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Citation: Journal of Applied Physics 115, 134315 (2014); doi: 10.1063/1.4870575
View online: http://dx.doi.org/10.1063/1.4870575
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/13?ver=pdfcov
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(Received 3 January 2014; accepted 25 March 2014; published online 7 April 2014)

We studied plasmonic features of bimetallic nanostructures consisting of gold nanoisland cores semi-coated with a chromium layer and explored how they influence emission of CdSe/ZnS quantum dots. We showed that, compared with chromium-covered glass substrates without the gold cores, the bimetallic nanostructures could significantly enhance the emission of the quantum dots. We studied the impact of the excitation intensity and thickness of the chromium layer on this process and utilized numerical means to identify the mechanisms behind it. Our results suggest that when the chromium layer is thin, the enhancement process is the result of the bimetallic plasmonic features of the nanostructures. As the chromium layer becomes thick, the impact of the gold cores is screened and the enhancement mostly happens mostly via the field enhancement of chromium nanoparticles in the absence of significant energy transfer from the quantum dots to these nanoparticles. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870575]

I. INTRODUCTION

Localized surface plasmon resonances (LSPR) in metallic nanoparticles (MNPs) have inspired significant amount of research and applications, ranging from fundamental physics to chemical and biological sensors,1–8 optical diagnostic,9–11 nano-devices,12–14 etc. Many of these studies are based on hybrid systems consisting of semiconductor quantum dots (QDs) and MNPs. These systems have been used for colorimetric measurements of DNA conjugations,15 energy transfer processes in superstructures formed via bio-molecules,16,17 construction of active nanostructures,18 etc. Plasmonic field enhancement via MNPs has also been used for various device applications, such as optical and plasmonic antennas,19–23 light emitting devices and photovoltaic,24–26 and coherent nanoantennas wherein coherent effects are used for detection and ranging of nanostructures.27

Majority of these research activities rely on plasmonic properties of MNPs fabricated from one type of metal. Recent research have explored bimetallic nanoparticles (bi-MNPs) consisting of two types of metals.28–30 For example, bi-MNPs consisting of Au cores and Ag shells have been used to reveal interesting effects, including tunable plasmonic resonance band, which can be useful for biocompatible multicolored dark field imaging.31 Bi-MNPs have also been investigated for their applications in Raman scattering,32 affinity sensors,33 fiber optic sensor devices,34 waveguides,35 and light traps.36

Our objectives in this paper are to study the plasmonic features of bi-MNPs consisting of core gold nanoislands semi coated with chromium (Cr) and investigate how these features influence emission of colloidal CdSe/ZnS QDs. We show that compared with glass substrates coated with the same thickness of Cr layer in the absence of gold nanoisland cores, such bi-MNPs can support significant amount of emission enhancement. Our results show that the nature of this process depends on the thickness of the Cr layer. For thin Cr layer, this process is correlated with the bimetallic plasmonic features of the MNPs. These include spectral broadening and red shift of the plasmonic absorption and electric field enhancement, as the thickness of the Cr layer increases. When such a thickness becomes significant, however, the effects of the gold cores are screened and the emission enhancement mostly occurs via the field enhancement as if the bi-MNPs were only made of Cr. Our results show that such a field enhancement process happens because of the increase in the mode volume of the plasmonic field and its spectral red shift towards the emission peak wavelengths of the QDs. This processes happen while the plasmonic absorption spectra of the bi-MNPs are blue shifted and smeared out, indicating the absence of efficient Forster resonance energy transfer (FRET) from the QDs to the MNPs. These results seem to be consistent with a recent report that showed when QDs were in the presence of Cr nanoparticles, their lifetimes were not changed, although their emission was enhanced.37

II. NUMERICAL INVESTIGATION OF PLASMONIC EFFECTS OF GOLD-CHROMIUM BIMETALLIC NANOPARTICLES

The bi-MNPs studied experimentally in this paper include Au nano-islands coated from the top with 1, 3, 7, or 50 nm of Cr, as explained in Sec. III. We are interested to study how the plasmonic effects of such MNPs influence the
emission of QDs which happened at about 639 nm. For this, we start our investigation by presenting the results of our numerical calculations for plasmonic effects of such MNPs obtained using COMSOL. The experimental results and the way they match with the outcomes of this section will be discussed in Secs. IV and V.

