Plasmonic Enhancement of Scattering and Emission of Light in Nanostructures: From Basic Science to Biomedical Applications

Sergey GAPONENKO
National Academy of Sciences of Belarus, B.I. Stepanov Institute of Physics
s.gaponenko@ifanbel.bas-net.by

***Abstract* — Advances and challenges of plasmonic enhancemen t of Raman scattering and fluorescence with metal-dielectric nanostructures are discussed. Theoretical predictions and experimental implementation are presented and compared. Reasonable agreement of experimental data with the theory is outlined. Special attention is given to biomedical applications including fluorescent and Raman immunospectroscopy.**

***Index Terms* — nanoplasmonics, metal nanoparticles, fluorescence, Raman scattering, quantum dots.**

I. INTRODUCTION

Metal nanostructures capable to support plasmonic excitation by incident light essentially modify light—matter interaction resulting in local concentration of incident light, modification of radiative and non-radiative transition rates, and the probability of photon scattering. Thus all types of secondary emission (spontaneous emission and scattering of photons) may experience considerable enhancement under certain conditions..

II. RESULTS

A rather general consideration of incident field concentration and photon density of states concentration provides a rationale for huge enhancement factors for Raman scattering (more than 1010) and noticeable enhancement factors for luminescence [1,2].

Based on joint incident field and photon density of states enhancements it is possible to assign definite physical notions to so-called “hot spots” in plasmonic nanostructures. These are such places on a nanotextured metal surface or near metal nanobodies where simultaneous spatial redistribution of electromagnetic field occurs both at the frequency of the incident radiation and at the frequency of scattered radiation. The first effect is the so-called “the field enhancement factor” whereas the second is local density of states enhancement.

“Hot spots” promise enormous enhancement of the secondary radiation emitted by molecules or other species located in the proper positions within plasmonic nanostructures. When multiplying incident field enhancement and photon local density of states enhancement, e.g. for a spheroidal metal particle, one can get the product exceeding 1012[2]. Such values can never be obtained for photoluminescence enhancement (because of the competitive non-radiative bypass) but these can even be exceeded in surface enhanced Raman experiments.

Experimental performance of luminescence for molecular systems and semiconductor quantum dots using randomized, multilayer and spatially organized metal-dielectric nanostructures is performed experimentally evidencing that one order of the magnitude enhancement factors can be performed routinely for high-yield species whereas up to 103-fold enhancement can be realized for low-yield (bio)molecules. Figure 1 shows an example of fluorescence enhancement for a representative model system, namely bovine serum albumin labeled with FITC. Such system reproduces to large extent the features of real antibodies with fluorescent markers. This means that routine medical analyses become feasible with approx. 10-fold enhancement in sensitivity.

Extensive modeling of luminescence and Raman scattering for simple but instructive systems is presented aimed at optimizing the design of metal nanostructures to get high net enhancement for desirable practical tasks. An overview can be found e.g. in Refs. [1,3].

During last decade, special attention is given to plasmonic enhancement of luminescence and Raman scattering for semiconductor nanocrystals (quantum dots) provided these are considered as promising fluorescent and Raman markers in biomedical application. High photostability of quantum dots as compared to organic fluorescent molecules stimulates extensive research towards conjugation of biomolecules with quantum dots. Data for plasmonincally enhanced Raman scattering for quantum dots is rather poor and further research is to be performed. Our recent experiments showed more that 104-fold overall enhancement of Raman scattering from ZnO nanocrystals on silver-based colloidal substrates (Figure 2). Well pronounced and relatively simple Raman spectra from quantum dots, its finger-print-like equidistant multi-phonon lines, readily conjugation with biomolecules make quantum dots promising Raman labels for immunospectroscopy.

Notably, advances in plasmonic enhancement of Raman scattering put forward the practical routine implementation based on simple and cheap Raman testers instead of complicated and expensive Raman spectrographs. Such targeted tester can include a special multiband selective filter (one filter for one task) instead of mono- or polychromator and a single photodetector instead of a CCD array. The concept of Raman testers (Figure 3) was recently presented in our paper [5].

