Enhanced photoluminescence in printed 2D polymer photonic structures via surface plasmon enhancement

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We report on a method to enhance the light-emission efficiency of printable thin films of polymer doped with semiconducting nanocrystals (NCs) and with dye chromophores via metallic nanoparticles and via nanoimprinted photonic crystals. The two nanocomposite materials, embossed by using nanoimprint lithography (NIL) process, showed very good imprint properties and enhancements in the spontaneous emission intensity of the incorporated emitters.

To prepare the printable polymers, small amounts of Au nanorods (NRs) with a double surface plasmon resonance were added to a mixture of PMMA-based copolymer and emitters. Figure 1 presents a schematic of the exciton-plasmon coupling in the nanocomposite polymer. A strong coupling is expected by matching the surface plasmon resonance frequency with the emission frequency of emitters. The photoluminescence (PL) intensity reported was recorded for different nanoparticles concentrations in the mixture. The measurements indicate an increase by a factor 1.7 in the emission intensity of the dye (Figure 2). This enhancement is attributed to an increased absorption and emission of R6G in presence of the metallic nanorods. A reduction of the lifetime confirmed the modification of the spontaneous emission rate of the emitters. Two dimensional silicon (2D) photonic crystal stamps with different lattice constants were successfully imprinted in the nanocomposite polymer by a standard NIL process. PL spectra of a nanoimprinted unpatterned sample without Au NRs, of a nanoimprinted unpatterned sample with the optimal concentration of Au NRs and of a 700 nm honeycomb lattice photonic crystal with the optimal Au NRs concentration. Imprint example is shown in Figure 3.

Similar results were obtained with the nanocomposite polymer containing the NCs. The additional challenge consisted to achieve a homogeneous dispersion of nanoparticules in the polymer matrix and to keep a good processability of the modified polymer for NIL process without altering their structural and chemical-physical properties of the nanoparticules. A challenging TEM cross-section of the polymer film showed a homogenous dispersion of (CdSe)ZnS nanocrystals after patterning was achieved with success. By controlling the concentration of NCs and Au nanorods in the PMMA-based copolymer, an optimum is achieved showing an enhancement in the PL intensity by a factor 5.5 thanks to the Au nanoparticules incorporation.

In conclusion, 36-fold enhancement of PL intensity compared to an imprinted unpatterned and unprocess sample is achieved at room temperature by using a printed photonic crystal in a dye-doped printable polymer and by coupling the dye emission to surface plasmons of metallic nanoparticles. An enhancement by a factor 14 has been achieved with semiconducting nanocrystals. Our results indicate that nanoimprint lithography is well suited to fabricate these challenging photonic structures in nanocomposite materials and that the combination of surface plasmons and nanoimprinted photonic structures in an active layer may lead to a new class of cost effective and high efficient OLEDs.

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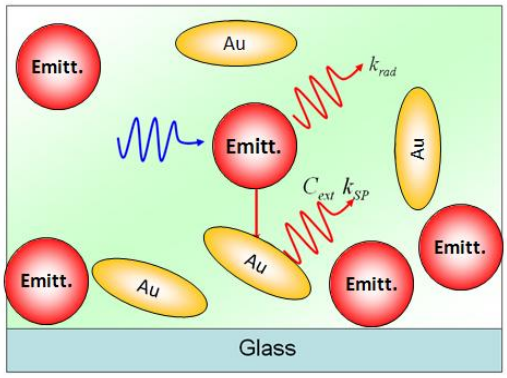

Figure 1: Schematic of the coupling between the metallic nanoparticules and the emitter [R6G],

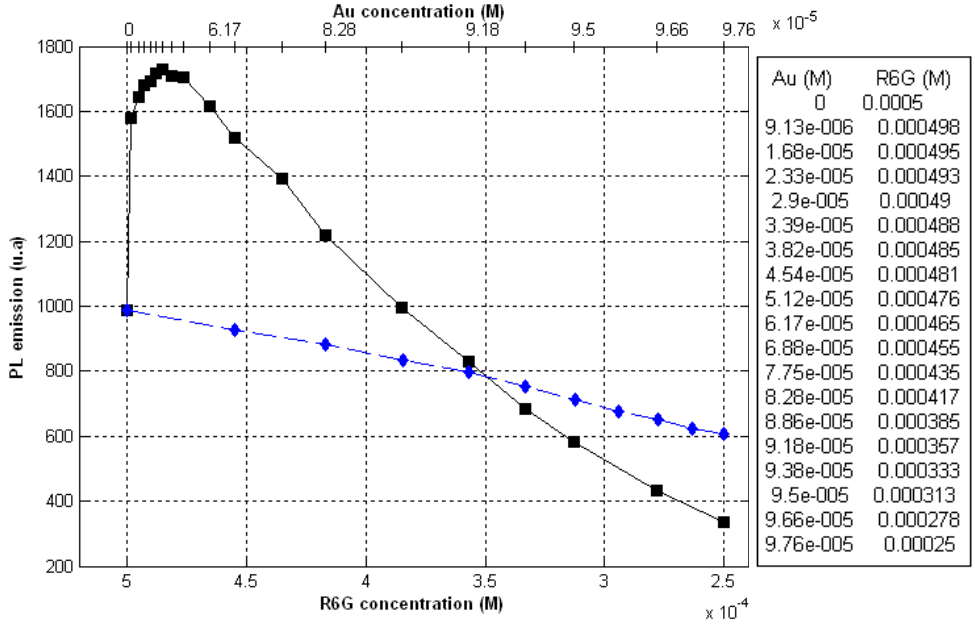

Figure 2: a/ Photoluminescence intensity of the functionalised polymer versus different Rhodamine and gold nanoparticles concentrations (curve with solid squares). The curve with full circles presents the PL intensity of R6G diluted in PMMA from a concentration from $5x10^{-4}$ to $2.5x10^{-4}$ M without Au nanoparticules. Table: concentration values of Au nanoparticules and R6G diluted in PMMA.

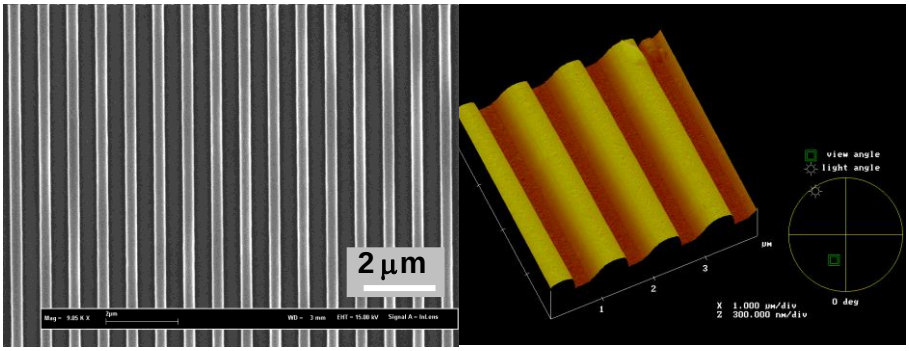

Figure 3: SEM micrograph of a nanoimprinted grating in mr-I PMMA, in which R6G and Au nanoparticles have been incorporated, b/ AFM image of the printed grating