

Distance-dependent fluorescence emission in solid hybrid structures of colloidal CdS Quantum Dots and Gold Nanoparticles: a study upon fluorescence enhancement related to proximity effect induced by Hexylamine

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Abstract

Fluorescence emission analysis in films of hybrid materials composed of quantum dots and metal nanoparticles is difficult to be conducted because of reasons involving reproducibility and consistency in the results. First and foremost, a previously prepared solution of quantum dots and metal nanoparticles must be dropped on a surface, namely a glass slide, and subsequently solvent annealed to give rise to a smooth layer. This process is affected by many factors that can cause differences among the obtained samples, even if they come from the same solution. For instance, humidity and temperature can cause a different result when the fluorescence emission of the glass slides is tested. Moreover, the intrinsic variability of the fluorometer apparatus, namely temperature affected variations in the emitted light or in the detected signal can pose some difficulties when the results are compared. For example, measures taken at very different instants of time can be non-reliably compared. The present work considers an alternative method based on the calculation of signal ratios with the aim to reduce the effect of the intrinsically present variation caused by the utilized equipment.

Keywords: CdS Quantum dots, Gold Nanoparticles, Raft copolymerization, Metal Enhanced Fluorescence, solvent annealing.

1. Introduction

The interaction between fluorescent Quantum Dots and Metal Nanoparticles has widely been investigated since it represents a very promising topic as far as the development of bioimaging and sensors is concerned. As affirmed by Andries Meijerink, “energy transfer between QDs and metal nanoparticles is a hot topic” [1] Even though numerous publications exist about studies on QDs-metal NPs interaction, a clear understanding of the behavior of excitons in QDs in the proximity of a metal nanoparticle is still missing. However, what can be asserted is that when analyzing the proximity of the mentioned components three main events are likely to occur and need to be considered. First of all, scattering is always present when metal NPs are stimulated by an incoming radiation. This is a fundamental point as far as the experimental section of this thesis is concerned. In fact, when the emission of a hybrid material composed of QDs and MNPs is measured, it is crucial to consider that MNPs are actually scattering light and it is necessary to find a way to distinguish the scattered light from the actual emission coming from QDs. Moreover, it is important to consider that the measured emission can be both increased or decreased by the action of the scattering components (i.e. MNPs). In fact, if a direct measure of a layer is performed (i.e. front – face analysis) the revealed signal is likely to be increased by the action of the metal. Therefore, the detector will receive a higher intensity compared to the one exclusively coming from the QDs. On the contrary, if a back – face analysis is conducted, the scattering action of MNPs is more likely to reduce the detected signal because the scattering direction is mainly opposite with respect to the detector’s position.

Secondly, the so-called auto absorption effect plays a fundamental role in the field of QDs-metal NPs interaction. In fact, if the emission wavelength of QDs is similar to the absorption wavelength of MNPs, some of the radiation emitted by QDs will be absorbed by MNPs and the detected signal will be lowered. For instance, GNPs characterized by a diameter of 3-5 nm present a main absorption wavelength of 520 nm. In turn, similar sized QDs emit mainly at the same wavelength. Therefore, the auto absorption effect can occur and some of the emitted radiation coming from QDs will be retained by GNPs before reaching the detector.

Finally, the plasmonic effect or field effect is a very interesting phenomenon which is able to increase the signal coming from QDs. This effect gave origin to the topic of Metal Enhanced Fluorescence (i.e. MEF) where the term “enhanced” has been implied to say that the presence of metal is able to strengthen the signal emitted by the fluorescent component (i.e. QDs). The MEF phenomenon has been explained by asserting that when metal nanoparticles are stimulated by a radiation, a local enhancement of the electric field around them takes place and consequently, a more efficient excitation of QDs occurs. In other words, MEF is caused by an increased excitation rate due to the enhanced local field experienced by QDs or fluorophores and the electromagnetic coupling with the metal NP situated nearby. [2] As a result, the fluorescence detected signal results to be increased.

All the previous effects are strongly related to the so-called Localized Surface Plasmon Resonance (i.e. LSPR) typical of metal NPs which is an important phenomenon occurring when an incoming radiation interacts with them. In particular, when a light beam hits a particle, it follows a mutual oscillation of electron charge in resonance with the visible light. This event is fundamental to explain the typical color of Gold nanoparticles, which depends on the absorbed and reflected wavelength, the consequent scattering phenomenon and the crucial increase of electric field around the particle, which gives rise to the aforementioned field or plasmonic effect providing what is defined as Metal Enhanced Fluorescence.

