Raman Characterization of Graphene Nanoparticles Infiltrated into the Synthetic Opal Pores

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Introduction

The presence of a periodic structure in photonic crystal (PC) leads to observations of the photonic stop bands due to light scattering on the periodically located scatters and enhanced electric field localization in the cavities of the PC (hot spots formation). The distribution of the local electric field can be controlled by the geometrical and optical parameters of the PC structure as reported from FDTD calculations in [1]. If nanoparticles or macrobiomolecules are placed in the cavities of such a system, this can lead to a change in the distribution of the field in the cavities and to an increase in the interaction of the electromagnetic field with nanoparticles or macromolecules.

Here we are going to clear up an influence of the PC structure and position of stop zone on the optical modes of graphene nanoparticles infiltrated into the interglobular cavities of the PC.

Materials and sample characterizations

Opal type photonic crystals were made by colloidal self-assembly method.
Spherical nanometer-size (D~240nm) SiO_2 particles with the relative standard deviation of ~5% were synthesized in colloid using a modified Stober method by hydrolysis of TEOS in the presence of ammonia as a catalyst: (C_2H_5OH (96%) - 25ml, TEOS - 1ml, H_2O – 13.25ml and NH_4OH (25%) - 0.89ml).
The PC with a size of 7×3×2 mm was used for the experimental study.
Between the spheres with diameter D packed in the closest packing, there are voids of two kinds - tetrahedral and octahedral. Their sizes are 0.225D and 0.414D respectively. Besides that, between the voids, there are narrow channels measuring 0.15D. Thus, the cavities between the PC globules have a wide range of cross-sections, from several to about 90 nm, and are interconnected.
Graphene nanoparticles (GNP) 0.7-1.8 nm (2-5 graphene layers) in thickness and about 20-50 nm in length fabricated by mechanochemical delamination were deposited from water-ethanol colloidal solution (concentration 0.2 mg/ml) on the surface of polished Si substrate as well in the pores of PC based on synthetic opal.

