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Chaitanya Indukuri, Arnab Mukherjee, and J. K. Basu

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Tailoring local density of optical states to control emission intensity and anisotropy of quantum dots in hybrid photonic-plasmonic templates

Chaitanya Indukuri, Arnab Mukherjee, and J. K. Basu

Department of Physics, Indian Institute of Science, Bangalore 560012, India

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We report results of controlled tuning of the local density of states (LDOS) in versatile, flexible, and hierarchical self-assembled plasmonic templates. Using 5 nm diameter gold (Au) spherical nanoantenna within a polymer template randomly dispersed with quantum dots, we show how the photoluminescence intensity and lifetime anisotropy of these dots can be significantly enhanced through LDOS tuning. Finite difference time domain simulations corroborate the experimental observations and extend the regime of enhancement to a wider range of geometric and spectral parameters bringing out the versatility of these functional plasmonic templates. It is also demonstrated how the templates act as plasmonic resonators for effectively engineer giant enhancement of the scattering efficiency of these nanoantenna embedded in the templates. Our work provides an alternative method to achieve spontaneous emission intensity and anisotropy enhancement with true nanoscale plasmon resonators. © 2015 AIP Publishing LLC.

Tailoring light-matter interactions, especially the ability to control spontaneous emission of quantum emitters (QE), has been actively pursued1–5 since the suggestion by Purcell6 of a strategy to enhance spontaneous emission rate, through the Fermi’s golden rule, by controlling the local density of photonic states (LDOS), $\rho$. Advances in technology have enabled development of various methods to control LDOS at the scale of optical electromagnetic radiation using photonic cavities and resonators.7–10 High values of Purcell factor, $F_P = Q/V$, have been achieved in several such resonator systems with dimensions $\sim \lambda$.11–13 Here, $Q$ is the quality factor of the cavity or resonator, $V$ is electromagnetic mode volume, and $\lambda$ is the wavelength of radiation. The emergent field of nanophotonics14,15 aims at studying and exploiting light-matter interactions at the nanoscale both for developing optical nanotechnologies and for an understanding of the feasibility of scaling of such interactions to such small spatial length scales. One of the major challenges confronting research in the deep subwavelength regime is to enhance $F_P$ so as to improve sensitivity to the level of single molecule or single photons for which nanoresonators with mode dimensions of few tens of nanometers or less are required. Plasmonic16–23 and metamaterial templates24,25 have been explored as possible nanoscale resonators which can provide large, $F_P$. While plasmonic nanoantennas appear to be the most promising candidates for achieving large $F_P$ enhancements due to the extremely small $V$ values26–28 achievable, in principle, it is well known that strong dissipative losses in such systems lead to simultaneous reduction of the $Q$ values leading to saturation of $F_P$ enhancement at the nanoscale. Hence, alternative strategies using hierarchical assembly methods are beginning to be developed to alleviate this problem.20–22

Here, we report the study of controlled LDOS tuning in a functional, flexible, and hierarchical self-assembled photonic-plasmonic template using extremely small gold (Au) nanoparticles of diameter 5 nm which by themselves are believed to be unable to produce any significant enhancement of emitter emission intensity. Using these Au nanoantenna elements polymer films a versatile, hierarchical two dimensional (2D) hybrid template has been developed which enables continuous tuning of the photoluminescence (PL) of Cadmium Selenide (CdSe) quantum dots embedded in this template, as a function of the composition of Au nanoparticles, $\phi_{Au}$. Experimentally, maximum PL enhancement of $\sim$4 has been demonstrated. However, finite difference time domain (FDTD) simulations indicate that, under appropriate conditions in these templates, the PL enhancement could reach a factor of 10–15. Coupled with such unexpectedly large enhancements for the small Au nanoantenna, we also observe reasonably strong polarisation anisotropy of emission lifetime of the quantum dots embedded in such templates which are otherwise isotropic. Experimentally, we observe maximum emission lifetime of $\sim$0.3 ms while in simulations this can be further extended to $\sim$0.7 ms for parameters not explored in experiments. The lifetime anisotropy can also be controlled by variation of template thickness. In addition, large enhancements in scattering efficiency of the embedded nanoantenna in such templates, with respect to their intrinsic scattering efficiency in air, is demonstrated through FDTD calculations further expounding the versatility and utility of these photonic-plasmonic templates as effective resonators for plasmonic nanoantenna and quantum emitters. Our work opens up a significantly different method to engineer large enhancements of emission intensity and lifetime of quantum emitters using assemblies of extremely small metal nanoparticles as nanoantenna elements which could help develop efficient nanoscale light sources and optical communication in the truly nanoscale regime.

