SYNTHESIS OF METAL NANOPARTICLES AND THEIR INFLUENCE ON FLUORESCENCE OF ORGANIC MATERIAL

Simona Streckaitė[1], Domantas Peckus [1, 2], Ramūnas Augulis[1], Tomas Tamulevičius[2],
Sigitas Tamulevičius[2] and Vidmantas Gulbinas[1]

[1]*Institute of Physics, Center for Physical Sciences and Technology,*
A. Goštauto Ave 11, Vilnius LT-01108, Lithuania, simona.streckaite@gmail.com
[2]*Institute of Materials Science of Kaunas University of Technology,*
Baršausko Ave 59, Kaunas LT-51423, Lithuania

In this work, synthesis of spherical AgNPs and their influence on optical properties of highly fluorescent organic dye rhodamine 6G (R6G) and low fluorescent conjugated polymer (RZ11) was investigated. Fluorescence changes of R6G was studied in solutions when concentration of AgNPs was increasing and fluorescence changes of RZ11 conjugated polymer was studied in thin films when layer of AgNPs was presented. Absorption and fluorescence spectra, and fluorescence decay kinetics of solutions and thin films were recorded by using steady-state and time-resolved spectroscopy. Fluorescence decay kinetics revealed that no energy transfer occur in solutions of R6G (10-6 M) and AgNPs (2.5x10-4÷7.5x10-4 M). In thin films with conjugated polymer, quenching of fluorescence with AgNPs was detected because of the energy transfer from fluorophore to metal due to short distances.

Introduction

Recently, silver nanoparticles (AgNPs) have attracted much attention because of their unique size and shape dependent optical, electrical and magnetic properties. Possible manipulations of these properties lead to various applications of nanoparticles (NPs) in optoelectronics [1,2], biosensing [3,4], catalysis, metal enhanced optical spectroscopies (metal enhanced fluorescence (MEF) [5–8], surface enhanced Raman scattering (SERS) [9]), as antimicrobials [10–12] and other.

Several previous experimental results supported by theoretical investigations showed that plasmon resonance band of NPs can be easily tuned over entire visible and near infrared (NIR) spectral range [13]. Despite AgNPs are successfully synthesized in many different sizes and shapes using various techniques, most of these methods have certain limitation controlling monodispersity and stability of the colloids. If no stabilizers are present, NPs are tend to form aggregates in colloidal solutions and such effects restrict their efficient long term use [14].

One of active fields of research using noble metal NPs such as silver (Ag) and gold (Au), which exhibit plasmonic resonance in a visible region, is altering emission properties of dyes. It was demonstrated that MEF is strongly depended on the distance between fluorophores and metal species, because plasmonic effects have impact on radiative and nonradiative decay rates. Nonradiative decay rates are usually due to fluorescence resonance energy transfer (FRET) or electron transfer from fluorophore to metal NPs. For this reason it dominates in short distances and causes strong fluorescence quenching. Increase in the distance can lead to the extreme fluorescence enhancement because of increased radiative decay [15–17]. Hence, for practical applications it is crucial to understand the influence of size, shape, aggregation, stability and other features of nanoparticles on their optical properties.

In this work, synthesis of spherical AgNPs and their influence on optical properties of highly fluorescent organic dye (rhodamine 6G (R6G) and low fluorescent conjugated polymer (RZ11) was investigated.

Experimental

Spherical AgNPs were prepared using two wet-chemistry techniques. First synthesis - reduction of silver salt: $AgNO_3 + NaBH_4 \rightarrow Ag + H_2 + B_2H_6 + NaNO_3$ [14]. AgNPs with absorption maximum at 390 nm (Fig. 1, black line) were obtained. Synthesized AgNPs (10-15 nm in diameter) are stabilized by a protective layer of borohydride anions (BH_4^-). However, solutions are stable only from few hours to few days when stored in dark in fridge (exposure of light causes immediate aggregation).
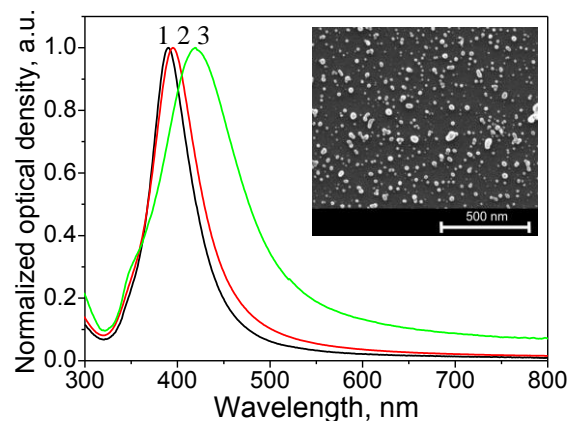

Fig. 1. SEM image of spherical AgNPs and absorption spectra of colloidal solutions: black line (1) - reduction of silver salt, red (2) – PVP (polyvinylpyrrolidone) influence for this solution, green (3) – Turkevich synthesis.