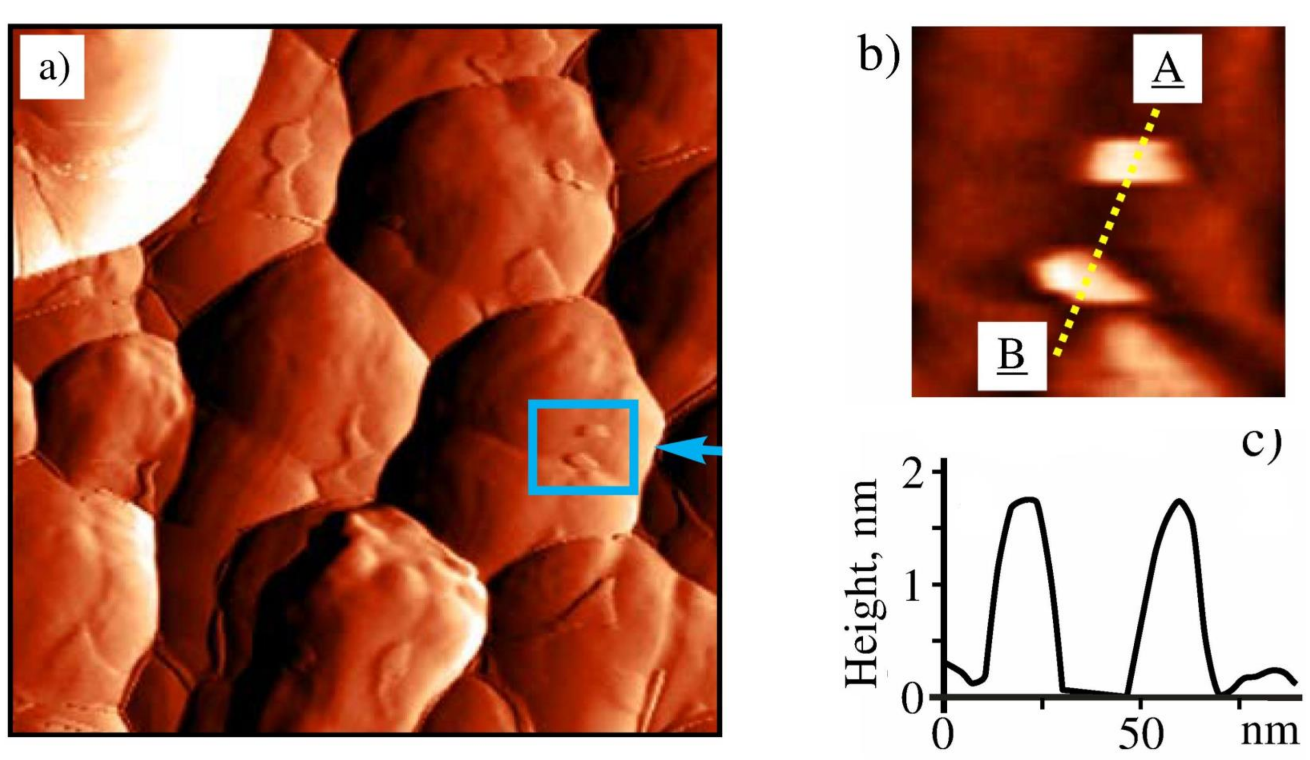

Fig. 1. (a) – AFM semicontact error image (0.8 × 0.8 μm²) of PC with GNP. (b) – fragment with 2D - nanoparticles of the corresponding topographic image of the surface area marked on (a).
Our estimations gave that essential (~7%) area of PC silica globules surface are covered with 2D graphene nanoparticles. These data allow us to estimate the volume fraction of GNPs in the near-surface layers as 0.5-1.5% of the volume of the cavities.

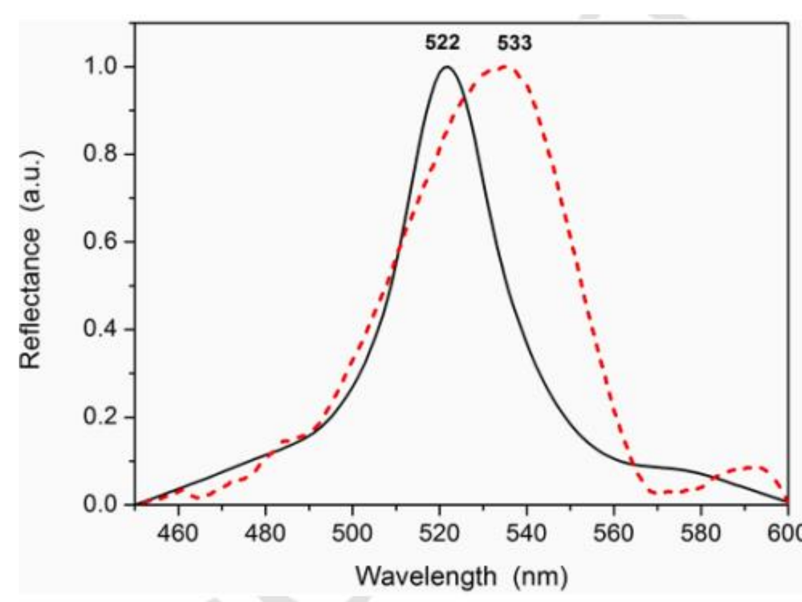

Fig. 2. Reflectance spectra of initial PC (solid line) and PC with GNP infiltrated (dashed line) in the photonic stop-band region (light incidence angle 10°). Initial sample's PSB occurs at 522 nm which agrees well with estimation for globules with D = 240 nm and $n_2 \approx 1.0$ (n_{eff} = 1.342).
Infiltrations of GNPs evokes a red-shift of PSB maximum to 533 nm which is caused by the effective refractive index increasing to $neff$ = 1.370 due to the presence of GNPs in the cavities of the PC.

