ENHANCEMENT OF THE FORWARD EMISSION OF LIGHT-EMITTING COMPOSITES BY SOFT NANOLITHOGRAPHIES

L. Persano, A. Camposeo, R. Cingolani and D. Pisignano

National Nanotechnology Laboratory of CNR-INFM and Scuola Superiore ISUFI, Università del Salento, via Arnesano I-73100, Lecce, Italy

Introduction

The combination of the wide tunability, processing, and chemical flexibility of light-emitting conjugated polymers, and the optical, mechanical and thermal stability of inorganic nanoparticles allows one to design and implement novel functional materials and systems with improved structural properties, and whose optical characteristics can be broadly tailored [1, 2].
However, nanostructuring of composites with nanocrystals embedded in light-emitting organic compounds still represents a challenge, though achieving reliable, high-resolution patterning of such materials is strategic to control the resulting surface wettability, and the optical properties via the optical density of states. Applications range from high-efficiency light-emitting diodes, to nanophotonics, lasers, and smart nanostructured surfaces.
To this aim, we develop soft, gentle nanolithographic methods for micro- and nano-structuring hybrid organic/inorganic nanocomposite materials, consisting of inorganic semiconductor and oxide nanoparticles incorporated in light emitting conjugated polymers. Accomplished resolutions are up to the sub-micrometer scale, thus being suitable for the fabrication of photonic crystals on the surface of the light-emitting nanocomposites.
Spectroscopy, rheometry, and scanning force microscopy are applied to optimize the processing parameters and to assess the tuned optical and structural properties of the nanopatterned materials. In particular, the emission properties of the nanocomposites are studied before and after nanopatterning to rule out material damages possibly induced by nanolithography processes and to relate the achievable luminescence to the printed photonic crystal structures. This allows us to demonstrate the enhancement of the forward emission from the nanopatterned, hybrid organic-inorganic active nanocomposite.

Experimental

Materials. We prepare our nanocomposites by blending several light-emitting conjugated polymers and oxide or semiconductor micro- and nanoparticles. Poly(methylmethacrylate) is optionally employed as matrix in order to improve the overall plastic behaviour of the nanocomposite. Solutions are generally prepared by dispersing polymers and nanoparticles in toluene with suitable relative concentrations (nanocrystals:conjugated polymer) between 3:2 and 1:4 in weight. Polydimethylsiloxane and other elastomeric compounds of controlled modulus are used for the realization of the soft lithography molds.
Lithography. A set of master structures is made by parallel stripes with period ranging from 560 nm to 4 μm, both by electron beam lithography and by optical lithography. Nanocomposite films are spin-cast onto cleaned quartz substrates from the toluene solutions. High-temperature molding lithography is carried out by placing the molds on the composite films under their own weight, and heating the samples at temperatures (> 150°C) higher than the softness characteristic temperature of the used nanocomposite. The patterning process is performed out under nitrogen atmosphere to prevent damaging of the active materials.
Atomic force microscopy (AFM) and optical characterization. The morphological characterization of the nanopatterned surfaces is carried out by tapping AFM in air, by using a Nanoscope III controller with a Digital Instruments Multimode head. Furthermore, angle-resolved cw photoluminescence (PL) of the nanocomposites before and after patterning is collected, together with the compound absolute quantum efficiency (Φ), by means of a fiber-coupled monochromator, equipped with a charge coupled device. An integrated sphere is used to measure the luminescence yield, allowing us to take into account the average emitted photons per solid angle, independent of their angular distribution The light-emitting nanocomposites are photoexcited by a He-Cd laser (λ = 325 nm) at near normal incidence and at room temperature.

Results and discussion

Our soft lithography approaches combine procedures and advantages of soft and nanoimprint methods [3] on active molecular materials and nanocomposites. We point out that the presence of incorporated nanoparticles generally disfavours the nanofluidic molecular flow occurring in imprinting procedures, thus requiring longer process intervals or higher temperatures for pattern transfer from the employed molds. The choice of the processing parameters in molding technologies is particularly critical for patterning light-emitting composites, since excess heating may lead to the degradation of the luminescence and conduction properties. Fig. 1 displays the optical micrographs of a prototypal grating on the mold and on a light-emitting nanocomposite after molding, evidencing the good fidelity of the achieved pattern transfer.
Importantly, printing a periodic nanostructure with wavelength-scale (sub-μm) features into the composite light-emitting film enhances significantly the forward output from the active material, since the emitted photons are preferentially scattered along certain forward directions, instead of being guided along the composite slab. The imposed photonic crystal pattern allows therefore the light, naturally trapped in waveguide modes in absence of periodic features, to be Bragg-scattered out of the film along the preferential forward direction, as shown in Figure 2. Analogous results are obtained by our group on different class of functional materials, including light-emitting organic films [4, 5] and electrospun nanofibers [6], thus demonstrating the wide flexibility of the conceived lithographic approaches.

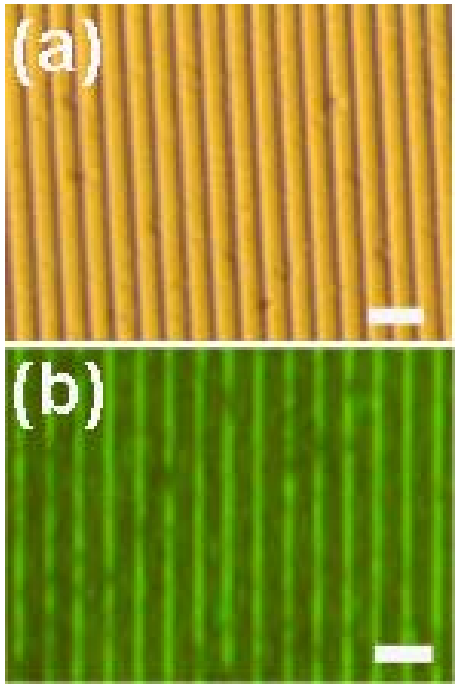

Fig. 1 Optical micrograph of 4 μm-period elastomer mold (a), and corresponding pattern transfer to a nanocomposite of ZnO microparticles and a green emitting polymer, imaged by fluorescence microscopy (b). Marker = 5 μm.

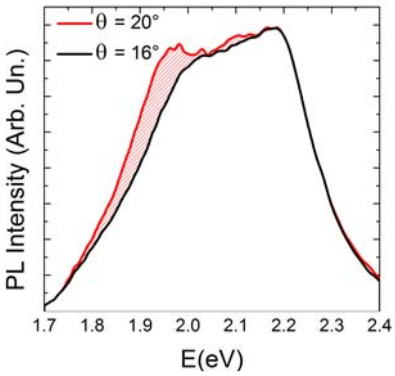

Fig. 2 Angle-resolved, normalized PL spectra of a prototype light-emitting composite film after nanopatterning, evidencing the angular dependence of the emission peaks induced by the imprinted grating.

Conclusions

We demonstrate nanostructuring of light emitting nanocomposite materials made by nanoparticles and conjugated polymers, resulting in the enhancement of the forward emission by pattern-induced Bragg-scattering. Further experiments are currently in progress for texturing composites with 100 nm lateral resolution.

References

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