The scope of the present work is to thoroughly analyze the role and influence of the distance between fluorescent Quantum Dots and a plasmonic component (i.e. gold nanoparticles) in the fluorescence emission phenomenon. Various studies have been conducted on the performance of light emitting Quantum Dots in the presence of metal nanoparticles. However, most of the current literature, only reports results about analysis conducted in solution. For instance, Farinha et al. observed an enhanced fluorescence emission in solutions of CdS QDs in presence of Gold NPs (GNPs) [3] and Huang et al. [4] affirmed that until when GNPs are under a certain amount, their action is intended to increase the PL because of the LSPR and field effect. As soon as a limit is reached, a contact between GNPs and QDs occurs which causes the quenching to happen. On the other hand, few investigations have been carried out as far as the case of a layer of solution deposited on a support is concerned. In fact, many factors must be taken into account when the solution is spread over a surface. Among them, the evaporation of the solvent and the structure of the layer around the Quantum Dots play a fundamental role in defining the actual performance of a layer with respect to the one of a stable solution. [5] [6] [7]

The present work suggests a promising approach to study the interaction between fluorescent and plasmonic components in a solid layer and was inspired by the previous study by Farinha et al. [3] In particular, it is based upon the comparison between an initial condition where GNPs are randomly dispersed among PS-CdS QDs and a condition where Hexylamine provides a closer proximity between these two components. Interestingly, this study approach turned out to be very useful in confirming that the addition of Hexylamine is effective in approaching nanoparticles and quantum dots. Specifically, the induced proximity is initially likely to provide a stronger auto absorption effect which is visible in the ratio between the emission of samples with QDs, GNPs and Hexylamine and the emission of samples with only QDs and GNPs, which is lower than 1. Subsequently, the increase in the quantity of gold, demonstrated that the close proximity between the two components causes an effect of photoluminescence enhancement, known as Metal Enhanced Fluorescence, observable in the ratio R which grows higher than 1. Less clear is the trend with high amounts of gold, probably due to variability caused by the scattering phenomenon. Moreover, when the specific role of gold was investigated, a clear auto absorption effect was observed which was more and more evident as the amount of gold increased. Furthermore, the current theory was supported by a similar and enhanced effect when homopolymer was added to the solutions. In particular, the latter provided an initial larger distance between QDs and GNPs and made the Hexylamine effect even more evident.

Finally, what can be defined as an auto correction property must be highlighted as an advantage of the applied method. In fact, when establishing the emission ratios, the action coming from the component equally present at the numerator and at the denominator, is deleted and other interesting effects are allowed to be observed. Despite some weak points related to reproducibility and uncertain reliability on samples comparison, the present study offers numerous perspectives on the investigation of the interaction between quantum dots and metal nanoparticles in films deposited on rigid supports.

2. Materials and Methods

Preparation of Polystyrene surrounded CdS QDs (PS-CdS)

In order to produce Polystyrene surrounded CdS QDs, also defined as CdS Quantum Dots Micelles (QDMs), a symmetric tetrablock copolymer was implied which was previously produced by Raft Copolymerization at “Centro de Química-Física Molecular” at Instituto Superior Técnico in Lisbon – Portugal. Specifically, the mentioned tetrablock copolymer presented the structure reported in figure 1, where the so-called TTC group stands for trithiocarbonate and is fundamental in the synthesis procedure of CdS QDs since it can be effectively cut by the Hexylamine by consequently providing the establishment of a bond between QDs and GNPs. The tetrablock copolymer was dissolved in filtered 1-4 dioxane to a concentration of 0.5% w/w. To provide a perfect solubilization, the dispersion was kept at 25° C overnight under a vigorous magnetic stirring. Thereafter, the formation of micelles with poly (cadmium acrylate) cores was induced by adding a 0.25 M solution of CdAc₂ in methanol to a stoichiometric ratio of 1 mol of CdAc₂ per mol of COOH group. Subsequently, in order to synthesize a quantum dot into the micelle core, the addition of a 1.9 M solution of Na₂S in a mixture of 1:1 methanol and water was necessary. Specifically, it was added to a ratio of 0.4 mol of Na₂S per 1 mol of COOH groups. The last step allows for the formation of a single QD into the micelle core which is surrounded by a PS corona. More precisely, the so-called quantum dot micelle (QDM) presents a “flower like structure” because each chain around the core looks like a petal which apex is characterized by the presence of the TTC group. The produced dispersion was kept overnight at 25° C under vigorous magnetic stirring. Moreover, protection from light was ensured by wrapping the vial in aluminum foil to prevent QDs photobleaching and the concentration was maintained unaltered by sailing the vial with Teflon tape.

