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# Metal oxide control of exciton-plasmon coupling

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## ABSTRACT

A key application of metallic nanostructures is enhancement of the radiative decay rates of quantum emitters. In this contribution we investigate control of emission dynamics of semiconductor quantum dots (QDs) using combination of both metal oxides and plasmonic effects of gold thinfilms. Different metal oxides, including Cu, Ag and Al oxides are investigated. We show how such oxides can dramatically change the decay of QDs via photocatalytic processes in the absence and presence of plasmonic fields. The outcomes show the distinct impact of such oxides, ranging from total annihilation of QD emission to their plasmonic revival via Purcell effect.

**Keywords:** metal oxides, plasmons, metallic nanoparticles, exciton-plasmon coupling, photocatalytic

## 1. INTRODUCTION

Depending on their sizes, metallic nanoparticles (MNPs) are characterized by their strong plasmonic absorption and scattering features. Significant interest has been devoted towards application of these features to suppress or enhance the emission of the semiconductor quantum dots (QDs).<sup>1-4</sup> These two competing processes have many useful applications, such as colorimetric measurements of DNA conjugations,<sup>5</sup> investigation of energy transfer processes in superstructures formed via bio-molecules,<sup>6</sup> device applications such as optical and plasmonic antennas,<sup>7,8</sup> and light emitting devices.<sup>9</sup> Recent studies have also shown that when QDs are placed in the vicinity of MNPs, plasmonic effects can enhance the rate of Forster resonance energy transfer (FRET) between donor and acceptor QDs.<sup>10-15</sup> This process has been studied in thin film QDs consisting of two monodisperse QDs separated, or mixed together, and in the presence of MNPs having various sizes.<sup>13, 15-17</sup>

Previous reports have shown that the fluorescence of QDs in the presence of MNPs is influenced by the contributions of two competing processes: enhancement of plasmonic near fields of the MNPs and FRET from the QDs to the MNPs.<sup>18-20</sup> Under different conditions, such as the MNP size distributions, QD emission wavelengths, and the distance between the QDs and MNPs, the outcome of this competition can lead to either enhancement of the QD emission or its suppression.<sup>4,21</sup> According to Refs. 11 and 17, in the presence of large gold MNPs a monodisperse QD solid exhibits emission enhancement,<sup>16</sup> but suppression is characteristic of FRET from the QD to the MNP for small MNPs. The results reported by of Li et al further supported this conclusion.<sup>22</sup>

In this contribution we investigate control of emission dynamics of QDs using combination of metal oxide and plasmonic effects of gold thinfilms with rough surfaces. Different metal oxides, including Cu, Ag and Al oxides are investigated. We show how such oxides can dramatically change the decay channels of QDs via different photocatalytic processes in the absence and presence of plasmonic fields. The outcomes show the distinct impact of such oxides, ranging from near total suppression of QD emission to their plasmonic revival. This study also shows how metal oxides can be used to control the defect environments of QDs and the way this can change the competition between plasmonic enhancement of decay rates of QDs and transfer of their energies to the metallic nanostructures.

Investigation of the impact of metal oxides can play a significant roles in device applications of plasmonic effects. This is related to the fact that application of Si/Al oxide charge barrier can suppress migration of photo-excited electrons from QD cores to the surface traps or defects in the substrate.<sup>23-25</sup> Our recent study has shown when such a charge barrier is put in close vicinity of a Schottky junction formed via contact of Au with Si, the outcome can be dramatic increase of quantum efficiency of QDs as the result of suppression of their defect environment via Purcell effect and hot electron capture by this junction.<sup>26-27</sup>

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## 2. METHODOLOGY

Samples were fabricated by sputtering 40 nm of Au on glass substrate followed by deposition of 25 nm of amorphous Si. On the top of the Si layer we then sputtered 1 nm of either Al, Ag, or Cr. After exposure to air, these layers were converted to oxide. The metal surface was rough, supporting localized surface plasmons resonances (LSPRs),<sup>28</sup> and the surface morphologies of Si and Si/metal oxides supported gains of oxides [27]. After depositing the oxide, a thin layer of CdSe/ZnS QDs was spin coated on the samples (Figure 1). The QDs were acquired from NN Lab INC and had emission wavelength of about 630 nm. The emission of the QDs were measured using a 514 nm laser and spectrometer. The time resolved measurements were done using a Time Correlated Single Photon Counter (TCSPC) system. This system included a 450 nm pulsed laser with about 30 ps temporal width, a single photo avalanche detector (SPAD), and a time tagging system (Picoquant Timeharp 260).