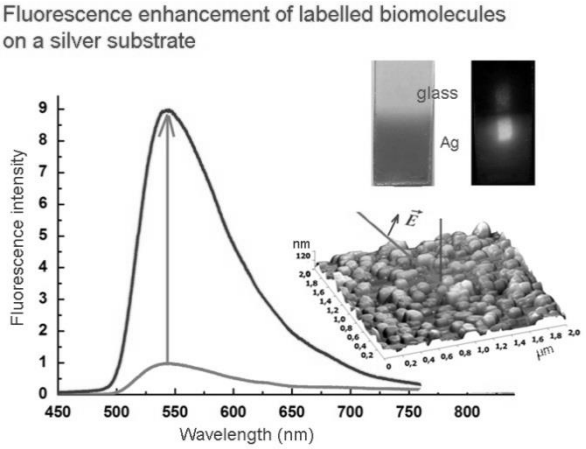

Fig.1 Enhancement of fluorescent signal from biomolecules labeled with fluorescein based dye. The figure presents emission spectra, AFM image of the substrate and photographic image of substrate on a glass plate with one half being free from silver nanoparticles for reference measurements.

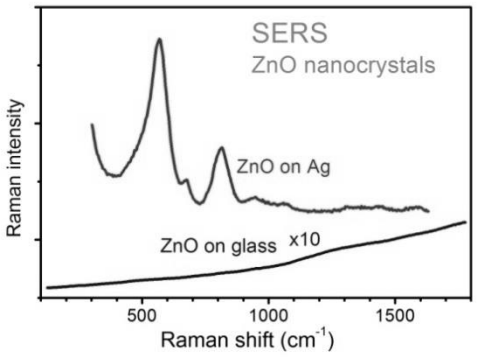

Fig.2 Enhancement of Raman scattering of ZnO nanocrystals with silver-based colloidal substrates [3].

III. CONCLUSION

In conclusion, nanoplasmonic enhancement of fluorescence and Raman scattering has become a mature field of research with high potential application in biomedicine, first of all in immunospectroscopy based on signal enhancement from labeled antibodies. Remarkably, quantum dots may not only substitute organic molecules as photostable fluorescent label but can also serve as promising Raman markers in ummune analyses based on evaluation of Raman rather than fluorescent labels attached to antibodies. Then cheap Raman testers can readily replace expensive Raman spectrometers.

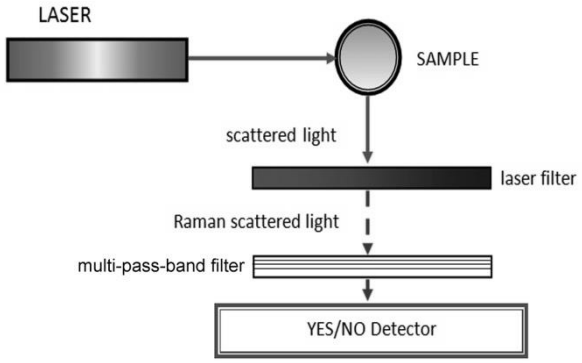

Fig. 3. A concept of the simple Raman tester based on multiband selective filter

ACKNOWLEDGMENTS

Cooperation with colleagues whose papers are cited in the list of References is acknowledged. The work has been supported by the Belarussian Foundation for Basic Research..

REFERENCES

[1] S. V. Gaponenko, Introduction to Nanophotonics. Cambridge University Press, 2010.

[2] S. V. Gaponenko and D.V. Guzatov. "Possible rationale for ultimate enhancement factors in single molecule Raman spectroscopy". Chem. Phys. Lett. Vol.477, no. 6, pp.411—414, July 2009.

[3] D.V. Guzatov, S.V. Vaschenko, V.V. Stankevich et al.,"Plasmonic enhancement of molecular fluorescence near silver nanoparticles: theory, modeling, and experiment",J. Phys. Chem. C., vol. 116, no. 19, pp. 10723-10733,April 2012.

[4] A. Rumyantseva, S. Kostcheev, P.-M. Adam et al. Non-resonant surface enhanced Raman scattering of ZnO quantum dots with Au and Ag nanoparticles, ACS NANO 2013 (in press).

[5] S. G. Kozhukh, S. V. Zhukovsky, I. I. Yurkevich, S. S. Stepkova, and S. V. Gaponenko. "Design of high-pass multiband multilayer filters for Raman spectroscopy". J. Nanophotonics, vol. 6, pp. 061704-1—4, October 2012.