CdSe quantum dots used for the experiment with two different PL maxima SCdSe (545 nm) and LCdSe (570 nm) were prepared according to the procedure already reported...
earlier; while Au nanoparticles with surface capping of trioctyl phosphine oxide (TOPO) were synthesized based on the method described previously. The plasmonic templates are based on Polystyrene (PS-300 KDa)-Poly vinyl pyridine (P4VP-125 KDa) diblock copolymer (BCP) templates of hexagonal arrays of vertically aligned cylinders prepared on silicon substrates using methods similar to earlier reports. The diameter of the cylinders and their average separation is specified in Table I. These templates were loaded with CdSe quantum dots inside the matrix, surrounding the P4VP cylinder. To create ordered porous BCP, we etched the P4VP resulting in a base template of order pores inside PS matrix. Room temperature etching leads to NPBCP templates, while high temperature etching leads to HPBCP templates. To create the desired plasmonic templates, we filled these templates with Au nanoparticles following methods described in Ref. 34. Details of the samples used in this study are specified in Table I. Typical thickness of the templates used in this report is 180 nm. Atomic force microscopy (AFM) measurements were performed in non-contact mode with NT-MDT-Integra AFM system. All PL spectral measurements on our samples were performed with WITec alpha SNOM confocal mode using the blue line (488 nm) of an Ar ion laser, in transmission mode as described earlier. The polarization dependent time resolved PL measurements were performed using time correlated single photon counting (TCSPC) system from Horiba Scientific (Fluoro cube-01-NL) system. UV-visible measurements on the films were performed in transmission geometry using a Perkin Elmer (LAMDA-750) spectrometer. Finite difference time domain simulations (Lumerical Solutions, Inc., Canada) were performed to calculate various quantities such as absorbance, electric field, LDOS, and Purcell factor with unit cell consisting of cylinders with and without the Au nanoparticles surrounded by PS matrix loaded with CdSe quantum dots. Further details regarding methodology of calculation of various quantities using FDTD are available in Ref. 35.

![Fig. 1](image)

**FIG. 1.** (a) Schematic diagram of plasmonic template defining the parameters $R$ and $d$ as well as showing the location of the Au nanoparticles and the CdSe quantum dots. (b) AFM image of NPBCPL film. Inset shows the corresponding FFT. (c) UV-Visible absorption spectra of various templates indicated in the panel. (d) Steady state PL measurements on the same templates as in (c) loaded with LCdSe quantum dots.