Because of the specifications of the Au nano-islands, in this section, we approximate them with oblate nanospheroid Au cores covered with a semi-shell of Cr layer. As in our experiments, we consider the Au nanospheroids are placed on a glass substrate and the Cr layer covered them from the top, as expected to happen when Cr is sputtered from the top. Fig. 1 shows the results for the field enhancement of such bi-MNPs at about 639 nm. We consider the major and minor radii of the Au cores are 50 and 25 nm, respectively, and the thickness of the Cr layer is 0 (Cr0), 7 (Cr7), and 50 (Cr50) nm. We also show the field enhancement for a nanospheroid with the same size as that of Cr50, but totally made of Cr (Fig. 1, all-Cr), as a reference. We do not consider 1 nm of Cr in our simulation, since in contact with air it becomes fully oxidized, and numerically treatment of such a thickness is more demanding.

A rather obvious conclusion inferred from Fig. 1 is that as the bi-MNPs become larger, their field mode volumes are increased. As a result, they can encompass larger numbers of QDs, leading to larger overall enhancement of QD emission. The fact that at 639 nm, we can still see a significant modal field volume for the all-Cr MNP is rather peculiar, as previous studies mostly noted this at much shorter wavelengths.37

The bi-metallic nature of the plasmonic effects of the bi-MNPs becomes clearer when we investigate their absorption ($\sigma_{\text{abs}}$) and scattering ($\sigma_{\text{scat}}$) cross sections and maximum field enhancement factor ($P_{\text{enh}}$). $P_{\text{enh}}$ is defined as the ratio of the maximum amplitude of the field in the vicinity of a MNP to that in the absence of the MNP at the same location. The results presented in Fig. 2 show that when the thickness of the Cr layer is zero (very close to our sample with 1 nm of Cr), we have distinct absorption and scattering around 530 and 545 nm, respectively (thin solid lines). Fig. 2(c) shows under these conditions, $P_{\text{enh}}$ can reach higher than 9 at about 555 nm, close to the wavelength of the scattering peak.

As the thickness of the Cr layer increases, we can identify two different regimes. The first regime is mostly caused by the bi-metallic nature of the plasmonic effects. This can be seen in the results for the Cr3 and Cr7 samples, wherein $\sigma_{\text{scat}}$ and $P_{\text{enh}}$ undergo broadening and red shift, while $\sigma_{\text{abs}}$ mostly smears out (dashed and dotted-dashed lines). For Cr7, in particular, the $P_{\text{enh}}$ peak reaches the emission wavelength of the QDs (vertical dashed line), with a value of about 6.

The second regime happens when the thickness of Cr is high enough such that the bi-MNPs mostly act as if they are made of Cr only. Such a regime can be seen for Cr50 (dotted lines). The results show that for this case, scattering, absorption, and field enhancement are very similar to that of the all-Cr case (thick solid line), suggesting the impact of the Au cores are nearly totally screened. Interestingly, however, here the peak of $\sigma_{\text{scat}}$ occurs at about 430 nm, while $P_{\text{enh}}$ peak happens around 700 nm, although both are broadened significantly. $\sigma_{\text{abs}}$, on the other hand, undergoes significant amount of broadening with frequency dependency resembling that of bulk Cr.

![FIG. 1. Field profiles of oblate spheroids of Au nanoparticles with 50 and 25 nm major and minor radii, respectively, coated with 0 (Cr0), 7 (Cr7), and 50 (Cr50) of Cr from the top. The “all Cr” profile refers to the case of an oblate spheroid with the same size as Cr50 but totally consists of Cr (no Au nanoparticles). In all cases, the spheroids are placed on a glass substrate and the field profiles were obtained at 639 nm.](image1)

![FIG. 2. Variation of absorption cross section (a), scattering cross section (b), and field enhancement factor (c) of nanospheroids considered in Fig. 1 (legends in (a)) as a function of wavelength.](image2)
III. SAMPLES AND EXPERIMENTAL METHODS

To study the impact of the bi-MNPs on the emission of QDs experimentally, as mentioned in Sec. II, we fabricated four types of samples. The Au nanoislands were fabricated on glass substrates by evaporating 13 nm of Au followed by thermal annealing at 500 °C for 30 min. We then sputtered 1 (sample Cr1), 3 (sample Cr3), 7 (sample Cr7), and 50 nm of Cr (sample Cr50) on the top of the gold nanoislands, forming Au MNPs covered with semi-shells of Cr. A typical SEM image of such nanoislands, as shown in Fig. 3, demonstrates the formation of isolated islands with average sizes of about 100 nm.

