# Carbon nanomaterials for holography

## Nanomateriales de carbono para holografía

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### Abstract

Holography is a technique to produce and store three dimensional images. It has awakened special interest since its inception as it has applications in several field such as the production of security labels, the development of sensor, in massive storage or in metrology and microscopy. Holography is based on the recording of interfering patterns onto photosensitive materials thus creating a hologram. The light employed as well as the composition of the photosensitive materials are key elements to produce holograms of high quality.

Due to their interesting electrical and optical properties, carbon nanomaterials have been widely studied for the fabrication of holograms of advanced properties.

This review summarizes the use of carbon nanomaterials in holography. A short introduction of the types of holograms as well as the most common photosensitive materials is described. Finally, the emerging of new technologies different to holography for the fabrication of diffractive materials based on carbon nanomaterials is briefly presented.

### Introduction

Classical photography involves the illumination of an object with light (sunlight or artificial) and the register of the diffused light by the object in a photographic plate composed of a photosensitive material (usually a gelatine that contains halide salts) that is modified by the action of the light coming from the object. The magnitude of the modification is proportional to the intensity of the emitted light by the object. After the adequate treatment of the photographic plate (developing, fixation and washing), it will have bright and dark zones related with shape of the object. However, as only the intensity is registered, the photograph will be a two-dimensional image of the object.

Looking for an improvement in the resolution of the electronic microscopy, holography appeared in the forties as a technique to produce and store three dimensional images.[1] It was first described by Dennis Gabor, who was awarded the Nobel Prize for Physics in 1971 for its discoveries.

Holography entails two steps, recording and reconstruction.[2] In the recording process, a photosensitive material is illuminated with a reference beam and the emitted wavefront from the object (object beam), in such a way that the two waves interfere at the surface of the material (Figure 1 A), thus becoming a hologram. After the adequate postprocessing treatment, if needed, the hologram contains fringes of bright and dark zones, similar to a photography; but thanks to the interference of the two beams, it contains information about the phase and amplitude of the registered wave and not only about the intensity of the light. In the reconstruction stage, the hologram is illuminated with a light beam, similar to the reference one, and the diffracted light generates the three-dimensional image of the object (Figure 1 B).

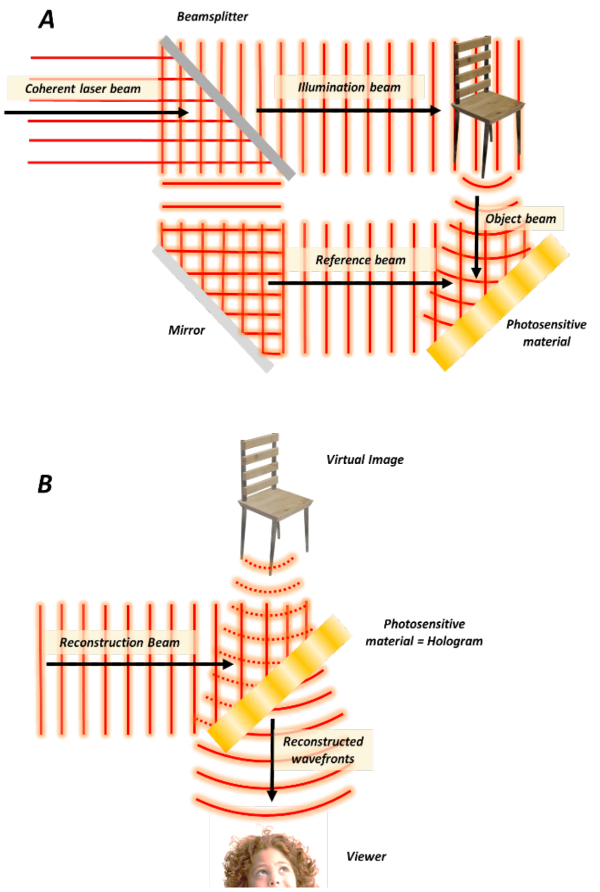


**Figure 1.** Holographic process steps: **A)** Recording and **B)** Reconstruction.

Although initially holography arose as a technique to register or store images, since its discovery, it has found applications in multiple fields such as virtual reality,[3] storage of information,[4] optical waveguides,[5] solar concentrators,[3] memories,[6] sensors,[7] holographic microscopy[8] or holographic spectroscopy.[9]

However, despite its great potential, real applications of holography have not totally taken off as the process requires certain requirements that still have ample room for further improvements. On one hand, the interfering waves should be coherent (the phase difference between them should be constant); and on the other hand, the photosensitive material that is modified by these waves should has high resolving power. This property is defined as the capacity of the material to distinguish the spatial frequencies of the interference pattern. That is, to correctly differentiate the bright and dark zones of the light that will eventually form the fringes of the hologram. The problems related with the coherence of light were solved with the discovery of lasers in 1962, and the ones related with the resolution of the materials are step by step being overcome with the development of new photosensitive materials.