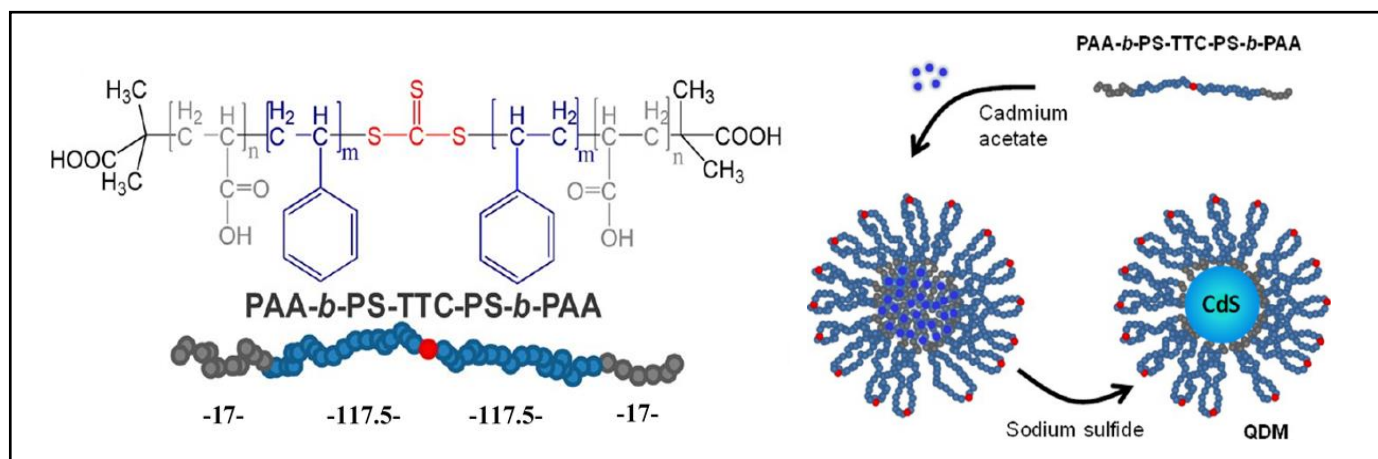


Figure 1 Tetrablock copolymer structure and PS-CdS synthesis procedure [3]

The produced PS-CdS QDs were characterized by applying UV-Vis spectroscopy in order to determine their dimension and by fluorometer analysis to investigate their optical properties following the same procedure described by Farinha et al. [3]

Preparation of Toluene based-GNPs

The well-established Brust method was applied to produce Gold Nanoparticles in the following way. First and foremost, it was necessary to produce an aqueous solution of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$. Specifically, in order to synthesize a 0.30 mM solution, 0.118 g of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ were mixed with 10 ml of deionized (D.I.) water. As far as this first step is concerned, it is important to underline how difficult and simultaneously fundamental it is to accurately measure the exact amount of material to achieve the desired final result. In particular, the extremely high reactivity of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ caused a visible interaction with the implied metallic spatula and it was arduous to transfer to the vial all the material picked up on the spatula surface. Therefore, it was extremely useful and functional to utilize, as a scoop, the upper part of a glass pipette which was less reacting in presence of $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$. The so produced solution was transferred to a 150-ml round bottom flask which was positioned on a magnetic stirring plate and kept on equilibrium with a cork round support. Moreover, a magnetic stirrer was inserted, and the solution was left under vigorous stirring for 15 minutes. Meanwhile, a solution of tetraoctylammoniumbromide (ToABr) in toluene was prepared. To achieve a molarity value of 50 mM, 0.729 g of ToABr powder were mixed with 26.7 ml of pure toluene. The present solution was independently stirred for 15 minutes and subsequently mixed with the aqueous solution of gold chloride to induce phase separation. The obtained solution was left under vigorous stirring for 30 minutes, after which an evident phase separation was observed, and all the gold was transferred within the organic phase. With the aim to provide colloidal stability, 67 μl of pure dodecanethiol were added dropwise and the solution was left under vigorous stirring until the bottom was clear. The amount of time that was necessary to accomplish this step varied according to the sample under production and was in a range of 10 – 20 minutes. Finally, a reducing agent must be added in order to transform the gold into gold nanoparticles. Therefore, a 0.4 M aqueous solution of sodium borohydride (NaBH_4) composed of 0.126 g of NaBH_4 and 8.33 ml of water was freshly prepared and added dropwise quickly to the previous solution. The role of NaBH_4 is to carry out reduction which is simultaneously controlled and finally arrested by the previously added dodecanethiol. The so produced solution was left under vigorous stirring at room temperature overnight and the obtained GNPs were dimensionally characterized by a JEOL transmission electron microscope with a LaB_6 filament. GNPs pictures were further elaborated by the software Image J.

