

Spatially selective broadband emission enhancement of quantum dots

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Abstract

We demonstrate broadband enhancement of quantum-dot photoluminescence through spatially selective photochemical deposition of silver nanoparticles on domain patterned ferroelectric crystals. This enhancement is a consequence of coupling of broadband plasmonic modes to the quantum-dot emission.

1. Introduction

Semiconductor quantum dots (QDs) are ideal fluorophores for multiplex photoluminescent applications owing to their broad excitation and narrow, tunable emission spectra, as well as high stability and good quantum yields. Spatially controlled, broadband enhancement of QD photoluminescence (PL) is desirable for demanding applications involving sensors, microarrays and single molecule studies [1, 2]. PL enhancement can be achieved by coupling to suitable metal nanoparticles, however, their generation with high throughput and a high spatial resolution at the same time remains an open challenge. Here, we propose and demonstrate ferroelectric domain engineered photochemical deposition to achieve arbitrary spatial control of PL enhancement over a broad spectral range.

2. Results and discussions

In our work we use photochemical deposition of silver onto the domains of ternary ferroelectric single crystal (PIMNT) to achieve high-spatial accuracy patterning of QD PL. First, a checkerboard pattern of $c+$ and $c-$ domains is created on the surface of the PIMNT crystal by applying a voltage to the tip of an atomic force microscope. Next, the crystal is immersed into a silver nitrate solution and irradiated with ultraviolet (UV) light. The UV illumination leads to an upward [downward] bending of the crystal's energy bands for the $c-$ [$c+$] domains, respectively. As a result, photo-generated electrons are driven towards the surface for the $c+$ domains, and away from the surface for the $c-$ domains, leading to the formation of silver nanoparticles on the surface for the $c+$ domains only. The generated silver nanoparticles have multifarious shapes and random sizes ranging

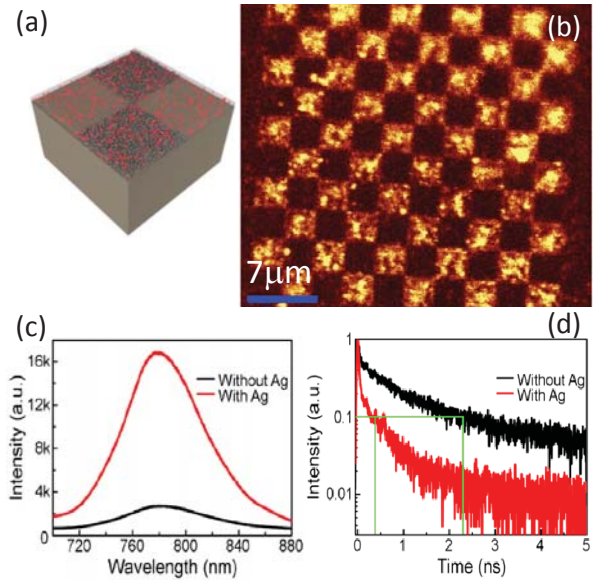


Figure 1: (a) Schematic of silver nanoparticles photo-deposited onto domain patterned PIMNT and covered by QDs. (b) Measured PL map of QDs, emitting at 800 nm, above a checkerboard pattern of regions with and without silver nanoparticles. (c) Typical PL spectra of QDs for a region with and without silver nanoparticles (red and black line, respectively). Normalised time-resolved photoluminescence at 800 nm for (red) region with QDs over silver nanoparticles and (black) region with QDs only. The green line is a guide for the eye.

from several to hundreds of nanometers [3]. Such mixture of silver nanoparticles supports inhomogeneously localized plasmonic excitations similar to those of percolating metal films [4]. Importantly, the spectrum of such modes is extremely broadband, allowing for high local-field enhancement over a large spectral bandwidth. After silver deposition, a uniform mixture of streptavidin coated QDs dispersed in polyvinyl alcohol (PVA) is spin-coated onto the ferroelectric. A schematic of the resulting sample geometry is shown in Fig. 1(a).