Silver halide sensitized gelatines, dichromated gelatine, photothermoplastics, photopolymers, photoresist and photorefractives have been used as photosensitive materials for storing holograms. Concretely, photopolymers highlight among other systems as they do not require complicated post-recording chemical treatments to form the hologram. Indeed, hologram is created in situ during the recording process, thus, photopolymers are self-processing. Other interesting materials are photorefractives, defined as any material that changes its refractive index under illumination due to electronic processes. The most interesting advantages of photorefractives is that they can be used for read-write applications (as they are optically "erasable") and in real-time holographic display, and do not require high optical power density to be processed. Photorefractive can be inorganic crystals or organic compounds, but liquid crystals stand out due to their high sensitivity to optical field as well as for their capacity to supply the hologram with superior properties. Nonetheless, photopolymers and liquid crystals materials are not absent of drawbacks and numerous research efforts are aimed to improve them in terms of increasing their resolving powers, diffractive efficiencies, or response rates. Different strategies are being addressed to get these objectives. Among them, some of the most interesting are their use in conjunction, thus called polymer-dispersed liquid crystals (PDLC),[10] and their doping with carbon nanomaterials.

Carbon nanomaterials have a noticeable standing among all the nanomaterials owing to the combination of dimension, structure and topology that translates into exceptional electrical, thermal, chemical, and mechanical properties. In holography, carbon nanomaterials are used to provide the photosensitive materials with superior properties due to their high refractive index and conductivity.

Here, we review the types of holograms, the use of photopolymers and photorefractive as photosensitive holographic materials and their doping with carbon nanostructures for the improvement of their performance. Finally, the use of carbon nanostructured to directly create holograms will be briefly discussed.

### Types of holograms

Holograms can be classified according to different criteria. On one hand, the classification can be carried out according to the properties of the incident light that are modified after the recording: the phase or the amplitude. When light hits the photosensitive material, it can modify its refractive index (n) or its thickness (d), thus becoming a phase hologram; or its absorption coefficient (α), thus becoming an amplitude hologram. Another classification responds to the physical characteristics of the hologram. In volume or thick holograms, the thickness of the recording material is much larger than the average spacing of the created fringes, while in surface or thin holograms, the thickness is negligible versus the fringe period. Finally, they can be classified as reflection or transmission holograms depending on the geometry of the holographic recording, that is, the direction of the recording laser beams. In transmission holograms, the two interfering laser beams enter the material from the same side, hence the fringes are perpendicular to the surface of the material (Figure 2 A). In reflection holograms the two interfering laser beams hit the material from their two opposite sides, thus fringes are parallel to the surface of the material (Figure 2 B).

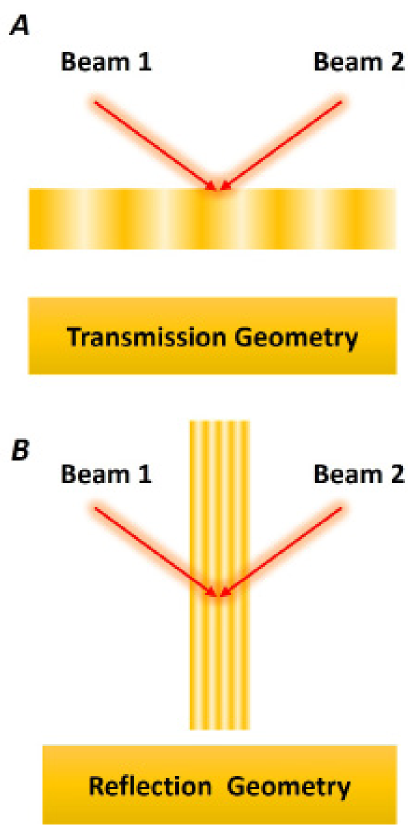


**Figure 2.** Formation of **A)** a transmission hologram and **B)** a reflection hologram.

### Fabrication of holograms with photopolymers and liquid crystals

Photopolymers are materials that polymerize by the action of light at a specific wavelength. In holography, photopolymers are normally composed of one or several monomers and crosslinkers, a photoinitiator and a plasticizer, all embedded in a binder (polymerized inert matrix). They are usually disposed as a film of specific thickness over a flat surface. Then, they are illuminated with the interfering beams to record the hologram. During the recording process, light provokes the polymerization of the monomers in the bright zones thanks to the photoinitiator. As the polymerization evolves, a simultaneous migration of monomers from the dark zones is produced. At the end of the register process, the fringes of the holograms consist of polymerized and non-polymerized zones that differ in their refractive index; consequently, phase holograms are created (Figure 3). As one can envision, multiple variables can affect to the hologram formation, since the characteristics of the recording process by itself (laser power, time, geometry, etc) to the composition of the photopolymers (kind and concentration of the reagents).

