PROCEEDINGS OF SPIE

SPIEDigitalLibrary.org/conference-proceedings-of-spie

Enhancement of exciton-plasmon coupling via functional plasmonic metal oxide metastructures

Seyed Sadeghi

Seyed M. Sadeghi, "Enhancement of exciton-plasmon coupling via functional plasmonic metal oxide metastructures," Proc. SPIE 12647, Active Photonic Platforms (APP) 2023, 126470J (4 October 2023); doi: 10.1117/12.2677527

SPIE.

Event: SPIE Nanoscience + Engineering, 2023, San Diego, California, United States

Enhancement of exciton-plasmon coupling via functional plasmonic metal oxide metastructures

Seyed M Sadeghi*
Department of Physics and Astronomy, The University of Alabama in Huntsville, Huntsville, AL 35899, USA

ABSTRACT

Plasmonic metal-oxide metastructures comprise arrays of Au nanoantennas embedded in Si layers, with a top ultrathin layer of Al oxide, supporting an Au/Si Schottky junction in the vicinity of a Si/Al oxide charge barrier. In such structures the hot electrons generated by nonradiative decay of plasmons can be captured by the Schottky junctions, forming an electrostatic field via charge accumulation in the Si layers. When thin layers of semiconductor quantum dots are placed on top of such structures, such a field suppresses their non-radiative decay rates, making them far more efficient emitters. We study the impact of plasmon modes of the Au nanoantennas on the exciton-plasmon coupling enhancement supported by such a material platform.

Keywords: Plasmons, Al oxide, excitons, exciton-plasmon coupling, hot electrons, arrays, metallic nanoantennas

1. INTRODUCTION

Enhancement of quantum efficiency of semiconductor quantum dot (QD) semiconductor is an important field of research with significant impact. Such an enhancement process can make QDs more efficient emitters, greatly improving their applications in optical devices, sensors, and even quantum computations [1,2]. The primary techniques include optimizing the fabrication techniques of such nanocrystals, applying optical cavities, and utilizing plasmonic effects [3-8]. To use plasmonic effects, one normally requires the application of near fields of metallic nanoantennas. While significant progress has been reported, the limitation of such a technique is that it mostly deals with the enhancement of radiative decay of QDs, which in turn reduces the contribution of their non-radiative decay, making them more efficient emitters [7,8]. Such a technique has also been used for enhancement of emission and absorption of two-dimensional transition metal dichalcogenide monolayers and graphene [9,10].

Recently, we presented a material platform that not only enhances the radiative decay of QDs but also suppresses their non-radiative decay [11-14]. This platform, referred to as plasmonic metal-oxide metastructures (PMOM), is formed when arrays of metallic nanoantennas are embedded on Si and topped up with an ultra-narrow layer of Al oxide (Fig. 1a). Such a structure supports an Au/Si Schottky junction and a Si/Al oxide charge barrier in close vicinity of each other (Fig. 1b). The main underlying physics behind such a structure is the application of the hot electrons, formed via the non-radiative decay of plasmons, to create an electrostatic field that suppresses the non-radiative decay of QDs by prohibiting the migration of their photo-excited electrons to the defect sites (Fig. 1b). This is achieved by using the Au/Si Schottky barrier to capture the hot electrons and employing Si/Al oxide charge barriers to keep such electrons in the Si layer. In the presence of a QD thin film on top of such PMOM (Fig. 1a), optical excitation creates excitons capable of exciting plasmons via exciton-plasmon coupling. A prominent impact of this process is the enhancement of exciton-plasmon coupling, which is a crucial ingredient for a variety of active optical devices [15]. In this contribution, we study the impact of plasmon modes of Au nanorods on the exciton-plasmon coupling enhancement supported by such a material platform. Through the analysis of emission polarization and lifetime measurements of the QDs, we demonstrate how the longitudinal and transverse plasmon modes of such nanoantennas influence the exciton-plasmon coupling enhancement, offering quantum super-emitters with enhanced emission via both Purcell effects and suppression of the defect environment with a strong sense of polarization.