**TABLE I.** Specification of PBCP-CdSe composite films. $\phi_{\text{CdSe}}$ and $\phi_{\text{Au}}$ are the volume fraction of CdSe quantum dots and Au nano particles in respective plasmonic template. $R$ and $d$ are average pore radius and inter pore separation in plasmonic template, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_{\text{CdSe}}$</th>
<th>$\phi_{\text{Au}}$</th>
<th>$R$ (nm)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPBCP</td>
<td>0.0135</td>
<td>0</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCP-Au1</td>
<td>0.0135</td>
<td>0.014</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCP-Au2</td>
<td>0.0135</td>
<td>0.048</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCP-Au3</td>
<td>0.0135</td>
<td>0.059</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>HPBCP</td>
<td>0.0135</td>
<td>0</td>
<td>28</td>
<td>95</td>
</tr>
<tr>
<td>HPBCP-Au1</td>
<td>0.0135</td>
<td>0.0207</td>
<td>28</td>
<td>95</td>
</tr>
<tr>
<td>HPBCP-Au2</td>
<td>0.0135</td>
<td>0.0647</td>
<td>28</td>
<td>95</td>
</tr>
<tr>
<td>HPBCP-Au3</td>
<td>0.0135</td>
<td>0.0712</td>
<td>28</td>
<td>95</td>
</tr>
<tr>
<td>NPBCPS</td>
<td>0.0135</td>
<td>0</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCPS-Au1</td>
<td>0.0135</td>
<td>0.014</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCPS-Au2</td>
<td>0.0135</td>
<td>0.048</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>NPBCPS-Au3</td>
<td>0.0135</td>
<td>0.059</td>
<td>20</td>
<td>95</td>
</tr>
</tbody>
</table>
Au nanoparticles in the template, with $\phi_{Au}$. We also modified the geometric parameter of the PBCP templates to change the R/d values. The larger P4VP cylinder volume leads to larger possible values of $\phi_{Au}$ and hence larger overall absorbance. Interestingly, large PL enhancement from the embedded CdSe quantum dots can be observed in Fig. 1(d). This is quite remarkable since such enhancements are achieved with Au nanoparticles which, by themselves, are not expected to give any enhancement at all.\cite{36,37} The enhancement, $F$, seems to scale with $\phi_{Au}$ and we have reached a maximum of $\sim 3$ with LCdSe based samples and $\sim 4$ with the SCdSe based samples [S6 in Ref. 35]. These values of $F$ are found to be further enhanced in the HPBCPL samples that have been studied experimentally. Interestingly, we find that despite having the same absorbance values as the LCdSe based samples the SCdSe samples shows higher $F$ for identical $\phi_{Au}$ indicating the possible role of LDOS in PL enhancement. Further we observe that although absorbance increases for the HPBCP template $F$ remains almost same as the NPBCPL templates for comparable $\phi_{Au}$ again suggesting LDOS being a crucial parameter in determining overall PL enhancement. We will discuss these aspects in more detail later. We now focus our attention on time resolved polarised and un-polarised PL measurements on these samples. The measurements were performed with samples in grazing incidence geometry with respect to the incident beam so that polarisation parallel and normal to the surface can be defined. Figure 2(a) shows PL lifetime data for the various samples with un-polarised excitation. The estimated total lifetime $\tau$ is also indicated in the respective panels. Clear reduction of the PL lifetime with increasing $\phi_{Au}$ is visible pointing to the role of the plasmonic template in controlled tuning of spontaneous emission decay rates of the quantum dots. The results of the polarisation dependent lifetime measurements on the same samples are also quite remarkable. A clear anisotropy in decay lifetime defined by $G$,\begin{equation}
 G_{Exp} = \frac{|\tau_p - \tau_s|}{|\tau_p + \tau_s|}, \end{equation}
is observed which also seems to increase with $\phi_{Au}$. In Eq. (1), $\tau_p$ and $\tau_s$ are average lifetimes\cite{38} of CdSe quantum dot with $S$ and $P$ polarized excitation, respectively. These issues will be discussed further. In the following, we describe, how the observed behavior of the spontaneous emission of the CdSe quantum dots in the hierarchical hybrid template can be understood and also predict the expected behavior for in terms of values of certain parameters which were not utilised in the experimental templates.

The total PL enhancement factor, $F$, can be defined as\cite{39,40}
\begin{equation}
 F = F_{abs}(\omega_{ex}) \times F_{em}(\omega_{em}), \end{equation}
where $F_{abs}(\omega_{ex})$ is absorption enhancement and $F_{em}(\omega_{em})$ is emission enhancement. To calculate the excitation enhancement $F_{abs}(\omega_{ex})$, we designed templates corresponding to our experimental samples, in FDTD and calculated the spatial distribution of electric fields, $E$. A typical spatial distribution of $E^2$ is shown in the [S11 (Ref. 35)]. $F_{abs}(\omega_{ex})$ is then calculated as
\begin{equation}
 F_{abs}(\omega_{ex}) = \int \frac{E_{Au}^2}{E_{base}} dx dy, \end{equation}
where $E_{Au}$ is spatial distribution of electric field in PBCP template with Au nanoparticle loading and $E_{base}$ is spatial distribution of electric field in PBCP template.

Another remarkable feature of these hybrid photonic-plasmonic templates is there ability to engineer giant enhancement of scattering efficiency of embedded small nano antenna. To capture this aspect, we have also calculated the ratio of scattering efficiency $C_s$ to the absorption efficiency $C_a$ for plasmonic nano antenna located in air or plain dielectric and with in the template. Figure 3(a) shows the ratio $C_s/C_a$ as a function of the diameter of the spherical nanoantenna, $D$, in air and in our NPBCP template. This ratio seems to almost independent of nano antenna diameter with in the template but the effective giant enhancement of this ratio with respect to the values of the nano antenna in air is remarkable. To estimate $F_{em}(\omega_{em})$, we calculated the spatial dependent Purcell factor $F_P$ for these templates by considering a quantum dot as a dipole emitter having spectral properties exactly matching the quantum dot. The total $F_P$ is calculated as the weighted average of the corresponding curves in Fig. 3(b) and the estimated spatial distribution of CdSe quantum dots inside the BCP template as estimated from transmission electron microscopy (TEM) images [S5 (Ref. 35)], The isotropy of the film along the plane normal to the thickness ensures that this spatial profile of $F_P$ is independent of the direction from the Au filled cylinders. From these profiles of $F_P$, we calculated the $F_{em}(\omega_{em})$ of CdSe quantum dots inside these plasmonic templates defined by