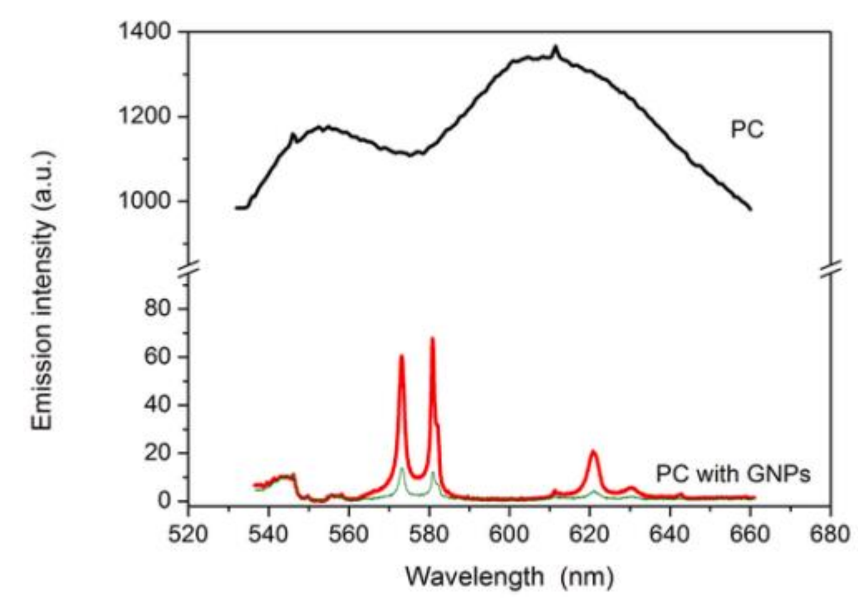

Fig. 3. Emission spectra of initial PC (luminescence) and PC with GNP infil - trated (Raman). Excitation with λ_{exc} = 532 nm at room temperature.
The excitation energy matches the PSB position.
For PC infiltrated with a small amount of GNP materials, a suppression of PC luminescence intensity resulting in clearing of Raman spectra of the material investigated is observed.