*seyed.sadeghi@uah.edu

Active Photonic Platforms (APP) 2023, edited by Ganapathi S. Subramania, Stavroula Foteinopoulou, Proc. of SPIE Vol. 12647, 126470J
 · 0277-786X · doi: 10.1117/12.2677527

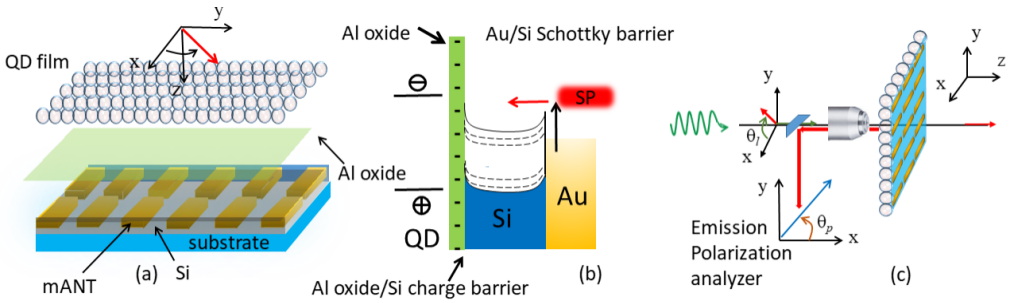

Figure 1. Schematics of fabrication processes and layer structures of a PMOP (a), and its electronic structure (b). (c) Experimental setup used to investigate the exciton-plasmon coupling.

2. METHODOLOGY

Samples consisting of Au nanorod (NR) arrays were fabricated using E-beam lithography. Each NR had a length of 890 nm, a width of 195 nm, and a thickness (height) of 40 nm (Fig. 2a). These NRs were formed on glass substrates and embedded in 15 nm of Si. On top of the Si layer, 1 nm of Al was then sputtered. After air oxidation, this layer converted into Al oxide, supporting a two-dimensional negative charge density (Fig. 1) [16,17]. Finally, a thin layer of CdSe/ZnS QDs was spin-coated on top of the Al oxide layer (Fig. 1a). Reference samples with a similar arrays structures were also fabricated but without the Al oxide layer. These reference samples are used to illustrate conventional plasmonic emission enhancement in comparison to those offered by PMOM. Fig. 2b shows the extinction spectra of such NR arrays when the incident light was linearly polarized along the x-axis (solid line) and the y-axis (dashed line). Along the x-axis (x-pol), the spectrum mostly refers to longitudinal modes of the NRs, while for the y-axis (y-pol), the longitudinal modes are excited in the range of about 600 nm. Additionally, the spectrum exhibits a sharp peak at about 750 nm, which is associated with the surface lattice resonance (SLR) of the NR arrays [18,19].

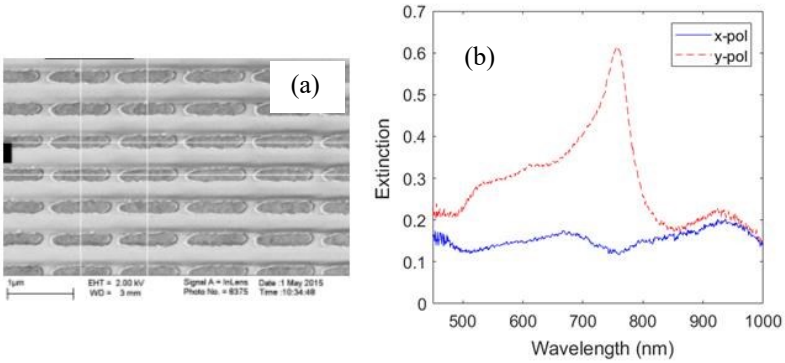

Figure 2. (a) SEM image of NR array. (b) Extinction spectra of the NR array when the incident light was polarized along the x-axis (solid line) and the y-axis (dashed line).