Preparation of a solid hybrid layer of PS-CdS and GNPs on glass slides

In order to produce a solid hybrid layer of PS-CdS and GNPs on glass slides, previous solutions were appositely prepared in separated vials. Specifically, 12 different solutions were synthesized which are summarized in table 1. In particular, solution 0 contained only as-produced PS-CdS, while solution 00 contained PS-CdS and 2.50 equivalent of Hexylamine per TTC group. In addition, two series of solutions were produced which were named A and B. Specifically, A identified a solution containing PS-CdS and GNPs, while B stood for a solution of PS-CdS, GNPs and Hexylamine. The ratio GNP/QDM increased from 0.001 to 0.01 and the five different ratios were indicated with numeric indexes from 1 to 5.

Once the vials were ready, 60 μl of each solution were drop casted on previously washed glass slides and the solvent annealing technique was applied. More specifically, the glass slides were positioned on a support inserted into a glass jar and the solution was carefully dropped onto them by using an adjustable pipette. Moreover, the bottom of the jar was filled with the same solvent utilized to synthesize the dropped solution (i.e. dioxane) and the jar was sealed with aluminum foil. Thus, a closed chamber was created which caused a slower evaporation of the solvent from the deposited solution onto the glass slides. This was due to the high amount of solvent vapor in the atmosphere all around the samples in the jar. Consequently, a smooth solid layer of deposited solution could be created once the solvent resulted to be evaporated. [9] In fact, in order for this to happen, different amounts of time were tested, and 24 hours were considered the minimum necessary time to produce a stable layer.

Three replicates were produced per each glass slide in order to average the results. Consequently, a single sample was constituted by 36 slides.

Moreover, Polystyrene Homopolymer was added in the last produced sample in a percentage of 50% w/w with respect to the added raft copolymer. This was able to enhance the Hexylamine effect by providing an initial larger distance between fluorescent and plasmonic component.

Sample name	GNP/QDM	PS-CdS	Hexylamine		GNPs	Replicates
1 A	0.001	x			x	3
1 B	0.001	x	x		x	3
2 A	0.0025	x			x	3
2 B	0.0025	x	x		x	3
3 A	0.005	x			x	3
3 B	0.005	x	x		x	3
4 A	0.0075	x			x	3
4 B	0.0075	x	x		x	3
5 A	0.01	x			x	3
5 B	0.01	x	x		x	3
0	0	x				3
00	0	x	x			3
						Tot: 36

Hybrid solid layer optical characterization method

In order to characterize the optical properties of the solid hybrid layer deposited on the glass slides and to evaluate the differences arising from the different compositions, a fluorometer analysis was performed. In particular, excitation spectra were obtained to investigate the maximum absorption wavelength and emission spectra were run at that specific wavelength to achieve the maximum emission provided by QDs in the different conditions, namely pure PS-CdS, PS-CdS + Hexylamine, PS-CdS + GNPs (within the different GNP/QDM ratios) and PS-CdS + GNP + Hexylamine (within the different GNP/QDM ratios).

An analysis procedure based upon the establishment of three different photoluminescence (PL) ratios was conducted where the ratios between emissions were plotted rather than the emission values itself. Specifically, the following ratios were defined.

Ratio R = B/A

This is the ratio between the maximum emission (i.e. at 520 nm) of samples with GNPs + Hexylamine and samples with only GNPs (i.e. B/A) and it was useful to study the effect of the reducing agent on an increasing amount of gold NPs.

Ratio R1 = A/0

This is the ratio between the maximum emission (i.e. at 520 nm) of samples with GNPs and samples with only PS-CdS (i.e. A/0) and it was useful to investigate the effect of GNPs addition and increase while in absence of Hexylamine.