RS mapping

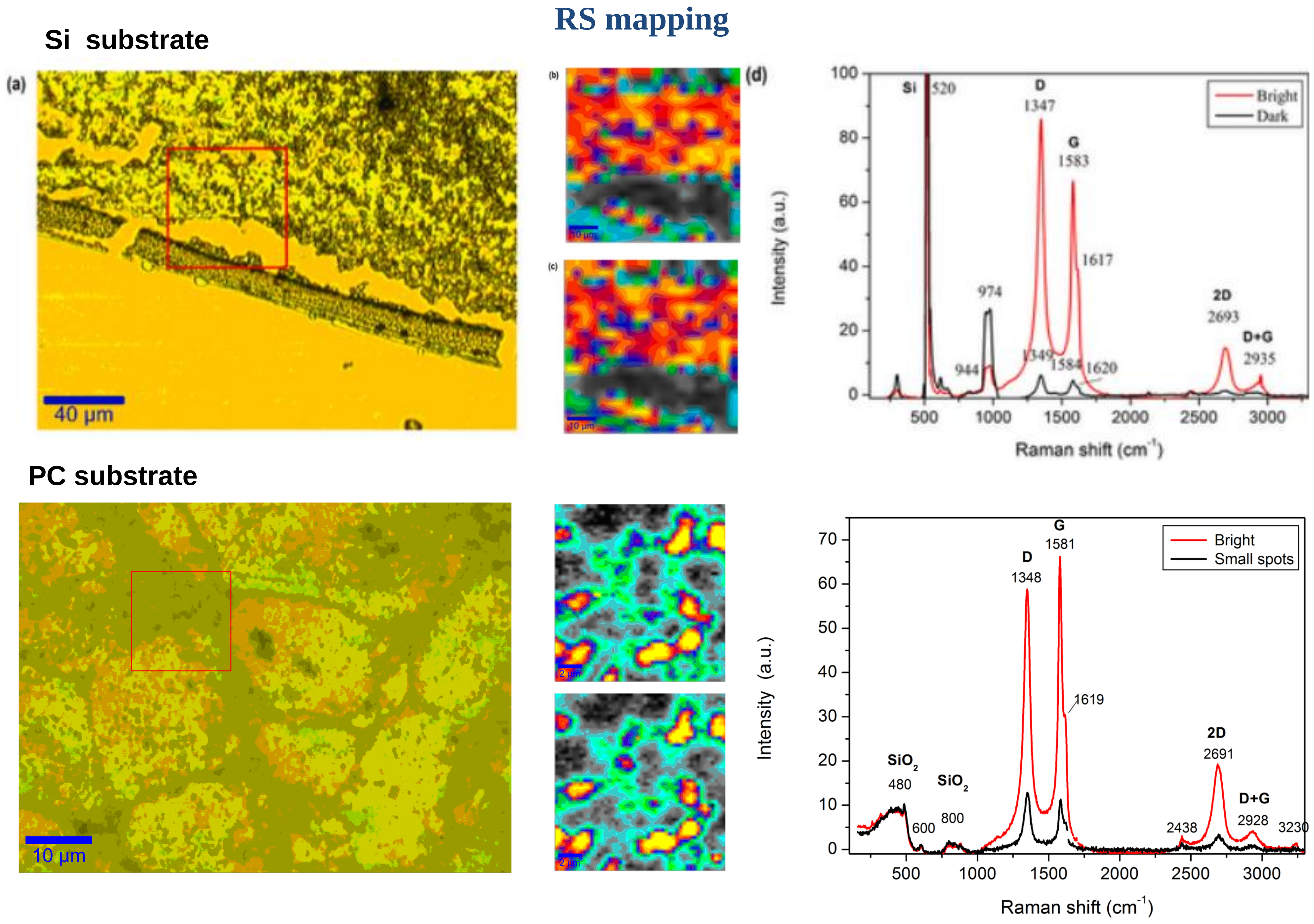

Fig. 4. Optical microscopy image (a), Raman mapping at D and G mode frequencies (b, c) and Raman spectra of graphene nanoparticles on Si and PC substrates averaged for high and low surface nanoparticles concentration regions (d).
Excitation with λ = 532 nm at room temperature .
The marker Raman bands of carbonaceous materials, namely D (1275-1355 cm^{-1}), G (1580-1600 cm^{-1}) and 2D (2550-2800 cm^{-1}) are observed.
The PC substrate provides better separation of the test substance, this will allow to distinguish smaller objects than on a flat substrate and avoid the distortion of spectra that is often observed in large aggregates of nanoparticles or macromolecules.