After deposition of the Cr layers, a thin film of CdSe/ZnS QDs was spin coated directly on the Cr layer. Such QDs were obtained in toluene solution from NN labs, LLC. They had emission wavelength at about 639 nm and were coated with octadecylamine ligands. Samples were illuminated with an Ar ion laser (514 nm) perpendicular to their planes and emission spectra were measured using a thermoelectrically cooled spectrometer. In each sample, the Au nanoislands covered the central region of the substrate, while the Cr layer was sputtered all over. This allowed us to measure the emission of QD on the bi-MNPs and on the glass parts covered with a smooth layer of Cr in the absence of such MNPs. For clarity, in the following, we refer to the former region as the ‘bm-QD region’ and to the latter as the control region (Cr-QD). The latter acts as a control or reference region.

IV. EXPERIMENTAL RESULTS

To study the impact of plasmonic effects of bi-MNPs on the emission of QDs, we measured emission spectra of the QDs under different laser intensities. Using these spectra, we then studied variations of their peak wavelength ($\lambda_{\text{peak}}$) and Full Width Half Maximum (FWHM). The results presented in Figs. 4(a) and 5(a) show the way emission spectra of the QDs in the presence of bi-MNPs (the bm-QD region) are changed for Cr3 and Cr50 samples. The unique features of these spectra become evident once they are compared with those of QDs in the Cr-QDs, wherein the effects of bi-MNPs do not exist (Figs. 4(b) and 5(b)). The results show that, in overall, the QDs in the bm-QD regions are much more efficient emitters than those in the control regions. This is clearly true even for the case of Cr50, wherein a thick layer of Cr covers the Au nanoislands.

In Fig. 6, we present the results for variation of emission peaks of QDs in the presence of bi-MNPs (squares) as a function of the laser intensity ($I_0$). For each sample, we also
show the results for its control region, i.e., in the Cr-QD region (circles). For Cr3, Cr7, and Cr50 samples, we can see emission of QDs in the presence of bi-MNPs is in overall more than those in their control regions. For the case of the Cr1 sample, however, the emission of the QDs in the control region increases nearly linearly. This happens while in the presence of the bi-MNPs, the emission of QDs undergoes a sharp initial rise followed by a strong roll off when $I_0 \sim 60 \text{ W/cm}^2$. When $I_0$ passes $\sim 120 \text{ W/cm}^2$, the emission of such QDs becomes less than those in the control region.

The ratio of the QD emission in the presence of the bi-MNPs to that in the Cr-QD region is called emission enhancement factor ($E_{\text{enh}}$). This factor highlights the plasmonic impact of the bi-MNPs. The results in Fig. 7(a) show that for the case of Cr1 sample, $E_{\text{enh}}$ is about 2.8 at $I_0 \sim 8 \text{ W/cm}^2$. After a slight rise it starts to decline, reaching about 0.3 when $I_0 \sim 200 \text{ W/cm}^2$. The enhancement seen here at low laser intensity is an indication of the impact of plasmonic effects on the emission of the QDs in the absence of heat. Note that in the case of this sample, the thickness of the Cr layer is so small that it cannot cause significant changes in the plasmonic field of the Au nanoislands. Therefore, we believe in this case the heat generated by absorption of the laser beam via such nanoislands plays a major role in the roll off of $E_{\text{enh}}$. Fig. 7(a) shows that for the Cr3 sample, when $I_0 = 8 \text{ W/cm}^2$, $E_{\text{enh}}$ can reach 5. In the cases of Cr7 and Cr50 samples, we observed $E_{\text{enh}}$ is, in overall, about 5. Although, our results showed the net amount of emission in the case of QDs in the Cr50 sample was much smaller. This issue will be discussed in Sec. V.

The spectral properties of the emission of QDs in the bm-QD and Cr-QD regions are highlighted in Fig. 8. The results in Figs. 8(a) and 8(a') show that in the case of Cr1 sample, $\lambda_{\text{em}}$ and FWHM of the QDs in the Cr-QD region

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**FIG. 6.** Variation of the emission peak of the QDs as a function of the laser intensity in the presence of bi-MNPs (squares) and in the control region (circles) for Cr1 (a), Cr3 (b), Cr7 (c), and Cr50 (d) samples.

**FIG. 7.** The ratio of emission of QDs in the presence of bi-MNPs (in the bm-QD region) to that in the Cr-QD region for Cr1 (circles), Cr3 (squares), Cr7 (triangles), and Cr50 (crosses) samples.

