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Direct characterization of polymer encapsulated CdSe/CdS/ZnS quantum dots

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ABSTRACT

Surface engineering advances of semiconductor quantum dots (QDs) have enabled their application to molecular labeling, disease diagnostics and tumor imaging. For biological applications, hydrophobic core/shell QDs are transferred into aqueous solutions through the incorporation of water-solubility imparting moieties, typically achieved via direct exchange of the native surface passivating ligands or indirectly through the adsorption of polymers. Although polymeric encapsulation has gained wide acceptance, there are few reports addressing the characterization of the adsorbed polymers and existing theoretical analyses are typically based on simple geometric models. In this work, we experimentally characterize and quantify water-soluble QDs prepared by adsorption of amphiphilic poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, MW ~ 9000) onto commercially available CdSe/CdS/ZnS (CdSe/CdS/ZnS-PMAT). Using X-ray photoelectron spectroscopy (XPS) we determined that ~15 PMAT molecules are adsorbed onto each QD and sum frequency generation (SFG) vibrational spectra were utilized to investigate the mechanism of interaction between PMAT molecules and the QD surface. Importantly, when employed together, these techniques constitute a platform with which to investigate any polymer–nanoparticle complex in general.

1. Introduction

As nanoparticles (NPs) in general, and semiconductor quantum dots (QDs) in particular, become an ever-present stalwart in the application of nanotechnology to the biomedical sciences, there has been an increasing surge in the literature regarding the need for more accurate analytical characterization of their structure, composition and biological effects [1–3]. Indeed, over the last decade there have been an increasing number of reports of QD application as bright luminescent labels for molecular diagnostics, ultrasensitive in vitro assays and tumor imaging [4–7]. Comprehensive characterization has become important to their successful engineering and application [8–10]. The notable characteristics of QDs include unique optical properties such as size-tunable narrow Gaussian emission line shapes, broad excitation spectra, robust photo-stability and high quantum yields [11–13]. High-quality II–VI CdSe cores with a thin protective overlayer of higher bandgap ZnS [14] (overall diameter [11] less than 10 nm) are commonly employed. The photo-generated exciton is confined to the lower bandgap fluorescent core while the surrounding ZnS shell enhances photoluminescence by confining the exciton and passivating the core; thereby attenuating photo-oxidation and surface defect effects [12].

A result of the high-temperature organometallic synthetic procedure used to produce monodisperse nanoparticles is the nanocrystal surface being passivated with a monolayer of hydrophobic surfactant ligands [15], yielding overall hydrophobic nanoparticles. However, to serve as biologically relevant probes, QDs must be transferred into aqueous solutions and often undergo conjugation with biological molecules such as small molecule ligands, nucleic acids and proteins. The two most widely used methods to achieve phase transfer are to perform ligand exchange, thereby exchanging native surface molecules with bi-functional water-solubility imparting ligands [16–20], or polymer encapsulation, wherein a polymer containing both hydrophobic and hydrophilic groups [15,21–23] is adsorbed over the native surface ligands. Since QD optical properties are intimately sensitive to surface physical and electronic structures, the ligand exchange process can result in a dramatic decrease in photoluminescence or particle precipitation [24], although it has been shown that multidentate ligands minimize or eliminate these negative side-effects altogether [20,25]. Importantly,

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polymer adsorption leaves the native ligand layer intact in a hydrocarbon bilayer thereby leaving the QD photoluminescence unaffected. As such, polymer encapsulated-nanoparticles have been successfully applied to biological studies using polyethylene glycol derivatized phospholipids [26], block copolymers [6] and amphiphilic polyanhydrides [22,27–29] encapsulating moieties. Afterwards, specific-targeting ability is gained through the conjugation of bioaffinity ligands such as antibodies or aptamers to the polymer-coated QDs. Ideally, by optimizing the molecular stoichiometry and orientation of the encapsulated polymer, improved biocompatibility and reduced non-specific protein binding to the QDs can be achieved.

A common assumption is that the encapsulating polymers orient so the hydrophobic domains strongly interact with alkyl chains of the ligands on the QD surfaces and the hydrophilic groups face outward, rendering the QDs water-soluble. Although polymer encapsulated QDs have been widely used, there are few detailed experimental studies that directly quantify and characterize the interaction mechanism of the adsorbed polymer [22,30,31]. It should be noted that many theoretical analyses in the literature are typically based on simple geometric models that presume an interaction mechanism between the polymer and QD. In this study water soluble QDs are prepared by encapsulating amphiphilic poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, MW ~ 9000) around commercially available CdSe/CdS/ZnS (CdSe/CdS/ZnS-PMAT).