Ratio R2 = B/00

This is the ratio between the maximum emission (i.e. at 520 nm) of samples with GNPs + Hexylamine and samples with only PS-CdS + Hexylamine (i.e. B/00) and it was useful to investigate the effect of GNPs addition and increase while in presence of Hexylamine.

The present procedure provided positive results because it was able to overcome the problem represented by the intrinsic signal variation due to the fluorometer apparatus. In fact, if different samples had been produced and orderly tested, the signal emitted by the first tested sample would have been hardly comparable with the signal emitted by the last sample since the fluorometer parameters could have been slightly changed because of temperature-related oscillations in the emission and detected radiations. Instead, by establishing and calculating ratios, possible artifacts deriving from long time separated measures would have been less likely to affect the final result.

3. Results and Discussion

Solutions for sample called LC1-114 were produced according to the previously illustrated method and 60 μ l of each solution were deposited on each glass slide. Three days were necessary to finalize the solvent annealing procedure for the three replicates since the solvent annealing chamber only allowed to anneal 12 glass slides at a time. Once replicate i, ii and iii were ready, the aforementioned fluorometer test was performed and the three ratios R, R1 and R2 were obtained. Figure 2 reports ratio R obtained from the average signal coming from the three replicates and the three signals non-averaged.

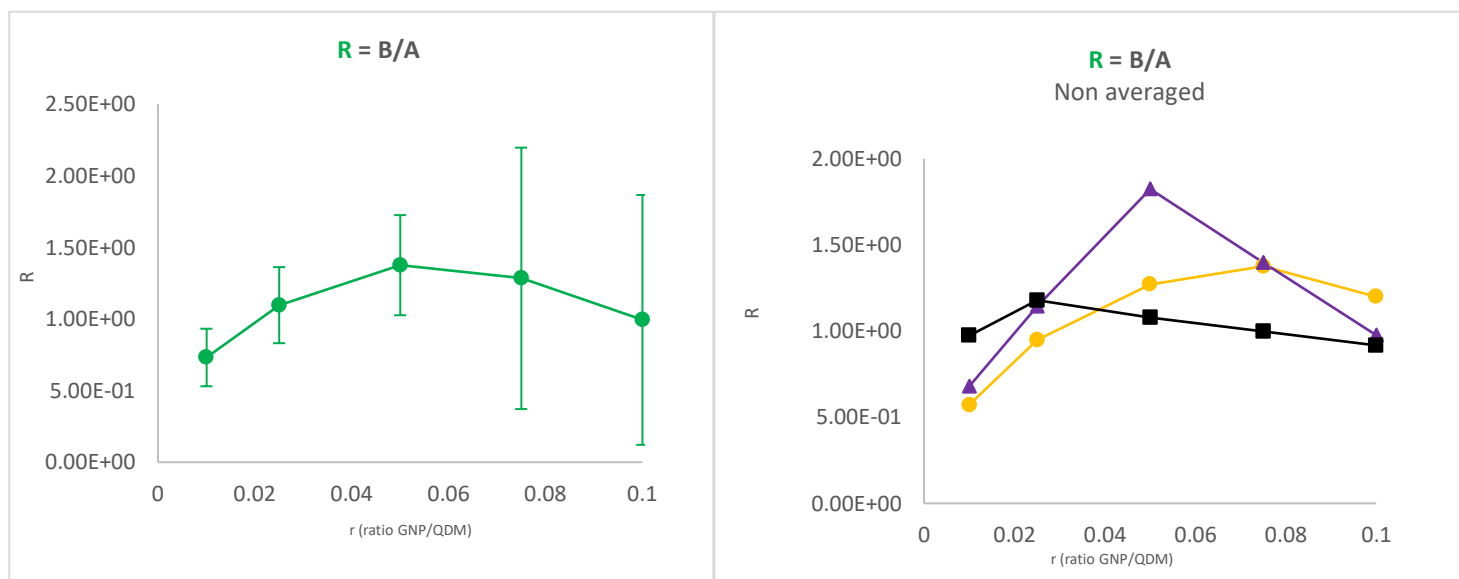


Figure 2 Ratio R averaged and non-averaged for sample LC1-114

As it can be seen, a ratio increase occurred from slide 1 to slide 3 as a consequence of the field effect caused by the proximity between QDs and GNPs induced by Hexylamine. However, as far as slide 1 is concerned, a ratio lower than 1 can be observed which is a clear sign that auto absorption effect is the dominant feature. As the amount of gold increases, field effect begins to be the most effective phenomenon. This is actually true until slide 4 when Hexylamine was no more able to establish a consistent difference between a random dispersion of GNPs among QDs and a preferential close proximity, resulting