Salts (NaCl, KI) disrupt the protective shield and also causes aggregation of AgNPs in solutions. One drop of 3% PVP (polyvinylpyrrolidone) in H_2O solution stabilizes 2 ml of AgNPs solution for months. Over-concentration of PVP also leads to aggregation. PVP causes small red shift of absorption band of AgNPs (Figure 1, red line). Plasmon resonance band shifts due to changes in dielectric constant of the surrounding environment of metal nanoparticle.

Second synthesis was done using Turkevich method: $4Ag^+ + Na_3C_6H_5O_7 + 2H_2O \rightarrow 4Ag° + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2$ [14]. AgNPs with absorption maximum at 420 nm were obtained. Synthesized AgNPs (35-50 nm in diameter) were stabilized by a protective layer of trisodium citrate (TSC, $Na_3C_6H_5O_7$), which also acts as reductant (Figure 1, green line). The advantage of this method is that TSC is non-toxic and more environmentally friendly than reducing agents used in other methods [5].

Influence of synthesized AgNPs on optical properties was investigated in solutions of R6G and in thin films of conjugated polymer. Chemical structures of these materials are shown in Figure 2.

All solutions were prepared using deionized water as solvent. Five different solutions were prepared: 10^{-5} M R6G, three solutions of 10^{-5} M R6G with 2.5×10^{-4} M, 5×10^{-4} M, 7.5×10^{-4} M AgNPs and 2×10^{-5} M R6G with 10^{-3} M AgNPs. AgNPs used for solutions were 35-50 nm diameter.

Thin films were prepared as follows. Glasses were cleaned, kept in plasma and silanized using 2% APTES (3-aminopropyltriethoxysilane) solution in acetone. Then, substrates were covered with colloidal AgNPs solution and kept for about 24h. Finally, half of the glass with AgNPs was cleaned and conjugated polymer was spin-coated on the substrate. Different samples of thin films were prepared: using two types of AgNPs (10-15 nm and 35-50 nm diameter) and various thicknesses (20-150 nm) of conjugated polymer layer.
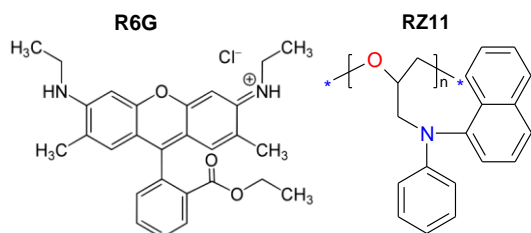

Fig. 2. Chemical structures of highly fluorescent organic dye rhodamine 6G (R6G) and low fluorescent conjugated polymer RZ11.

Solutions and thin films were studied by using SEM imaging, steady-state and time-resolved absorption and fluorescence spectroscopy. UV-visible absorption spectra of all samples were measured with a Jasco V-670 spectrometer. The steady state fluorescence spectra and fluorescence decay kinetics were recorded with the Edinburgh Instruments Fluorescence Spectrometer F900. The picosecond pulsed diode lasers EPL-375 and EPL-470 emitting at 375 nm and 470 nm respectively, were used for excitation of the samples. Fluorescence decay kinetics were measured using Time Correlated Single Photon Counting (TCSPC) method.