![FIG. 2. (a) Unpolarized time resolved PL of QD in NPBCPL. Polarization dependent time resolved PL on (b) NPBCP template. (c) NPBCP Au1, (d) NPBCP Au2 and (e) NPBCP Au3 template.](Image)
Using FDTD simulations, we also calculated, as can be seen from Fig. 3(c), the maximum absorbance for the NPBCPL samples which matches quite well with the experimentally observed values shown in Fig. 1(c). The versatility of our templates can be further understood by observing the extended range of parameter space that can be explored in them of varying the ratio $R = d$ through control of etching process. We were able to change LDOS by changing $R = d$ as shown in Fig.4(a). The LDOS variation explains the anomalous observation in Fig.1(d) of large increase in the UV-Visible absorbance of HPBCPL samples with incommensurate increase in corresponding PL. For instance, the F value for HPBCPLAu$_2$ sample is 2.5 which it is 2.9 for NPBCP sample despite the fact the $\phi_{Au}$ for the NPBCPAu$_3$ former is larger than the later. Similarly, the spectral tunability of LDOS, as represented through the spectral dependence of $F_P$ (S12 (Ref. 35)), lead to a larger enhancement of quantum dot emission occurring close to the $F_P$ maxima. This can be seen from the fact that $F$ for SCdSe samples at same $\phi_{Au}$ as compared to LCdSe based samples is much larger, as was stated earlier. All these measurements and the corresponding calculation indicate the tunability of the photonic properties of plasmonic templates to control the emission of embedded quantum dot. It should be noted here that the values of various quantities, like $F_P$, calculated here is averaged over two distinct polarization states of the emitters. These are typically 3–4 times smaller than the maximum possible values for the same configuration if perpendicular polarisation of the emitters and a location close to the cylinders is assumed.

To understand the anisotropic decay, we calculated the polarization dependent LDOS in our photonic-plasmonic templates over the spectral span of the dipole emission as shown in Fig. 4(b). This is done by orientation of dipole momentum vector along Z axis and XY plane to calculate $q_z$ and $q_{xy}$, respectively. We observe the change in the DOS with polarization and the difference between them increasing with Au concentration in the template well agreement with the experimental results. The total LDOS is calculated by integrating the wavelength span of the dipole. From these polarization dependent DOS, we have calculated the $GF_{FDTD}$ defined as

$$GF_{FDTD} = \frac{\rho_z - \rho_{xy}}{\rho_z + \rho_{xy}}.$$  

The experimental and calculated values of the anisotropic factors are shown in Fig. 4(c). The simulation results are in reasonable agreement with the experimental values. Additional simulations performed with various thickness seems to suggest that this anisotropy is geometric in origin with larger $G_{FDTD}$ value observed for larger film thickness (implying cylinders with larger aspect ratio) at identical $\phi_{Au}$.

In conclusion, we report the systematic studies of $GF_{FDTD}$ for various films indicate that this value increases with increasing $\phi_{Au}$ for a fixed thicknesses. We report the study of
controlled LDOS tuning in a functional, flexible, and hierarchical self-assembled photonic-plasmonic template using extremely small Au nanoparticles of diameter 5 nm. Using these Au nanoantenna elements in a 2D polymer template, a photonic-plasmonic template has been developed which enables continuous tuning intensity and lifetime anisotropy of the quantum dots embedded in this template, as a function of the composition of Au nanoparticles. It is also demonstrated that these hybrid templates enhance the scattering efficiency of embedded nano antennas significantly. We have explored the anisotropy in the templates using the polarization dependent time resolved PL measurements. We demonstrated that the decay dynamics in the plasmonic templates can be controlled in a facile manner by changing the filling fraction of the Au nanoparticles. This polarization dependent anisotropic decay dynamics for the quantum emitters is determined by polarization dependent LDOS of the plasmonic templates as demonstrated by FDTD simulations which shows reasonably good agreement with experimental results. This type of control over emission is likely to be very useful in various applications like plasmonic solar cells, high efficiency display devices, and optical communication.

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35See supplementary material at http://dx.doi.org/10.1063/1.4916548 for details of sample preparation, TEM images of quantum dots in solution and in templates and FDTD simulation.