in a dominant auto absorption effect and a ratio decrease. Furthermore, this could have also been caused by scattering events which are more likely to be evident with high amount of GNPs and which made results deriving from slide 4 and 5 not easily to be interpreted. In addition, there is a substantial difference among the three replicates, especially for slide 3. In fact, slide 3Bii was seen to be turbid meaning that scattering could have occurred resulting in an increased signal and a higher B/A ratio. This explains the ambiguous position of ratio R for replicate ii of slide 3. Instead, the large error bar appearing in sample 4, is the result of a large error deriving from the multiplication of the relative B error (i.e. 71 %) and the ratio B/A. Differently, for sample 5, the large error bar was caused by a

large error relative to A (i.e. 87 %). However, even if the last two samples are somehow difficult to be explained, sample 1-3 suggest a clear field effect.

About ratios R1 and R2, a comparison is reported in figure 3. Specifically, R1 shows a clear decreasing trend from sample 1 to 4 which can be interpreted as an evident auto absorption effect becoming more significant as the amount of gold increases, while a slight increase occurred in sample 5 which was probably due to scattering. R2 showed a similar pattern with a slight increase for sample 3 and 5. Due to the large error bars which are often superimposed, it is hard to formulate a certain theory. However, the main result is represented by sample 1 where the difference between R1 and R2 is more appreciable. In other words, the obtained first ratio is already lower in the case where Hexylamine is implied. This could be explained by saying that if Hexylamine is added and a small amount of GNPs is present, the occurring auto absorption effect is more evident.

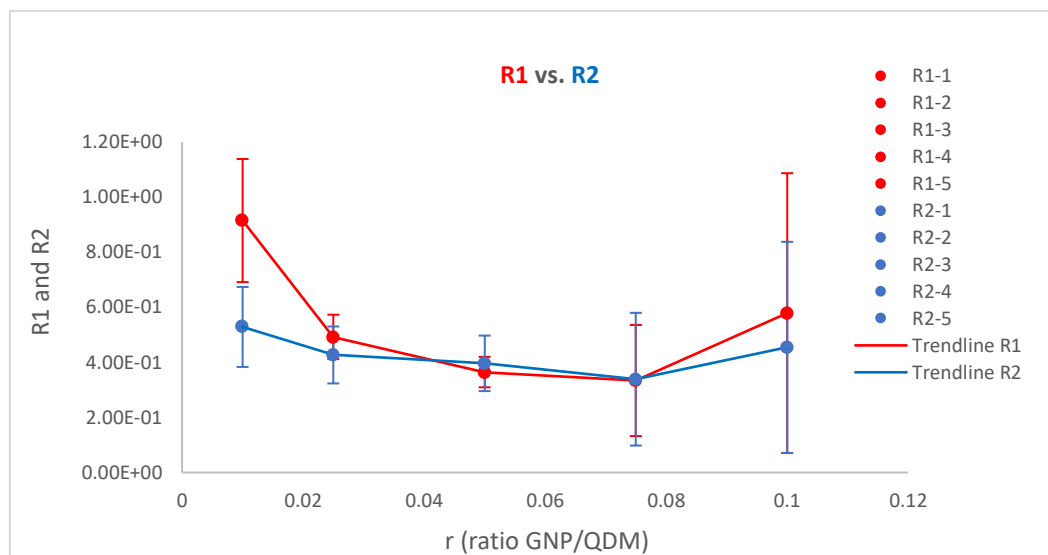


Figure 3 Comparison between R1 and R2 in sample LC1-114

In order to confirm the elaborated theory for sample LC1-114, sample LC1-116 was produced by adding Polystyrene Homopolymer in a percentage of 50% w/w with respect to the added raft copolymer. The effect of the homopolymer is to provide an initial larger distance between GNPs and QDs by eventually enhancing the proximity effect provided by the Hexylamine.