We have optically characterized the samples using micro- PL-mapping, PL-spectroscopy, and time-resolved PL measurements. A confocal PL map of QDs emitting at 800 nm on top of a checkerboard pattern of deposited silver is shown in Fig. 1(b). It is evident that the QD emission above the deposited silver patterns is enhanced (yellow regions) compared to emission in regions without silver nanoparticles. Typical QD photoluminescence spectra of the regions with and without silver nanoparticles are shown in Fig. 1(c). The photoluminescence of the QDs is enhanced roughly sixfold by the silver nanoparticles. Additional experiments have been performed to eliminate the possibility of photoluminescence from silver nanoparticles on PIMNT. Furthermore, insertion of an analyzer into the photoluminescence detection path shows that presence of silver nanoparticles does not affect the photoluminescence polarization. Nor was the photoluminescence polarization affected by rotation of the incident polarization of the pump beam by 90° .

Time-resolved photoluminescence was also performed to determine the total PL enhancement factor. Figure 1(d) shows typical time-resolved photoluminescence, measured at 800 nm. Because the QDs are randomly distributed in the PVA film, a single-exponential fit cannot account for the emission decay of an ensemble of QDs. Instead, as a quantitative measure of the lifetimes we consider the time it takes for the normalized intensity to drop to 10%. We find that the lifetime is 0.4 ns for the QDs emission in the region with silver nanoparticles, while it is approximately 2.3 ns for the region with only QDs.

The photoluminescence enhancement of a mixture of QDs emitting at 655 nm and 705 nm is also demonstrated in Fig. 2. The QD photoluminescence is enhanced about tenfold. This photoluminescence enhancement demonstrates the potential of ferroelectric photo-deposited silver in enhancing fluorophores with emission wavelengths spanning a broad spectral bandwidth. Moreover, comparing both curves in Fig. 2 we can conclude that the enhancement factor appears practically independent of the wavelength.

In order to explain our experimental results we recall that the enhanced QD photoluminescence is comprised of two effects: an electric field enhancement and plasmon-fluorophore coupling. In the former, metal particles concentrate the local electric field near the sharp edges of the particles leading to an increase in the rate of excitation of fluorophores and consequently in the photoluminescence emission. The photoluminescence lifetime is unaffected by this mechanism. In the latter, the fluorophore couples to localised plasmon modes of the silver nanoparticles, where the coupling interaction is confined to distances of about 20 nm. This leads to an increase in the photoluminescence emission of the metal-fluorophore system due to an enhanced Purcell factor. Additionally, the enhanced Purcell factor leads to a reduction in the photoluminescence lifetime (Fig. 1(d)). The observed lifetime reduction strongly indicates coupling between the QDs and the surface plasmon modes of the silver nanoparticles, and results in in-

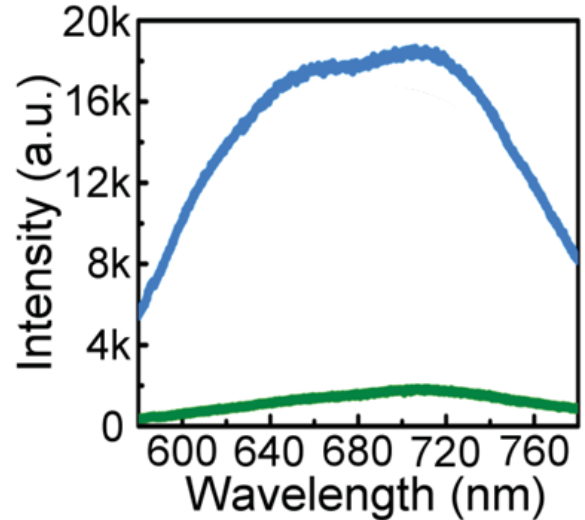


Figure 2: Typical photoluminescence spectra for: (blue line) a region with QDs over silver nanoparticles and (green line) a region with QDs only. A mixture of QDs emitting at 655 nm and 705 nm is used.

creased photo-stability and photon flux. The strength of coupling is dependent on the spectral overlap of the fluorophores emission spectrum and the plasmonic resonances of the metal nanoparticles. Typically, for narrowband plasmonic excitations, this leads to a photoluminescence enhancement that strongly depends on the emission characteristic (spectrum) of the fluorophore. In our case, however, because of the continuum-like collection of localized plasmon modes, the overlap between the emission of the different kinds of QDs and the plasmon modes of silver nanoparticles remains comparable over the entire measurement spectral range.

3. Conclusions

In conclusion, our results demonstrate that coupling of QDs to silver nanoparticles generated via area-selective ferroelectric photochemical deposition allows for spatial control of broadband enhancement of QD PL that may prove useful in diverse applications in multiplex detection of biomolecules.

Acknowledgement

We acknowledge financial support from the Australian Research Council.

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