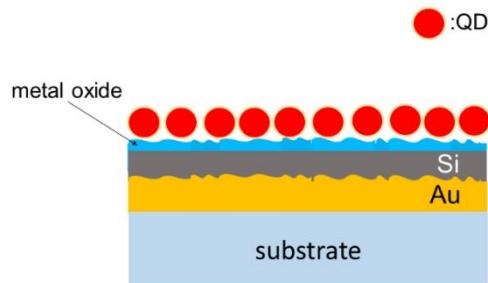


Figure 1. Schematic of the structure used for investigation of impact of metal oxides on exciton-plasmon coupling. The thickness of the Au thinfilm is 40 nm and the Si layer is 25 nm thick.

## 3. RESULTS

Figure 2 shows the results for the case when the metal oxide was Al oxide. These results suggest significant emission enhancement for case of QDs on Au/Si compared to those on Si. In fact for this case the plasmonic emission enhancement factor (PEF), defined as the ratio of emission of QDs in the presence to those in the absence of QDs, is equal to 16.5. This is due to the optimized spacing between the QDs and the Au thinfilm, which provides large amount of Purcell factor and small rates for FRET.

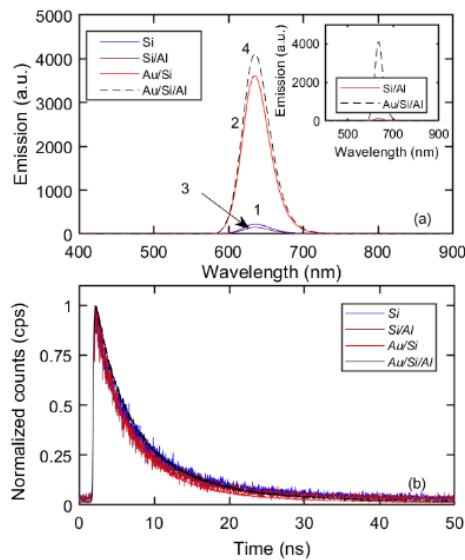


Figure 2. Emission spectra (a) and decay (b) of the QDs on the structure shown in Figure 1 when the metal oxide is Al oxide. Lines 1, 2, 3, and 4 refer to the case of QDs on Si, Au/Si, Si/Al ox, and Au/Si/Al ox, respectively.

For the case of Si/Al ox and Au/Si/Al the amount of PEF reaches about 28 (Figure 2 inset). This demonstrates the impact of having the Au/Si Schottky junction close to the Si/Al oxide charge barrier.<sup>26</sup> As schematically shown in Figure 3, for the structure considered in Figure 2 the hot electrons formed via decay of plasmons have the chance to be transferred to the Si layer. Because of the Si/Al charge barrier which has negative charge, such electrons can become accumulated in this layer, forming an electrostatic barrier that can prevent migration of electrons from the QDs. This leads to suppression of Auger recombination and increase of PEF. The results in Figure 2b show that the lifetimes of the QDs in all four cases are more or less similar. The significance of these results is that this happens while the emission of the QDs are quite differently, particularly for the very high emission enhancement supported by Au/Si/Al oxide.

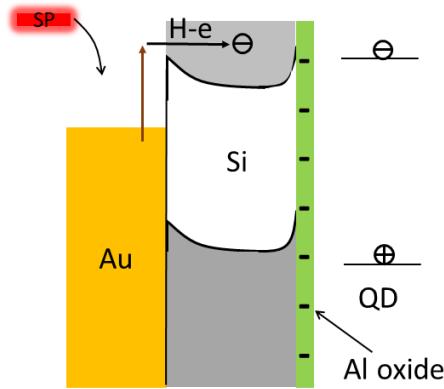


Figure 3. Schematic of the band structure of the structure considered in Figure 1 when the oxide is Al oxide. This figure shows how the decay of plasmons leads to formation of hot electrons, which can be transferred to the Si layer.

The results for the case of Cr oxide are presented in Figure 4. Here the amount PEF for the case of Si and Au/Si is very similar to the case seen in Figure 2. The value of PEF for the case of Si/Cr ox and Au/Si/Cr ox is also found about 23. The key difference between the results in Figures 2 and 4, however, is that in the former case (with Al oxide) the absolute value of emission intensity of the QDs was quite large, even larger than the case of Au/Si. For the case of Figure 4 (Au/Si/Cr ox), however, the emission of QDs is far less, about 1/3 of what seen for the case of Au/Si.

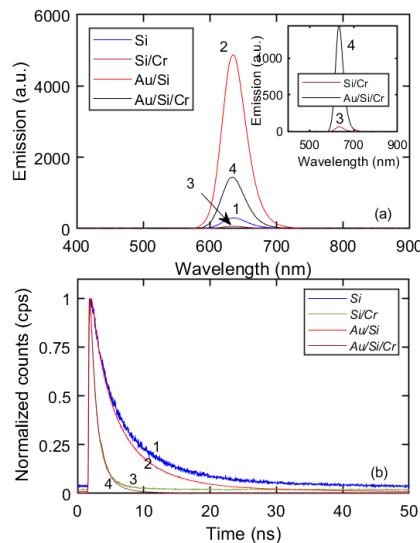


Figure 4. Emission spectra (a) and decay (b) of the QDs on the structure as shown in Figure 1 when the oxide is Cr oxide. Lines 1, 2, 3, and 4 refer to the case of QDs on Si, Au/Si, Si/Cr ox, and Au/Si/Cr ox, respectively.

