

Well-Controlled Arrays of Core-Shell Quantum Dots with Tunable Photoluminescence Properties

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INTRODUCTION

Metal surfaces influence the manner in which photoexcitation is converted to fluorescence emission from photoactive molecules through a complex interplay of enhancing and quenching mechanisms.¹ Of fundamental scientific interest and technological importance is the possibility to precisely modify the electronic states in emitters by surface plasmons in metals. This capability could facilitate the development of extremely sensitive devices for potential applications in biotechnology, optoelectronics, and nanophotonics through “sub-wavelength” manipulation of light. However, this endeavor demands novel approaches to tailor the plasmonic behavior of metals and luminescence properties of fluorophores as well as in-depth understanding of parameters that govern plasmon-exciton interactions.

We report two studies that aim to modulate the photoluminescence (PL) properties from arrays of quantum dots (QDs) by controlling the spatial organization of QDs with respect to the underlying metal (Au or Ag) surface. The first study explores the use of polypeptides and organic-peptide conjugates as two linkers with well-defined heights to attach QDs at known separations to the metal surface. This approach demonstrates a molecular biomimetic approach toward nanophotonics by integrating inorganic, organic, and biomolecular constructs to form hybrid nanostructures through template-directed self-assembly. In the second study, QDs are attached onto arrays of metal nanostructures. This approach affords the tailoring of localized surface plasmon resonance (LSPR) spectra of metal nanostructures as well as the tuning of vertical separation of QDs from the metal surface through layer-by-layer self-assembly.

RESULTS AND DISCUSSION

Peptide-mediated formation of well-controlled arrays of QDs.

Peptide-based assembly of inorganic nanostructures offers a powerful approach to form hybrid nanostructures.² Apart from their self-assembly and recognition characteristics, peptides are robust and can be genetically engineered to tailor their functionalities such as binding. In addition to 20 commonly occurring amino acids, there are variants and synthetic analogues available to produce a virtually unlimited variety of peptides and polypeptides. Furthermore, functional groups (for example, carboxyls and amines) appended to the amino acids can be exploited for different chemical reactions. In recent years, hybrid nanostructures composed of QDs and peptides have become a subject of considerable interest. While much work has been accomplished in solution, little effort has been invested to construct peptide-QD heterostructures on the substrate.

Our approach is unique in the use of genetically engineered polypeptides and organic-peptide conjugates as linkers. In comparison to self-assembled monolayers (SAMs) or electrostatically charged polymers commonly used as linkers for the attachment of QDs, the unparalleled benefit of combinatorially selected polypeptides is their potential ability to identify elemental composition, crystallographic structure and orientation, and morphology of an inorganic surface. In this work, gold-binding polypeptide (GBP, 42 amino acids, [MHGKTQATSGTIQS]₃), isolated by cell-surface display, is biotinylated to create a bifunctional biomolecular construct (bio-3GBP) which serves as a binder for specific adsorption to the Au substrate as well as a receptor for streptavidin (SA) functionalized CdSe@ZnS QDs through bio-SA formation.

Two schemes were formulated to vary the spacing between QDs and Au substrate (i.e., linker length) and to examine the functionality of bio-3GBP when covalently bonded with π -conjugated organic molecules (Figure 1A). In both cases, Au substrate patterned by μ CP of SH-(OCH₂)₃OH provides a template to allow the sequential assembly of linkers and QDs in a site-specific fashion. In the first scheme, bio-GBP was immobilized onto the Au substrate through surface recognition. In the second scheme, bio-3GBP was immobilized by covalent bonding between -NH₂ groups on bio-3GBP and -CHO end-groups of the SAM of (10-mercaptomethyl-9-anthryl)(4-aldehydephenyl)acetylene (MMAPA) through Schiff base formation.

