise NPs respectively. The resultant precursor solution was transferred into a vitreous vessel, heated to 160 °C and kept for 15 min by microwave irradiation. The system was then cooled to room temperature naturally, and purified by centrifugation and dialysis (3 kDa) to remove the residual reagents. The final concentration of the aqueous Si NP dispersion was determined by UV–vis absorption measurement [34].

To synthesize Si-yellow NPs, 102.7 *g* of APS and 20 *g* of 1,8-naphthalimide were dispersed in 1 L of distilled water to serve as reaction precursors [34]. Under continuous UV irradiation at 365 nm for 40 min, the reaction solution exhibited strong fluorescence, indicating the generation of fluorescent Si NPs. The resultant solution was purified *via* centrifugation, dialyzed to remove residual reactants, and then dried and weighed, yielding ∼10 *g* of Si-yellow NPs.

2.3. Fabrication of Lipid/NP composite membranes

Powders of lipids, DOPC, DOPC/DOPG, DOPC/DOTAP (DOPC/charged lipid = 9/1 by mol) or Diyne-PC, were firstly dissolved in chloroform at 2.0 mg mL^{-1}, dried under N_2 flow, and kept in vacuum overnight for complete evaporation of the solvent. They were then dissolved in distilled water to a concentration of 2.0 mg mL^{-1} with the aid of bath-sonication at 90 W for more than 6 h to give clear solutions. Lipid vesicles were supposed to form in the solution. After that, a certain volume of Si NP dispersion was added to each lipid solution, vortexed completely and sonicated for another 1.5 h. The concentration of Si NPs in the final bulk solution varied from 0 to 0.24 mg mL^{-1}. Such bulk solutions was used for the assembly of the composite films with various NP contents. To obtain a composite membrane, 10 μL of a bulk solution was cast on a pre-cleaned Si wafer surface, which was kept in vacuum for the fast evaporation of solvent.

2.4. Characterizations

The NPs were characterized with Zeta-potential (Malvern Zetasizer Nano ZS90, UK), transmission electron microscopy (TEM; Hitachi HT7700, Japan), dynamic light scattering (DLS; Malvern Zetasizer Nano ZS90, UK), UV–vis absorption (Shimadzu UV3600, Japan) and photoluminescence (PL; HORIBA Jobin Yvon FluoroMax-4 spectrophotometer, France) tests. The lamellar structure of the membranes was examined by X-ray reflectivity (XRR) on an in-door X-ray diffraction equipment (Empyrean PANalytical, Holland) with a wavelength of 1.54 Å. The in-plane ordering of the NPs within the composite membranes was examined by grazing incident X-ray diffraction (GIXRD), which was performed on the Small Angle X-ray Scattering Station (BL16B) at Shanghai Synchrotron Radiation Facility (SSRF; $\lambda = 1.24$ Å). Fluorescence lifetime test of the NPs was performed on a FL3-TCSPC spectrofluorometer ($\lambda ex = 380$ nm; HORIBA Jobin Yvon, France). The lipid Diyne-PC [21] was used for the TEM sample fabrications as detailed in the ESI. All the experiments were carried out at room temperature of 22 °C.

2.5. Data analysis

The PL stability of the Si NPs within composite membranes was examined through analyzing the time-dependent changes of fluorescence intensity of each sample under UV irradiation. All the samples, with various NP types and concentrations, were exposed continuously under UV irradiation in dark ($\lambda ex = 380$ nm) and an image was captured every the other 30 min within a duration of 3 h. The values of the fluorescence intensity of a certain sample were calculated through integrating the fluorescence intensity within the sample scope in the