**FIG. 8.** Variation of the emission peak wavelengths (a, b, c, and d) and FWHM (a', b', c', and d') of QDs in the presence of bi-MNPs (squares) and in the Cr-QD region (circles) as a function of the laser intensity for the types of samples studied in this paper.
remain nearly unaltered with the laser intensity (circles). This indicates that 1 nm Cr layer does not cause significant amount of heat, as also shown in our numerical calculations presented in Sec. VI. In the case of QDs in the presence of bi-MNP (bm-QD region), however, \( \lambda_{\text{em}} \) and FWHM are increased by about 8 and 12 nm, respectively. This, again, confirms the profound effects of the heat generated by the Au nanoislands as the laser intensity increases. The results presented in Fig. 8 show that as the thickness of the Cr layer increases, the amount of red shift and FWHM of emission of QDs in the bm-QD region are increased. These happen while the differences between such QDs and those in the control regions become small. For the cases of Cr7 ((c) and (c')) and Cr50 ((d) and (d')) samples, the spectral variations of the emission of the QDs in the bm-QD and Cr-QD regions become quite similar.

V. GOLD-CHROMIUM BI-METALLIC PLASMONIC EFFECTS ON QDs

The results presented in Sec. IV demonstrated enhancement of emission of QDs in the presence of bi-MNPs compared with those in the control regions. To continue our investigation, in this section we focus on the results obtained; \( I_0 \) was small (8 W/cm²). Using the simulation results presented in Sec. II, here we study the mechanism behind \( E_{\text{enh}} \) seen in Fig. 7 when the impact of heat is ignorable.

To start in Fig. 9(a), we show the absorption spectra of the bi-MNPs in the bm-QD regions for different thicknesses of Cr. For the case of the Cr1 sample, we see a sharp peak, indicating the presence of distinct plasmonic features. This is consistent with the results shown in Fig. 2(a) (thin solid line). As the thickness of the Cr layer increases, however, the peak starts to smear out and broaden. For the case of Cr50 sample, the thickness of Cr was so high that its absorption showed no clear feature (not shown). In Fig. 9(b), we show the results for the absorption spectra of the control region when the Cr thicknesses were 1, 3, 7, or 50 nm. The results show the expected, nearly featureless, absorption of Cr within the wavelength range considered in this study. These results suggest that the plasmonic structural features of bi-MNPs are fairly distinct up to 7 nm of Cr. Beyond this, these features are smeared out, becoming dominantly determined by Cr. These results are, in overall, consistent with our simulation results in Fig. 2(a).

In regard to the results shown in Fig. 9, note that the QD thin films in our samples were very thin. As a result, their effects in the absorption of the control regions were insignificant. Because of the plasmonic effects, however, this was not the case for the bm-QD regions. In these regions, the characteristic decay lengths of the plasmonic fields were very small. Therefore, although the QD films were very thin, they could change the effective refractive index experienced by the bi-MNPs. As a result, the actual absorption peaks of such MNPs in the absence of QDs happened at shorter wavelengths than those seen in Fig. 9(a).

Considering these results and those presented in Sec. II, the reason behind the large enhancement of QD emission in the case of the Cr3 sample can be related to the increase in the plasmonic mode volumes, as depicted in Fig. 1, and the large field enhancement of the bi-MNPs at the emission wavelength of the QDs. For the case of this sample, as shown in Fig. 2(c) (dashed line), the peak of field enhancement is close to the emission wavelength of the QDs, increasing their radiative decay rate. For the case of the Cr7 sample, \( E_{\text{enh}} \) reduces, leading to smaller enhancement of QD emission (Fig. 2(c), dashed-dotted line). Here, however, the peak of \( E_{\text{enh}} \) clearly happens around the emission wavelength of the QDs.

For the case of the Cr50 sample (similar to the all-Cr sample), because of the significant increase in the absorption of the bi-MNPs around the QD emission wavelength (Fig. 2(a), vertical dashed line) and efficient heat generation, the net emission of the QDs was lower than the cases of Cr3 and Cr7 samples. This happened despite the increase in the plasmonic mode volumes of such MNPs (Fig. 1). In our analysis, however, \( E_{\text{enh}} \) scales emission of the QDs in presence of these bi-MNPs with those in the control regions, which exhibited similar absorption. Therefore, in Fig. 7(b), \( E_{\text{enh}} \) reveals the impact of the field enhancement in case of the Cr50 sample, which based on Fig. 2(c) (dotted lines) should peak around the QD emission wavelength. Additionally, for such a sample, \( \sigma_{\text{abs}} \) becomes very broad, lacking distinct plasmonic feature. This may confirm the results reported recently that suggested Cr nanoparticles can support enhancement of emission in the absence of energy transfer.37