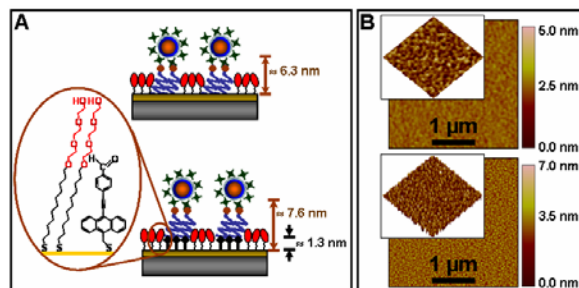


Figure 1. (A) Schematic illustration of the attachment of QDs using bio-3GBP (top) and MMAPA/bio-3GBP conjugates (bottom) as two linkers with well-defined heights to attach QDs at known separations from the Au substrate. (B) Distinct morphological features of self-assembled bio-3GBP (top) and chemically grafted bio-3GBP on MMAPA (bottom).

Distinct morphological features of self-assembled bio-3GBP and chemically grafted bio-3GBP dictate the assembly of QDs (Figure 2). Higher number density of QDs on the surface presented by grafted bio-3GBP may be attributed to the greater surface density of biotin functional groups (which brought the QDs into a closer proximity). For quantitative comparison, we combined AFM with PL spectroscopy to determine the relative contributions of linker length and QD number density to the PL from each array (Au/bio-3GBP/SA-QD and Au/MMAPA/bio-3GBP/SA-QD).

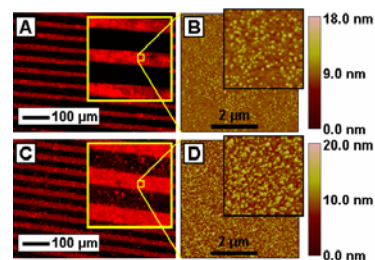


Figure 2. Assembly of QDs using bio-3GBP (A, B) and MMAPA/bio-3GBP conjugates (C, D) as linkers. From the analysis of fluorescence images, emission intensity from arrays of hybrid nanostructures with MMAPA was stronger. Based on AFM results, number of QDs attached through MMAPA-GBP was ~ 24% higher per given area.

Spatially resolved PL measurements from QDs arrays were performed on an inverted high-resolution microscope. Emission intensity from arrays of hybrid nanostructures with MMAPA (Au/MMAPA/bio-3GBP/SA-QD) was found to be about 27% stronger than that from arrays of hybrid nanostructure without MMAPA (Au/bio-3GBP/SA-QD). While both linker length and number density of QDs affected the fluorescence properties of QD arrays, emission intensity was mainly contributed by the number density of QDs, as seen in Figure 3. After normalization with respect to the number density of QDs calculated from AFM characterizations, the difference in the emission intensities from QD arrays decreased to about 5%.

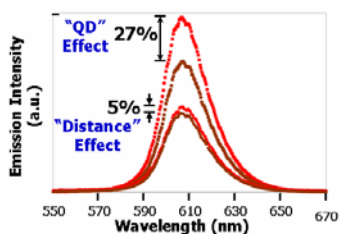


Figure 3. Emission spectra of QD arrays upon excitation by a 532-nm continuous wave laser.

Well-controlled arrays of QDs on tunable plasmonic platforms. Optical properties of metal nanostructures can be applied in many areas of technological importance including surface-enhanced spectroscopies, optics and optoelectronics, chemical and biological sensing, and probes/labels for imaging. The inherent optical property of a metal nanostructure is LSPR, which occurs when the photoexcitation at a correct wavelength (i.e., resonant condition) gives rise to the collective oscillation of conduction electrons.⁴ LSPR excitation manifests in two consequences: selective photon absorption and scattering, and generation of locally enhanced electromagnetic field at the surface of a metal nanostructure. As a result, metal nanostructures could serve as antennas for concentrating and transferring electromagnetic energy onto QDs with a possibility to coherently control the excitation and consequently emissive characteristics of QDs. Both QDs and metal nanostructures could be independently engineered, creating opportunities to design and develop LSPR-based QD devices by taking advantage of both quantum confinement phenomena and LSPR effects.