Results and Discussion
Silver nanoparticles in solutions

Study of R6G fluorescence changes in solutions due to increased AgNPs concentration was performed. Absorption and fluorescence spectra, and fluorescence decay kinetics of solutions are shown in Fig. 3 and Fig. 4. It was noticed that fluorescence intensity decreases with the increase of concentration of AgNPs in the solution. Similar experiment was made earlier [15], were authors state that distance dependent energy transfer was the reason of the reduced fluorescence. However, they did not show fluorescence decay kinetics to prove such effect of R6G and AgNPs coupling. In Fig. 4 we see that no changes occur in decay time of R6G fluorescence due to greater NPs concentration. We assume that no energy transfer is observed and that fluorescence decrease is determined by strong light absorption by AgNPs.
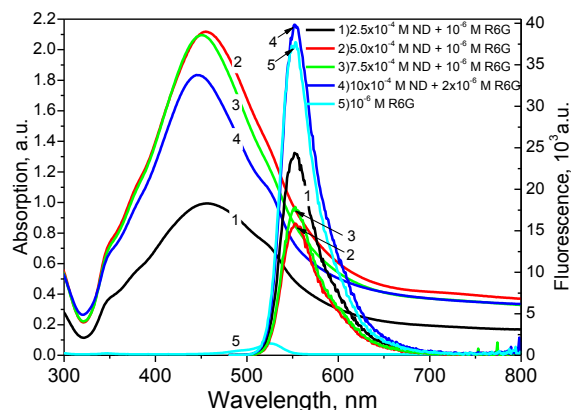

Fig. 3. Absorption and fluorescence (λ_{ex}=470 nm) spectra of R6G solutions with spherical AgNPs (synthesized using Turkevich method).
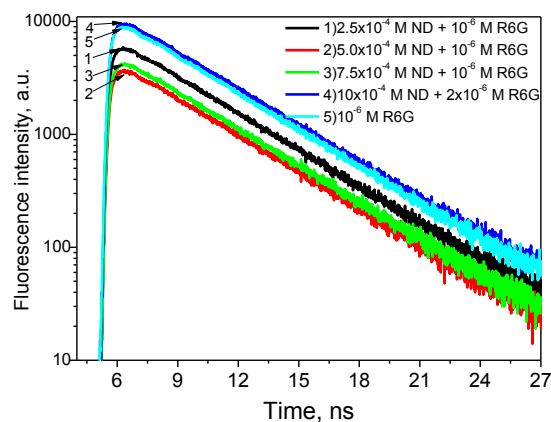

Fig. 4. Fluorescence decay kinetics at 550 nm (λ_{ex}=470 nm) of R6G solutions with spherical AgNPs (synthesized using Turkevich method).

Silver nanoparticles in thin films

Investigation of fluorescence changes of RZ11 conjugated polymer due to AgNPs layer in thin films was performed. Fluorescence spectra and fluorescence decay kinetics of thin films are shown in Fig. 5 and Fig. 6. All samples with conjugated polymer showed faster fluorescence decay when AgNPs were covered on glass. Also, most of the samples showed decreased fluorescence intensities due to presence of AgNPs. Only sample with the thickest RZ11 layer and the largest AgNPs shows small fluorescence intensity increase, which may

appear due to thicker polymer layer on rougher side of the glass were AgNPs were covered.

For plasmonic effect of NPs, decreased lifetimes as well as increased fluorescence intensities has to occur. Such increase is caused by enhanced fields around metal NPs and efficient emission of fluorophore ant plasmon complex.
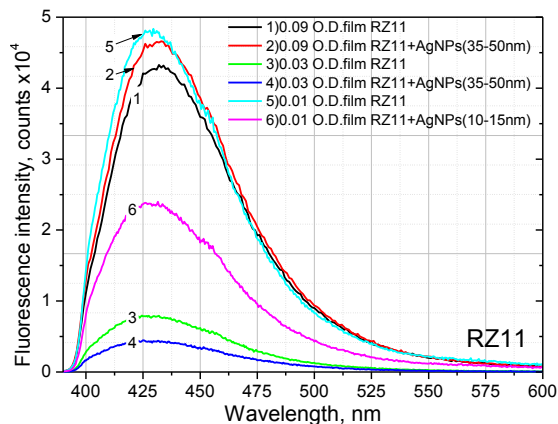

Fig. 5. Fluorescence (λ_{ex}=375 nm) spectra of RZ11 conjugated polymer thin films with ant without AgNPs.
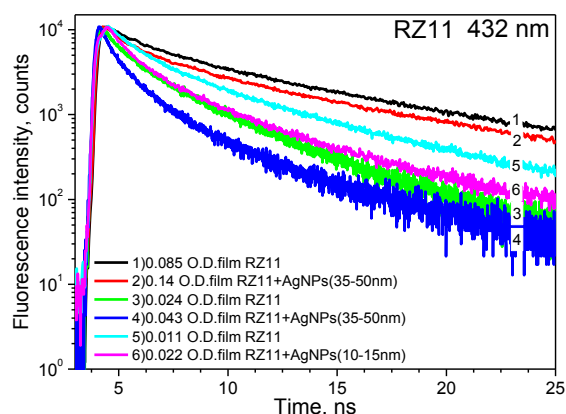

Fig. 6. Fluorescence decay kinetics (λ_{ex}=375 nm) of RZ11 conjugated polymer thin films with ant without AgNPs.