VI. DISCUSSION

The results shown in Fig. 6 suggest that as the laser intensity increases, the heat generated by bi-MNPs in the bm-QD region and Cr layers in the Cr-QD region can become
significant. Such a heat can reduce the emission yield of the QDs and cause red shift and broadening of their spectra. The results in Sec. IV suggest that for cases of Cr7 and Cr50 samples when \( I_0 = 120 \) and 80 W/cm\(^2\), respectively, the amounts of heat in both bm-Cr and Cr-QD regions were so significant that they made the QD emission quite low. These results also showed that as this happened the emission spectra of the QDs in these regions became very similar to each other, although in the former the QDs emitted \( \sim 5 \) times more. For the case of Cr3 sample in the Cr-QD region, we see the spectra of such QDs start to catch up with those in the bm-QD region (Figs. 8(b) and 8(b')) and in the case of Cr1 sample, they are very different (Figs. 8(a) and 8(a')).

To discuss these results, we estimated the amount of the heat generated in the Cr-QD region for different thicknesses of Cr using COMSOL. For this, we defined a three-dimensional model and then added the heat transfer module. The geometry (diameter and thickness), the glass material, chromium layer, and an effective quantum dot layer were defined and the boundary conditions were set. A suitable mesh was chosen and its convergence was checked. The results of simulation presented in Fig. 10 show that for 1 nm thick Cr layer, when the laser intensity is 200 W/cm\(^2\), the temperature increase is only couple of Kelvin. When the thickness increases to 3 nm, the local temperature increases to about 30 K. For the cases of 7 and 50 nm thick Cr layers, the temperature rise can be as larger as 50 and 110 K, respectively.

Considering the results in Figs. 2 and 10, we can present a rough assessment of the results presented in Fig. 8. To start note that the laser wavelength used to excite the sample was 514 nm. Such a wavelength is fairly close to the plasmonic peak of the bi-MNPs when the Cr layer is very thin or does not exist (Fig. 2(a), thin line). Therefore, one expects significant heat generation via plasmonic absorption of the laser field. For the case of Cr1 in glass (in Cr-QD region), however, we do expect to see significant heat generation, as shown in Fig. 10 (circles). This explains, to some extent, why in Figs. 8(a) and 8(a') the QD emission wavelength and FWHM in the bm-QD region undergo red shift and broadening while those in the Cr-QD region do not.

As the thickness of Cr increases, however the plasmonic absorption of the bi-MNPs is smeared out. Under this condition, their absorption resembles absorption of the Cr layer on glass. For the Cr50 sample, in particular, this allows the absorption spectra of QDs in the bm-QD and Cr-QD regions become similar (Fig. 2(a), thick and dotted lines). Around 639 nm, the wavelength of the QDs, we observed a steady rise of absorption for both bm-QD (Fig. 2) and Cr-QD regions (Fig. 9(b)). In both cases, most of the laser energy was absorbed leading to similar amount of heat and, therefore, similar spectra changes.

Note that the bi-MNPs discussed in this paper can offer a wider control over the plasmonic effects than those made of a single type of metal (Au or Cr). In this regard, the unique spectral changes of the absorption and field enhancement of such MNPs with the thickness of the Cr layer can provide us useful avenues to manipulate optics and carrier relaxation of QDs. Additionally, using such bi-MNPs, we can investigate how combination of the catalytic properties of Cr (and Cr oxide) and plasmonic effects can influence the photochemical and photophysical properties of colloidal QDs. In fact, recently, we have shown Cr oxide can accelerate photo-oxidation of such QDs.\(^{38,39}\) Therefore, if instead of about 1 s of irradiation, as the case of this paper, we irradiate these QDs over a much longer period of time (several minutes), their core sizes shrink rapidly and their emission undergoes significant blue shifting.\(^{38}\) It has also been shown that such a photo-oxidation process can suppress plasmonic enhancement of energy transfer between QDs.\(^{39}\)

VII. CONCLUSIONS

We studied emission enhancement of colloidal QDs in the presence of bi-MNPs consisting of Au core and semi-coated with Cr. Our results showed that for thin layer of Cr, we observed significant variation of plasmonic properties of the bi-MNPs. As the thickness of this layer reaches 50 nm, the impact of the Au core is relatively smeared out. Our results also showed that as the thickness of the Cr layer increases, the spectral features of QDs on glass substrates coated with the same thickness of Cr become similar to those with Au core. This suggested that although the bi-MNP systems offer field enhancement, they may offer similar rate of energy transfer broadening. The results also showed that up to 7 nm of Cr, we can see strong frequency-dependent plasmonic features.