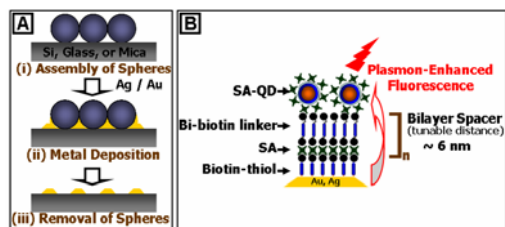


Figure 4. Schematic representation of NSL (A) and layer-by-layer self-assembly of molecular spacers (B).

In this work, based on a combination of parallel nanofabrication scheme and layer-by-layer self-assembly process, we studied the surface-plasmon-enhanced PL of QD arrays. Physical attributes (i.e., shape and size) strongly determine the LSPR excitations in metal nanostructures. Because nanosphere lithography (NSL)⁵ allows a flexible fabrication of arrays of metal nanostructures with different physical attributes including the material from which they are made and the substrate on which they are supported, NSL-fabricated substrates serve as tunable plasmonic platforms (Figure 4A). Although NSL's capability to tailor the localized surface plasmon resonance (LSPR) spectra of Ag nanostructures has been demonstrated for surface-enhanced sensing and spectroscopy, we showed the application of NSL as a route to 2-D and 3-D arrays of QDs with tunable surface-plasmon-modulated luminescence properties. To precisely control plasmon-exciton interactions, we employed layer-by-layer assembly of molecular spacers to ensure incremental separation between QDs and NSL-derived nanostructures (Figure 4B). We used alkane linkers (~1.35 nm in height) and streptavidin molecule (~5 nm in height) as linkers with well-defined heights to accomplish short- (~1.35 nm), mid- (~5 nm) and long-range (multiple of ~6.35 nm when alkane linkers and streptavidin molecule are taken as a bilayer spacer) separations. As a result, through “mix-and-match” combinations, we were able to assess a large range of defined separations between QDs and NSL-derived nanostructures, from below 2 nm to beyond tens of nanometers.

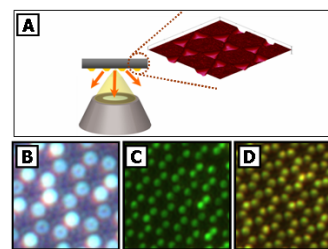


Figure 5. NSL-fabricated substrates as tunable plasmonic platforms. (A) Resonant Rayleigh scattering spectroscopy for characterization of NSL-derived nanostructures. (B-D) Arrays of metal nanostructures with distinct light scattering properties.

Along with the need for approaches to precisely manipulate plasmon-exciton interactions, the use of techniques for spatially resolved measurements of LSPR response with a high signal-to-noise ratio is essential. We relied on resonant Rayleigh scattering spectroscopy for simultaneous imaging and spectroscopic detection of the LSPR response of individual nanostructures within the arrays. In scattering efficiency measurements, a dark-field condenser is used for evanescent excitation by focusing a hollow light cone at such an angle onto the sample that only the scattered light can be collected by a high-magnification objective (Figure 5A). No light from the excitation sources is directly collected, enabling an image with an extremely low background and a high signal-to-noise spectrum to be acquired simultaneously. Physical attributes of metal nanostructures can be systematically altered to produce tunable plasmonic platforms with distinct light scattering properties as shown in Figure 5 B-D. Fluorescence image of QDs attached onto arrays of metal nanostructures with a separation of one bi-layer spacer (~7.5 nm) is shown in Figure 6.

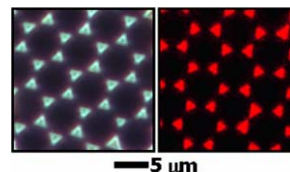


Figure 6. Dark-field image of metal nanostructures (Left) and fluorescence image (Right) after the assembly of QDs.

CONCLUSIONS

Understanding of field-matter relationships (for example, photoluminescence enhancement and quenching) are central issues in photonics and plasmonics. Our efforts are directed toward understanding plasmon-exciton interaction in arrays of QDs. Studies are underway to establish spectral relationships between native emission spectra of QDs and extinction spectra of metal nanostructures so that metal/semiconductor heterostructures can be predicted reliably.

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