**Holographic organic-inorganic nanomaterials for functional diffraction gratings**

O. Sakhno, T. Smirnova

Organic-inorganic photopolymerizable nanocomposites based on acrylate monomers with embedded inorganic or metal nanoparticles (NPs) have been developed for holographic fabrication of volume structures with submicrometer and nanometer resolution. The nanomaterials containing NPs of different nature and properties (metal oxides, phosphates, semiconductors, noble metals) in transparent polymer matrices allow designing efficient and functional diffraction elements possessing optical, photonic and non-linear properties suitable for special applications. As a photoactive organic part of the nanomaterials the two-component photocurable mixtures, consisting of acrylic monomers having a single and multiply double-bonds, and a photoinitiator, are used. These mixtures provide efficient light-induced spatial diffusion redistribution of the NPs in low-viscous organic matter according to and during irradiation by the interference pattern.

The holographic structuring governed by the photopolymerization-diffusion mechanism, where the periodical distribution of the NPs, which have higher or lower refractive indices compared to that of polymer matrix, allows fabricating the grating structures with high refractive index contrast (*n1*) in the spatial period range of 400 nm-5 *μ*m. Moreover, due to their various optical, chemical and physical properties, the NPs of different nature bring additional functionality to the gratings. The commercially available as well as in the lab synthesized inorganic and metal NPs were used in the study.

The parameters of the NP core and shell, property of photocurable organic matrices as well as the holographic patterning conditions strongly influence the gratings efficiency, optical quality and stability. The key problem, the compatibility of inorganic and metal NPs with organic monomers (polymers) was successfully solved by capping the NPs surface with properly designed organic outer shells. This results in the possibility to introduce up to 50 wt.% of inorganic NPs (SiO2) in the organic media. The optimization of the technology (organic outer shell, the NP size and their content in the monomer mixture, properties of the organic part of the nanomaterial, holographic inscription parameters) allows fabricating permanent highly efficient transmission gratings with low optical losses. The *n*1 of the gratings fabricated from the nanomaterials modified with metal oxides NPs possessing high refractive index (TiO2, ZrO2, etc.) was obtained in the range of 0.014 to 0.024 dependently on the NPs nature, the outer shell, the NPs content, etc. Typical content of these NPs in organic matrix was in the range of 15-25 wt.%. Exemplary, the highest diffraction efficiency, of about 98%, in the 20 *μ*m thick gratings, was achieved using the nanomaterial with 18 wt.% of ZrO2 NPs. The nanocomposite with SiO2 NPs, having lower refractive index compared to that of the polymer, is suitable for the fabrication of highly selective holograms of excellent optical clarity in thick, up to 300 *μ*m, layers. The presence of metal oxides NPs in the polymer matrix reduces the shrinkage of the layer during holographic photopolymerization thus minimize optical distortion of the gratings. Not only 1D grating as well as 3D structures can be created using holographic exposure of the developed organic-inorganic nanocomposites.

Application of the specially designed functional NPs makes it possible not only to fabricate effective diffractive gratings but also to introduce other features into holograms, such as luminescence or non-linear optical properties. Efficient holographic structures containing regularly arranged luminescent REN X-green (LaPO4:Ce,Tb) NPs, emitting in the green spectral range upon UV irradiation, have been demonstrated. The diffraction efficiency of about 90% in the 20 µm films and *n*1 of 0.014 was achieved introducing of 25-30 wt.% NPs loading into polymer matrix. The ability to create efficient holographic gratings containing spatially ordered luminescent NPs in a hundreds nanometer scale allows manufacturing of holographic security features to improve the security level. Currently the similar NPs are applied for the fabrication of special photonic crystals structures as a basic part of resonance sensor for optical detection of small amount of hazard agents.

The two, *ex situ* and *in situ,* NP formation methods were developed for the introduction of noble metal (Au and Ag) NPs in polymer matrices. Holographic periodic structures were formed either using ready NPs added to the monomer mixture (*ex situ* method) or the NPs have been synthesized in an already solid polymer matrix from a metal precursor, presented in the monomer mixture and spatially distributed upon holographic exposure (*in situ* method). The holographic structures based on the noble NPs provide not only unusual optical and holographic characteristics but also pronounced non-linear optical properties.

The nanocomposite containing only 1.5 wt.% of the Au NPs of a 1.7±0.3 nm size provides *n1* of about0.007 and of approximately 0.0085 in the case of the Au NP with a larger (2.7±0.8 nm) size. It was found that the Au NPs play a two-functional role in the grating formation: they participate in the material transfer under holographic exposure and also significantly affect the polymerization process, increasing the depth of monomer conversion, the segregation of a monofunctional monomer from the polymer network and, accordingly, *n*1. The peaks on the absorption spectrum, corresponding to the excitation of the localized surface plasmon resonance (LSPR) of the Au NPs, appears only using a nanocomposite with the Au NPs of 2.7 nm size. It suggests that the local field amplification affects the polymerization process and an increase in *n*1.

The holographic structures containing the Ag NPs created with the *in situ* method shown very high, up to 0.018, value of *n*1. In order to obtain a periodic distribution of silver NPs in polymer the holographic ordering of a metal precursor in the polymer matrix was combined with the subsequent photo-/thermo-induced reduction of the Ag NPs in the areas predominantly enriched with the Ag-precursor. The influence of the forming polymer matrix on the size and localization of the NPs was established. It was found that the Ag NPs are localized mainly in the dark areas of the layer and they are practically absent in the areas corresponding to the bright areas of the interference pattern. The size of the NP can be vary using other photoinitiators in the formulation and holographic exposure of other wavelength making possible to control the parameters of the structures and, consequently, their plasmonic and nonlinear optical properties.

Both types of the nanocomposites perform nonlinear optical properties. In the case of the Au NPs doped nanocomposites the nonlinear response occurs only by using the material with the NPs of 2.7 nm size, in which LSPR is observed. The nonlinear response of a 5 nm Ag NPs containing nanocomposite governs through the absorption saturation. The nonlinear refractive index has a positive sign, which leads to the self-focusing of laser radiation in the nanocomposite layer. Generally, the nonlinear effects of the developed nanocomposites with Ag and Au NPs are explained by the local field amplification due to the excitation of "hot" electrons in the conduction band of the metals.

Thus, in our technology we could combine an easiest, mostly one-step, photostructuring of soft organic compounds with physical properties of inorganic substances in new photosensitive nanocomposite materials. The flexibility of the holographic patterning method allows the fabrication of monofunctional and multifunctional 1D as well as multidimensional passive and active optical and photonic elements. Dependently on the NP properties, the organic-inorganic nanocomposites can be used either to fabricate permanent efficient diffractive optical elements for visible and NIR spectral range or to create functional elements for modern optical, photonic, optoelectronics and sensoric applications.