Few other effects may occur due to metal-fluorophore interaction. For example, surface-plasmon coupled emission (SPCE), when intensities and lifetimes using ~40 nm thick metal layer are not considerably changed. In this case polarization properties must be studied, because plasmons radiate at defined angle into the sample [17].

Decreased fluorescence intensities and lifetimes may be caused by energy transfer from fluorophore to metal, when distance is small enough. It was noticed that fluorescence decays slower when polymer layer is thicker, because fluorophores located in longer distances from metal are not effected with energy transfer.

Hence, distance and particle size is crucial parameters for fluorescence enhancement. Some researches have demonstrated that small nanoparticles have no effect or quenches fluorescence, while bigger ones – lead to increase [16, 17]. To minimize quenching, distance between

fluorophore ant metal nanoparticle has to be increased.

Conclusions

Steady-state absorption spectra showed that R6G causes aggregation in AgNPs solution because of Cl⁻ ion, which disrupts the borohydride protective layer around NPs when they are synthesized from reduction of silver salt. Turkevich method enables to obtain bigger AgNPs, which are stabilized by a protective layer of trisodium citrate.

It was noticed that PVP, used for stabilization of AgNPs, cause small (~5 nm) red shift for all samples due to change in dielectric constant of surrounding environment of metal.

No energy transfer occur in solutions of R6G (10^{-6} M) and AgNPs (2.5×10^{-4}-7.5×10^{-4} M). Fluorescence intensity decrease in relation to increased AgNPs concentration due to strong laser light absorption by AgNPs.

In thin films with conjugated polymer, AgNPs quench fluorescence because of energy transfer from fluorophore to metal due to short distance. Increased polymer layer thickness leads to slower fluorescence decay because fluorophores in larger distances from AgNPs are not effected with energy transfer. In order to achieve metal enhanced fluorescence, larger distances and bigger NPs may work.

References

1. *Hsu C. W., Zhen B., Qiu W. et al //* Nat. Commun. 2014. V.5. P.3152.
2. *Tan H., Santbergen R., Smets A. H. M. et al //* Nano Lett. 2012. V.12. P.4070.
3. *Shi W., Ma Z. //* Biosens. Bioelectron. 2010. V.26. P.1098.
4. *Malinsky M. D., Kelly K. L., Schatz G. C. et al //* J. Am. Chem. Soc. 2001. V.123. P.1471.
5. *Wang X., He F., Zhu X. et al //* Sci. Rep. 2014. V.4. P.4406.
6. *Sorokin A. V., Zabolotskii A. A., Pereverzev N. V. et al //* J. Phys. Chem. C. 2014. V.118. P.7599−7605.
7. *Ming T., Chen H., Jiang R. et al //* J. Phys. Chem. Lett. 2012. V.3. P.191.
8. *Aslan K., Wu M., Lakowicz J. R. et al //* J. Am. Chem. Soc.- 2007. V.129. 1524.
9. *Wu W., Liu L., Dai Z. et al //* Sci. Rep. 2015. V.5. P.10208.
10. *Agnihotri S., Mukherji S., Mukherji S. //* RSC Adv. - 2014. V.4. P.3974.
11. *Agnihotri S., Mukherji S., Mukherji S. //* Nanoscale. - 2013. V.5. P.7328.
12. *Pallavicini P., Taglietti A., Dacarro G. et al //* J. Colloid Interface Sci. 2010. V.350. P.110.
13. *Franckevicius M., Gustainyte A., Kondrotas R. et al //* J. Nanopart. Res. 2013. V.967. P.7431.
14. *Rashid M. U., Bhuiyan K. H., Quayum M. E. //* Dhaka Univ. J. Pharm. Sci. 2013. V.12. P.29.
15. *Shemeena Basheer N., Rajesh Kumar B., Kurian //* J. Lumin. 2013. V.137. P.225.
16. *Guzatov D. V., Vaschenko S. V., Stankevich V. V. //* J. Phys. Chem. C. 2012. V.116. P.10723.
17. *Lakowicz J. R., Ray K., Chowdhury M. et al //* Analyst. 2008. V.133. P.1308.