To study the emission of the QDs and exciton-plasmon coupling, we utilized an optical setup shown in Fig. 1c. In this setup, a laser field with a wavelength of 517 nm was focused on the arrays using a microscope objective. The emission of the QDs was then collected by the same objective and directed towards a polarization analyzer and a collective lens, which further directed the QD emission to a sensitive spectrometer. The angle of the axis of this analyzer (θp) was measured from the long axis of the NRs (the x axis). This allowed us to study the impact of polarization on the emitted light from the QDs and exciton-plasmon coupling effects. Additionally, we employed a Time Correlated Single Photon Counter (TCSPC) system to measure the lifetime of the QDs.

3. RESULTS

The emission results for the reference samples (Au/Si/QD and Si/QD) are presented in Fig. 3a. These findings demonstrate a moderate enhancement in the emission of the quantum dots (QDs) through the near fields of the NR arrays. As depicted in Fig. 4a, this enhancement in emission occurs concurrently with a reduction in the QDs' lifetimes. This outcome is in line with previous studies [3-8]. The reduction in QDs' lifetimes can be attributed to the enhancement of their radiative decay rates. As a result, the QDs become brighter, and the contribution of non-radiative decay is reduced. This phenomenon is responsible for the observed increase in emission efficiency in the presence of the NR arrays, as seen in Fig.3a.

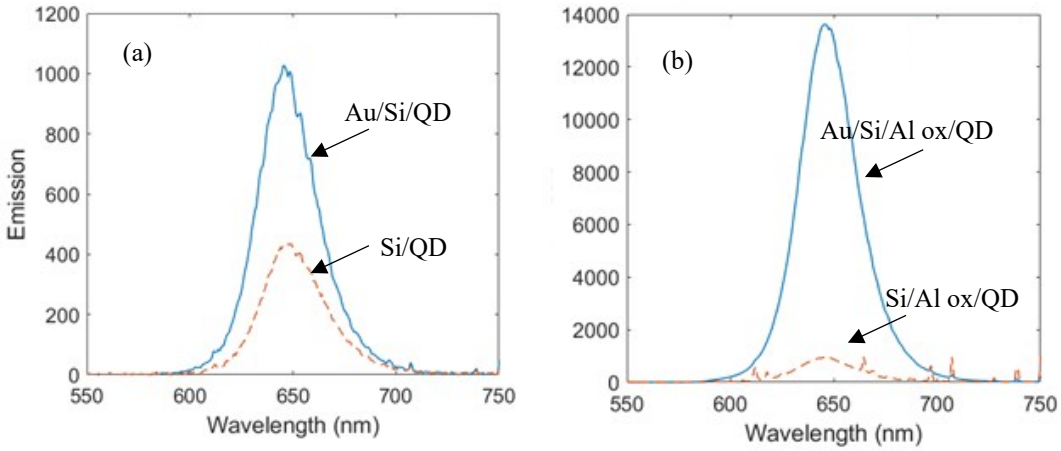

Figure 3. Emission of QDs in the presence (solid lines) and absence (dashed lines) of NR arrays. In (a) the structure does not have the Al oxide layer, while in the case of (b) the 1 nm Al oxide was deposited on the top of the Si layer.

The results obtained for the Si/Al oxide and Au/Si/Al oxide cases present a striking difference. As depicted in Fig. 3b, the emission of QDs on Au/Si/Al oxide (solid line) is significantly higher compared to that on Au/Si (Fig3a, solid line). Furthermore, when compared to the cases without NRs (Fig.3b, dashed line), the emission enhancement on Au/Si/Al oxide is much more pronounced. These findings suggest that the plasmonic metal-oxide metastructures (PMOM) offer a far more efficient enhancement for QD emission. A closer examination of the results in Fig. 4b indicates that this enhancement process is associated with an elongation of the QDs, indicating that PMOM can effectively suppress the impact of defect effects while simultaneously increasing the rate of radiative decays of QDs.