The key reason behind the large PEF seen in the case of Cr oxide is that, as shown by us before,<sup>29</sup> such an oxide can effectively oxidize both cores and shells of CdSe/ZnS QDs. Therefore, it drastically reduces the quantum efficiency of the QDs. This can be seen clearly in Figure 4, wherein the emission of QDs on Si/Cr ox is quite small. Because of the significantly small amount of quantum efficiency, the plasmonic effects can play a greater role, increasing the PEF of the QDs.

The lifetimes of QDs in the case of Cr oxide highlight its impact. As seen in Figure 4b, in the case of QDs on Si the lifetime is rather relatively long (line 1). For the case Au/Si (line 2) we found similar decay, as in the case of Figure 2b. Addition of Cr oxide, however, reduces the lifetime of the QDs significantly (line 3). Addition of the Au thinfilm to Si/Cr oxide seems to cause no significant change in the lifetime of the QDs compared to the case of Si/Cr oxide, except for the slow decay part occurring after 5 ns of the scale. This can be associated with the impact of the Purcell effect.

The results for the case of Ag oxide is rather more dramatic. The results shown in Figure 5a indicate that in the case of this oxide, while the emission of the QDs on Si and Au/Si remains similar to the cases seen in Figures 2 and 4 (lines 1 and 2), the amount of light emitted by QDs on Si/Ag oxide is strongly suppressed (inset, line 3). The results in Figure 5 (inset) show, however, that in the presence of the Au thinfilm, the emission of QDs is revived to some extent (line 4). This indicates the impact of Purcell effect that makes the radiative lifetimes of the QDs shorter, allowing it to compete better with the profound impact of Ag oxide. Figure 5b shows such an oxide dramatically reduces the emission of the QDs (Figure 5b, line 3), reaching a range of about 250 ps. The presence of Au thinfilm further reduces the lifetimes of QDs further (Figure 5b inset, line 4). These results suggest the very strong photocatalytic degradation caused by Ag oxide.<sup>30</sup>

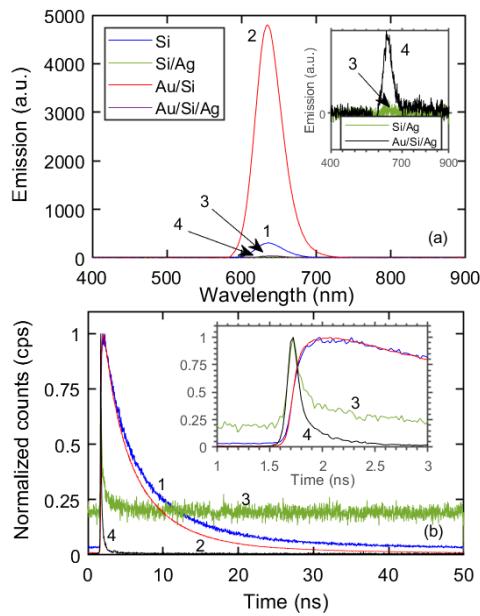


Figure 5. Emission spectra (a) and decay (b) of the QDs on the structure as shown in Fig.1 when the oxide is Ag oxide. Lines 1, 2, 3, and 4 refer to the case of QDs on Si, Au/Si, Si/Ag ox, and Au/Si/Ag ox, respectively.

The cases studied above highlighted the impact of Si/metal oxide on the way QDs interact with plasmons. The two clear distinct cases are Si/Al oxide and Si/Ag oxide. Our results showed that when Si/Al oxide comes in close vicinity of Au/Si junction, the plasmonic effects and, therefore, exciton-plasmon coupling is enhanced.<sup>26</sup> This can impact on a wide range of application of such a coupling,<sup>31</sup> ranging from suppression of quantum decoherence<sup>32</sup> and formation of plasmonic metaresonances<sup>33,34</sup> to rectification and bistability,<sup>35,36</sup> coherent control of optical population<sup>37</sup> and quantum sensors.<sup>38</sup>

#### 4. CONCLUSIONS

In this contribution we studied the impact of various metal oxides on the way QDs interact with Au thinfilm with rough surfaces. The roughness supported localized surface plasmon resonances, causing variations of the emission intensities and lifetimes of the QDs. Our results showed that Al oxide can promote exciton-plasmon coupling via suppression of the defect environment of the QDs. On the other hand, Ag oxide can lead to profound oxidation, leading to near total annihilation of the QD emission. In the presence of plasmonic effects part of this emission is revived via Purcell effect.

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