Therefore, except for the HP addition, sample LC1-116 was prepared according to the usual procedure and 60 μ l were dropped on each glass slide. Ratio R was plotted with the average values and in figure 4 (A) it is easy to recognize the same trend already discussed for sample LC1-114 where the field effect due to the addition of Hexylamine is clearly evident from sample 1 to 3. As far as ratios R1 and R2 are concerned (figure 4 (B) and (C)), it is confirmed that the Hexylamine addition enhanced the observed auto absorption effect which caused a substantial signal decrease from sample 1 to 3 and a following increase probably due to the scattering determined by the large amount of gold. More importantly, it is possible to observe how the addition of the Homopolymer confirmed the theory elaborated on ratios R, R1 and R2 for sample LC1-114. In fact, as far as ratio R is concerned, a confirmation of the previous theory was obtained because a more consistent field effect was observed from slide 1 to 3. In fact, the purple plot corresponding to the sample with HP reaches a maximum with slide 3 which is higher than the one obtained in the case without HP. In other words, when the HP is added, the initial interparticle distance between QDs and GNPs is enlarged and consequently, the action of Hexylamine in approaching and connecting them is more evident. In particular, this evidence is observed by the higher R ratio which means a larger gap between the signal of B (with Hexylamine) and the signal of A (with no Hexylamine). About R1 and R2, instead, it is easy to notice that the addition of the HP lowers the ratios. In fact, this means that the signal difference between A and 0 (for ratio R1) and between B and 00 (for ratio R2) is more pronounced since the emission of sample A and B is further decreased. In other words, an enhancement of the auto absorption effect was observed for almost all the GNPs amounts.

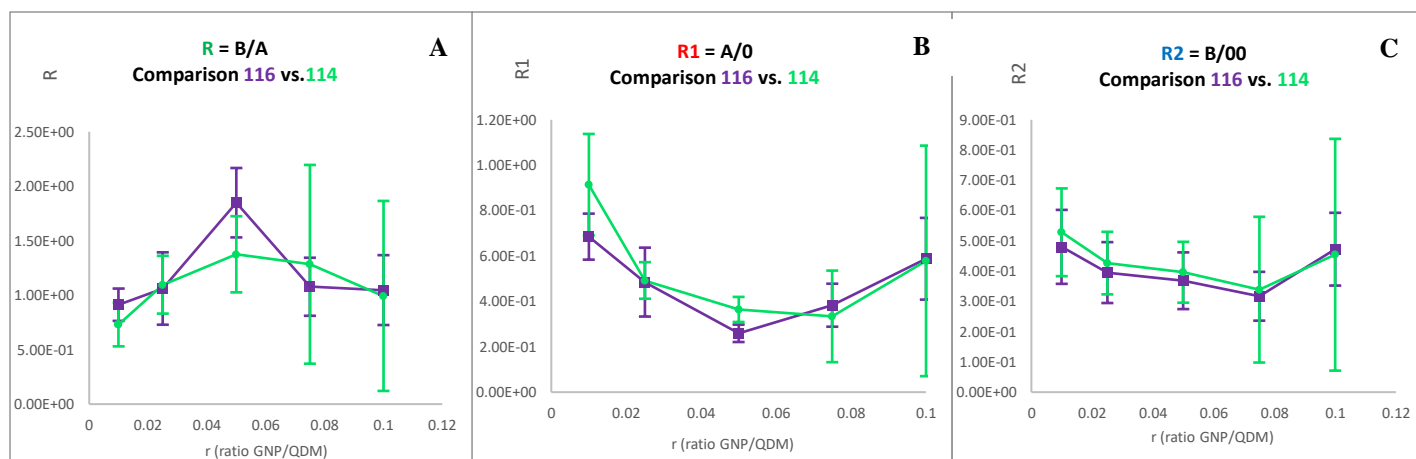


Figure 4 Comparison of ratio R (A), R1 (B) and R2 (C) between samples 116 with HP and 114 without HP