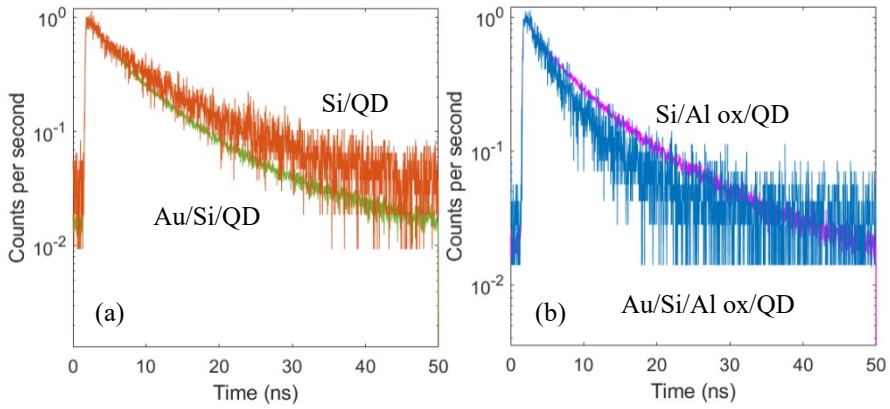

Figure 4. (a) The decay of QDs on Si and Au/Si. (b) Decay of QDs on Si/Al oxide and on Au/Si/Al oxide.

To study the exciton-plasmon coupling and its enhancement process, we investigated the degree of polarization of QD emission using the setup shown in Fig. 1c. In this study, we measured the peak intensity of QD emission while varying the angle of the polarization analyzer. The results presented in Fig. 5a show variations of the emission enhancement factor, defined as the ratio of QD emission in the presence of PMOM to that on Si/Al oxide, as a function of θp. When the axis of the analyzer was along the x-axis, i.e., θp=0°, the emission enhancement was slightly above 16. However, the emission enhancement factor increased to about 27 when the axis of the analyzer was aligned along the y-axis, i.e., θp=90°. The associated schematics depicting the exciton-plasmon couplings in these two cases are shown in Fig. 5b and 5c, respectively. For the case of θp=0°, mostly longitudinal modes of the NRs can be excited. Since such modes are quite off-resonant from the QD bandgap, only weak exciton-plasmon coupling is formed. For the case of θp=90°, however, since QDs and transverse modes of the NRs have similar wavelengths, the formation of excitons happens along strong coupling to plasmons, leading to a very high enhancement factor. Note that the high emission enhancement factor seen in Fig.5a is also associated with the presence of Si/Al oxide charge barrier, which tends to passivate QD via electrostatic field of surface surfaces [6].