In recent years there has been increased interest in developing methods for characterizing the surface chemistry of NPs [32], but most of the method development has focused on XPS analysis of alkyl thiol covered gold NPs [33–35]. These studies represent significant advances in our ability to quantify NP surface chemistry, however, some of these approaches cannot be easily extended to the multi-shell configuration of QDs, especially since the shells in QDs contain high atomic number elements that can have a significant effect on the photoelectrons emitted from the elements in the NP core [36]. Methods that can be applied to XPS characterization of QDs include ones previously developed for NP catalyst characterization [8,37] or ones such as simulated electron spectra for surface analysis (SESSA) [38]. However, as XPS measurements are made in ultra-high vacuum the overlayer thicknesses measured by XPS can differ from the overlayer thicknesses measured in solution due to hydration of the overlayer [39]. In this study XPS is used to directly quantify the PMAT/QD ratio. Sum frequency generation (SFG) vibrational spectroscopy, another powerful technique for characterizing polymer encapsulated NPs [40], is used to obtain additional information about the ordering and orientation of PMAT on the QD surface. This combination of techniques serves as a platform that can be extended to directly characterize any generic polymer/nanoparticle complex.

2. Materials and methods

2.1. Reagents

Poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, MW ~ 9000), chloroform, hexane, methanol and sodium borate were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Boric acid was purchased from Fisher Scientific and used as received. CdSe/CdS/ZnS (622 nm emission) QDs synthesized by the successive ion layer adsorption and reduction (SILAR) [8,41,42] method and purified using standard hexane/methanol extraction [41,43] were obtained in powder form as a gift from Ocean Nanotech (Springdale, AR).

2.2. PMAT-encapsulation

Hydrophobic CdSe/CdS/ZnS QDs were dissolved in chloroform and mixed with a 250–500 M excess of PMAT. QD concentration was estimated from absorption measurements as previously discussed by Peng and coworkers [44]. A few drops of methanol were added to the chloroform mixture to aid in PMAT dissolution. After thorough mixing for a few minutes on a vortexer, the chloroform was evaporated under vacuum, yielding CdSe/CdS/ZnS-PMAT QDs. The resultant residue was resuspended in 50 mM borate buffer (1:1 mixture of sodium borate and boric acid, pH 8.5) for 5 min without agitation to allow base-mediated ring-opening of the anhydride groups to yield highly-negatively charged carboxylic acid functionalized water-soluble CdSe/CdS/ZnS-PMAT QDs. Afterwards, the solution was vortexed to fully resuspend the water-soluble QDs. Excess PMAT was removed by two rounds of ultra-centrifugation at 45,000 rpm for 45–60 min using a Beckman Coulter Ultracentrifuge (Fullerton, CA). The resulting soft pellet (100–150 μL) was collected each time and resuspended in fresh borate buffer.

2.3. Hydrodynamic radius and optical analysis

Nanoparticle hydrodynamic radii were obtained by light scattering analysis performed on a Malvern Zetasizer NanoZS (Worcestershire, UK). Hydrodynamic size data were obtained from a number-weighted size distribution analysis and was reported as the standard error of the mean. A UV-2450 spectrophotometer (Shimadzu, Columbia, MD) and a Fluoromax-4 fluorometer (Horiba Jobin Yvon, Edison, NJ) were used to characterize the absorption and emission spectra of CdSe/CdS/ZnS before and after PMAT encapsulation. True-color fluorescence images were obtained with an IX-71 inverted microscope (Olympus, San Diego, CA), 100× oil-emersion objective (NA 1.40) and a Q-color5 digital color camera (Olympus) using broad-band near-UV excitation provided by a mercury lamp. A long-pass dichroic filter (400 nm) and emission filter (420 nm) were used to pass the Stokes-shifted fluorescence signals (Chroma Technologies, Brattleboro, VT).

2.4. Sample preparation for electron microscopy and surface analysis

For transmission electron microscopy (TEM) and XPS analyses CdSe/CdS/ZnS QDs were dissolved in hexane. For TEM analysis 10–20 μl was drop cast onto a TEM grid. For XPS analyses 20 drops (10 μl each) were sequentially dropped onto a clean silicon wafer substrate every 2 min and dried under ambient conditions. Two drops (100 μl each) of CdSe/CdS/ZnS-PMAT QDs in borate buffer were dropped onto a clean silicon wafer substrate for XPS analyses and dried under vacuum. The samples were stored in a desiccator prior to the surface analysis experiments. For SFG, the QDs were drop cast onto one side of an equilateral calcium fluoride prism and dried under ambient conditions.

2.5. Transmission electron microscopy (TEM)

TEM analysis was carried out at the University of Washington Molecular Analysis Facility using a FEI Tecnai G2 F20 TWIN 200 kV TEM equipped with an EDAX detector. A dilute solution of QDs in hexane or water was dropped onto a Formvar-coated copper grid and allowed to dry under ambient conditions. TEM images were obtained with Gatan Digital Micrograph software. The diameter of the QDs was measured by manually segmenting the nanoparticles with image processing software, then measuring the areas of 50 QDs using ImageJ.

2.6. X-ray photoelectron spectroscopy (XPS)

XPS data were acquired with a Surface Science Instruments S-probe spectrometer. This instrument has a monochromatized Al Kα X-ray source, hemispherical analyzer, multichannel detector and low-energy electron flood gun for charge neutralization. The X-ray spot size used for these experiments was approximately 800 μm × 800 μm. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. Spectra used to determine surface elemental compositions were acquired at an analyzer pass energy of 150 eV. The high-resolution C 1s spectra were acquired at an analyzer pass energy of 50 eV. The take-off angle (the angle between the substrate normal and

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