FDTD simulations

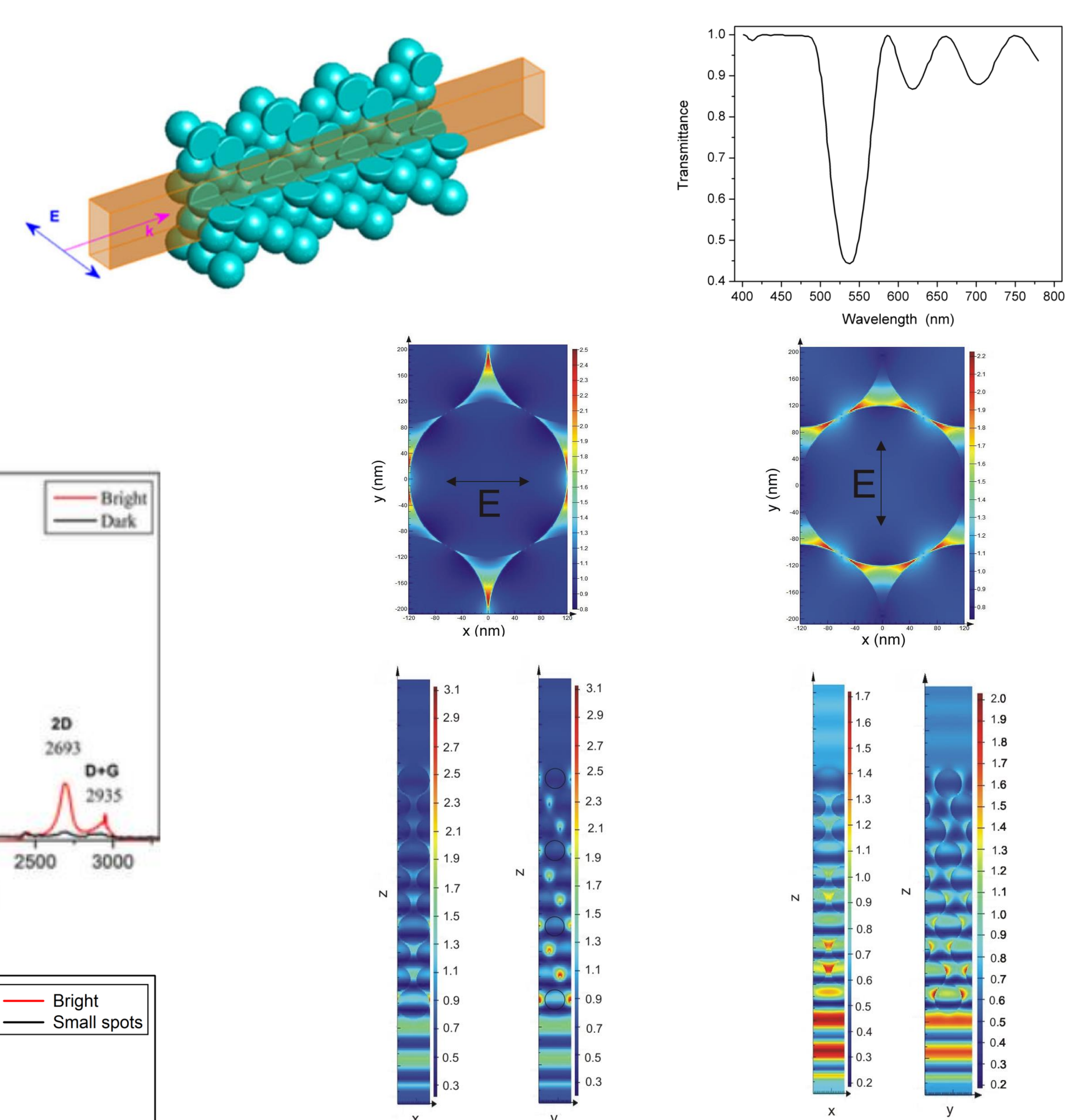

Fig. 5. Near-field relative electric field magnitude distribution in XY, XZ and YZ planes for p-polarized and s-polarized wave with λ=532 nm. Pulse propagates in Z direction. PC consists of spherical 240 nm globules with fcc arrangement. Refractive index for globules n = 1.46 and n = 1.0 for cavities.
When excitation occurs with energy match the PSB, light penetrates to a depth of about 10 monolayers of globules, and when excited outside the stop zone – much deeper.
At the same time the so-called "hot spots" with high electric field intensity are formed, although in the second case the field intensity is lower.

Conclusions

- Synthetic opal photonic crystal infiltrated with graphene nanoparticles were fabricated
- About 7% of silica globules area on the surface of PC are covered with 2D graphene flakes
- Graphene NPs suppress opal luminescence intensity and make Raman spectra more distinct and enhanced
- Photonic crystal matrix as a substrate provides better conditions for RS investigations
- Point globule arrangement defects generate a locally enhanced electromagnetic field

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