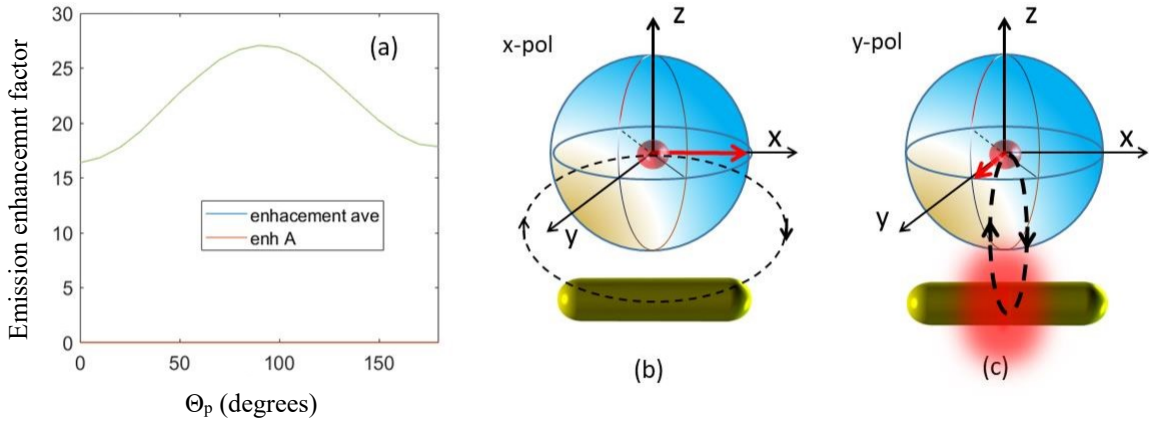

Figure 5. (a) Variations of emission enhancement of QDs on Au/Si/Al oxide (PMOM). (b) and (c) Two cases associated with exciton-plasmon coupling associated with longitudinal and transverse modes of the NRs.

4. CONCLUSIONS

We investigated exciton-plasmon coupling in the PMOM platform, demonstrating a significant polarization-dependent enhancement of this process. Such enhancement occurred via field-effect passivation of the QDs combined with Purcell effect, indicating the profound impact of the increased exciton lifetime on the efficiency of the exciton-plasmon coupling. We studied the effects of the plasmon modes of the nanoantennas, demonstrating strong polarization dependency of QD emission via selective coupling of excitons with such modes. The ability to control and tailor exciton-plasmon coupling through such adjustments in the PMOM platform opens up unique possibilities for various applications. This process can enhance the performance of active optical devices and sensors, as well as advance fundamental processes in controlling light-matter interactions.

Acknowledgments: This work is supported by US National Science Foundation under grant no. ECCS-1917544. The author acknowledges contributions of Drs Rithvik Gutha and Waylin Wing.

REFERENCES

[1] Cadusch, Jasper J., Evgeniy Panchenko, Nicholas Kirkwood, Timothy D. James, Brant C. Gibson, Kevin J. Webb, Paul Mulvaney, and Ann Roberts. "Emission enhancement and polarization of semiconductor quantum dots with nanoimprinted plasmonic cavities: towards scalable fabrication of plasmon-exciton displays." *Nanoscale* 7, no. 33, 13816-13821 (2015).