4. Conclusion

The proximity between GNPs and PS-CdS has been observed to be effectively provided by the addition of Hexylamine. [3] The reported study enabled to formulate a theory about the role of Hexylamine in a solid hybrid layer of QDs and GNPs. From this, it could be concluded that since the quantity of GNPs is low, the close proximity induced by Hexylamine mainly causes an auto absorption effect visible in a ratio $R < 1$. Oppositely, when the amount of GNPs is increased until a GNP/QDM ratio of 0.005, the close proximity seems to provide a clear field effect observable in a ratio $R > 1$. About higher GNP/QDM ratios, it is hard to formulate any theory. However, it is probable that the high amount of Gold enhanced the scattering effect which could have been more consistent for slides belonging to category A which could have reduced the R ratio. Furthermore, the increased scattering could be the cause for the large error bars. In fact, scattering is a very unpredictable phenomenon which could have caused different effects in the different samples. Instead, about R1 and R2, the general decreasing trend suggests that GNPs can effectively absorb the radiation emitted by QDs, or rather provide auto absorption effect. Specifically, R1 decreases until a GNP/QDM ratio of 0.0075 (i.e. slide 4) by confirming that a higher amount of GNPs can absorb more efficiently, while a GNP/QDM ratio of 0.005 (i.e. slide 5) gave a slightly higher ratio probably due to scattering. However, the obtained R1 ratios are all abundantly below 1 meaning that slides A are emitting less than slide 0 because of the mentioned auto absorption. Finally, the obtained trend for R2 is very similar and the previous explanation can be applied. However, the consistent gap existing between ratio R1 and R2 for a GNP/QDM ratio of 0.001 (i.e. slide 1) suggests that when a low amount of GNPs is implied, the close proximity enhances the auto absorption effect. In other words, when few GNPs are present, if Hexylamine is added, they can more efficiently absorb part of the radiation emitted by QDs. Similarly, with the addition of Hexylamine, a stronger auto absorption effect is observable with few GNPs. This confirms the observation reported with ratio R according to which auto absorption dominates with few GNPs while field effect becomes more important as the amount of GNPs increases. As far as the addition of the Homopolymer is concerned, this was useful to confirm the elaborated theory by increasing the initial interparticle distance and making the Hexylamine effect more evident.

Some minor drawbacks were present in the applied method, which caused some points to remain unresolved. For instance, a component of results uncertainty and unreliable comparability remained because of various reasons. Firstly, considerable differences affected replicates of samples which were averaged, and which were supposed to have the same features. Instead, because of synthesis issues related to solvent annealing, they presented inequalities which rendered the results affected by a large error which made the comparison not always significant. Specifically, the long time elapsing from the production of the first and last sample

was not advisable since different conditions of temperature, humidity and pressure could have seriously affected the obtained results. Moreover, a more reliable and precise drop casting method should have been applied to reduce thickness inequalities which could have caused unwanted differences among results. However, despite the presence of minor problems, a good and thorough study on the relation between QDs and GNPs was conducted together with a deep investigation on the role of their reciprocal distance. The latter opened good perspectives on the possibility of improving the fields of sensors and biological imaging based on the use of PS-CdS which performance could be improved by GNPs as a plasmonic component providing Metal Enhanced Fluorescence.

References

- [1] A. Maijerink, "Exciton dynamics and energy transfer processes in semiconductor nanocrystals," in *Semiconductor Nanocrystal Quantum Dots - Synthesis, Assembly, Spectroscopy and Applications*, Munich, SpringerWienNewYork - Andrey L. Rogach , 2008, pp. 277-310.
- [2] A. C. a. D. D. Fang Xie, "Plasmonic fluorescence enhancement by metal nanostructures: shaping the future of bionanotechnology," *Physical Chemistry Chemical Physics*, pp. 15709-15726, 2013.
- [3] M. M. T. R. a. T. P. J.P.S. Farinha, "Enhanced Photoluminescence from Micellar Assemblies of Cadmium Sulfide Quantum Dots and Gold Nanoparticles," *The Journal of Physical Chemistry*, pp. 3122-3133, 10 January 2013.
- [4] C. Y. Y. Z. C.-H. C. J. L. H.-C. K. Z. W. J. L. Y. F. a. C. C. Jun Yin, "Effect of the surface-plasmon–exciton coupling and charge transfer process on the photoluminescence of metal–semiconductor nanostructures," *Nanoscale*, pp. 4436-4442, 2013.
- [5] S. P. M. H. M. J. a. P. F. N. Xiaoying Liu, "Hybrid nanostructures of well-organized arrays of colloidal quantum dots and a self-assembled monolayer of gold nanoparticles for enhanced fluorescence," *Nanotechnology*, pp. 285-301, 2016.
- [6] Q. C. F. H. M. Lidong Li, "Controllable metal-enhanced fluorescence in organized films and colloidal system," *Advances in Colloid and Interface Science*, pp. 164-177, 2014.
- [7] J. K. B. ., D. J. G. a. G. P. W. M. Haridas, "Photoluminescence spectroscopy and lifetime measurements from self-assembled semiconductor-metal nanoparticle hybrid arrays," *Applied Physics Letters*, p. 083307, 2010.