[2] Wang, Hongyue, Yangyang Guo, Jianyang Zang, Hongxing Hao, Le Wang, Taihong Liu, Hongtao Bian et al. "Nanoantennas involved optical plasmonic cavity for improved luminescence of quantum dots light-emitting diodes." *ACS Applied Materials & Interfaces* 13, no. 37, 44760-44767 (2021).
[3] Chen, Yeechi, Keiko Munechika, Jen-La Plante, Andrea M. Munro, Sara E. Skrabalak, Younan Xia, and David S. Ginger. "Excitation enhancement of CdSe quantum dots by single metal nanoparticles." *Applied Physics Letters* 93, no. 5 (2008).
[4] Werschler, Florian, Benjamin Lindner, Christopher Hinz, Frieder Conradt, Pascal Gumbsheimer, Y. Behovits, C. Negele et al. "Efficient emission enhancement of single CdSe/CdS/PMMA quantum dots through controlled near-field coupling to plasmonic bullseye resonators." *Nano Letters* 18, no. 9, 5396-5400 (2018).
[5] Sadeghi, Seyed M., Rithvik R. Gutha, and Christina Sharp. "Amplified plasmonic emission enhancement of PbS quantum dots via Al-oxide/PMMA heterostructures." *Nano Futures* 6, no. 4, 045006 (2022).
[6] Patty, K., Sadeghi, S.M., Nejat, A. and Mao, C.B. "Enhancement of emission efficiency of colloidal CdSe quantum dots on silicon substrate via an ultra-thin layer of aluminum oxide". *Nanotechnology*, *25*(15), 155701 (2014).
[7] Rakovich, Aliaksandra, Pablo Albella, and Stefan A. Maier. "Plasmonic control of radiative properties of semiconductor quantum dots coupled to plasmonic ring cavities." *Acs nano* 9, no. 3, 2648-2658 (2015).
[8] Biteen, Julie S., Luke A. Sweatlock, Hans Mertens, Nathan S. Lewis, Albert Polman, and Harry A. Atwater. "Plasmon-enhanced photoluminescence of silicon quantum dots: simulation and experiment." *The Journal of Physical Chemistry C* 111, no. 36, 13372-13377 (2007).
[9] Alamri, Mohammed, Bo Liu, Seyed M. Sadeghi, Dan Ewing, Amy Wilson, Jennifer L. Doolin, Cindy L. Berrie, and Judy Wu. "Graphene/WS2 nanodisk Van der Waals heterostructures on plasmonic Ag nanoparticle-embedded silica metafilms for high-performance photodetectors." *ACS Applied Nano Materials* 3, no. 8, 7858-7868 (2020). [10] Lu, Rongtao, Annika Konzelmann, Feng Xu, Youpin Gong, Jianwei Liu, Qingfeng Liu, Melisa Xin, Rongqing Hui, and Judy Z. Wu. "High sensitivity surface enhanced Raman spectroscopy of R6G on in situ fabricated Au nanoparticle/graphene plasmonic substrates." *Carbon* 86, 78-85 (2015).
[11] Sadeghi, Seyed M., Waylin J. Wing, Rithvik R. Gutha, Ryan W. Goul, and Judy Z. Wu. "Functional metal-oxide plasmonic metastructures: Ultrabright semiconductor quantum dots with polarized spontaneous emission and suppressed Auger recombination." *Physical Review Applied* 11, no. 2, 024045 (2019).
[12] Sadeghi, Seyed M., Rithvik R. Gutha, Ali Hatef, Ryan Goul, and Judy Z. Wu. "Ultrahigh brightening of infrared PbS quantum dots via collective energy transfer induced by a metal-oxide plasmonic metastructure." *ACS applied materials & interfaces* 12, no. 10, 11913-11921 (2020).
[13] Sadeghi, Seyed M., Waylin J. Wing, Rithvik R. Gutha, Jamie S. Wilt, and Judy Z. Wu. "Balancing silicon/aluminum oxide junctions for super-plasmonic emission enhancement of quantum dots via plasmonic metafilms." *Nanoscale* 10, no. 10, 4825-4832 (2018).
[14] Sadeghi, Seyed M., Rithvik R. Gutha, Ali Hatef, Ryan Goul, and Judy Z. Wu. "Ultrahigh brightening of infrared PbS quantum dots via collective energy transfer induced by a metal-oxide plasmonic metastructure." *ACS applied materials & interfaces* 12, no. 10, 11913-11921 (2020).
[15] Cao, En, Weihua Lin, Mengtao Sun, Wenjie Liang, and Yuzhi Song. "Exciton-plasmon coupling interactions: from principle to applications." *Nanophotonics* 7, no. 1, 145-167 (2018).
[16] Simon, Daniel K., Paul M. Jordan, Thomas Mikolajick, and Ingo Dirnstorfer. "On the control of the fixed charge densities in Al2O3-based silicon surface passivation schemes." ACS applied materials & interfaces 7, no. 51, 28215-28222 (2015).
[17] Schmidt, J., A. Merkle, R. Brendel, Bram Hoex, MCM van de Sanden, and W. M. M. Kessels. "Surface passivation of high-efficiency silicon solar cells by atomic-layer-deposited Al2O3." Progress in photovoltaics: research and applications 16, no. 6, 461-466 (2008).
[18] Sadeghi, S. M., W. J. Wing, and Q. Campbell. "Normal and anomalous plasmonic lattice modes of gold nanodisk arrays in inhomogeneous media." Journal of Applied Physics 119, no. 11, 114307 (2016).
[19] Gutha, Rithvik R., Seyed M. Sadeghi, and Waylin J. Wing. "Ultrahigh refractive index sensitivity and tunable polarization switching via infrared plasmonic lattice modes." *Applied Physics Letters* 110, no. 15, 153103 (2017).