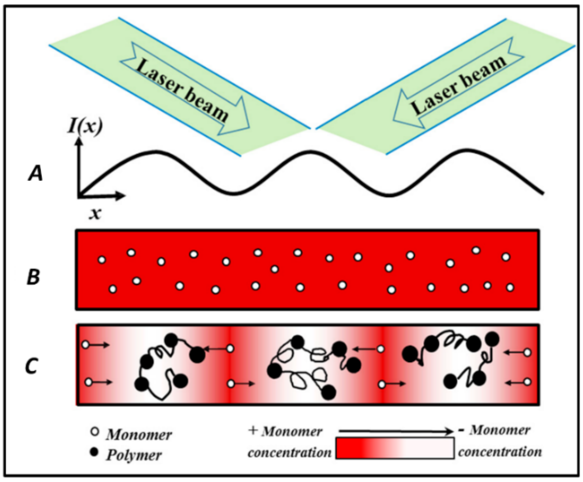


**Figure 3.** Formation of gratings in a photopolymer material: **A)** the sinusoidal illuminating intensity distribution at the plate; **B)** the uniform photopolymer before recording; and **C)** the photopolymer during recording (mass transport and polymer chains). Reprinted with permission from *Polymers* **2017**, *9*(8), 337. Copyright © 2017, MDPI.

In polymer-dispersed liquid crystals, photopolymers are doped with liquid crystals forming a homogeneous material. In this way, when polymerization is taking place and monomers are migrating from dark to bright zones, a concurrent relocation of the liquid crystals from the bright to the dark zones is generated, where they remain as droplets (Figure 4 A). This process is called photo-polymerization induced phase separation process and the photosensitive material for the formation of the holograms is called H-PDLC (Holographic Polymer-Dispersed Liquid Crystals). Apart from the improvement of the structural consistency of the layer, the decrease in the shrinkage processes, and the increase in the refractive index modulation of the holograms, the hallmark of the H-PDLC is that, due to the optical anisotropy introduced by the liquid crystals, the holograms adopt new electro-optical properties, and their response can be modified by the application an external electric field. That means that the electrical field can modify the diffraction efficiency of the hologram, so it can be useful for the development of optical switching devices. The modification is produced by the reorientation of the LC droplets within the electric field (Figure 4 B).

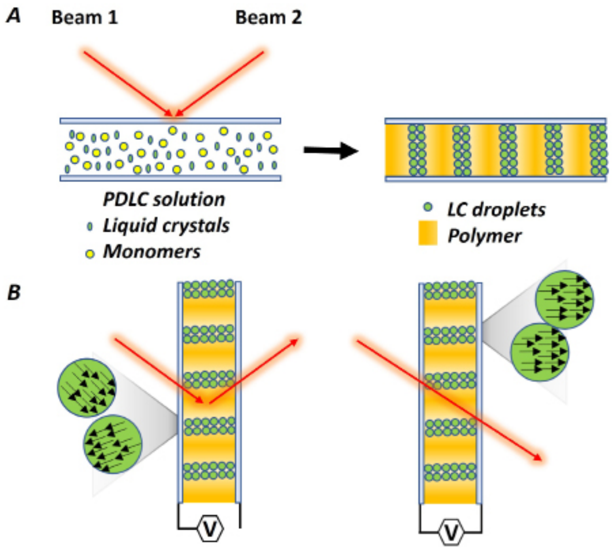


**Figure 4. A)** Formation of gratings in a solution of PDLC: Photopolymerization takes place in bright zones while LCs migrate to dark zones as droplets. **B)** Detailed scheme of the reorientation of the LC droplets in gratings in the presence of an external electric field. When the voltage is off the light is diffracted, while it is transmitted when the voltage is on.

## Carbon nanostructures as additives in holographic photopolymers

Carbon nanomaterials have been added to photopolymers mainly to generate a higher modulation of the refractive index in the photosensitive materials with the aim of increasing their diffraction efficiency. Tomita et al. added nanodiamonds (NDs) to photopolymers to increase the modulation of the refractive index (Δn) of the material and, thus, improve its diffraction efficiency.[11] They fabricated unslanted volume transmission holograms with the monomers tri- and tetrapentaetrythritol acrylate and a single functional ionic liquid monomer dopped with NDs at different proportions. Photopolymerization, triggered by the interfering waves, causes a migration of the NDs to the dark zones while photopolymer is formed in the bright zones, thus increasing the refractive index modulation. In addition, they performed slow-neutron diffraction experiments, observing that the fabricated gratings were excellent candidates for their use in neutron optics as they showed DE > 20 % (Figure 5). In a recent study, Guo et al. incorporated single-walled carbon nanotubes (CNTs) in a mixture of trimethylolpropane triacrylate (TMPTA), trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), and 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO) to fabricate volume transmission holograms.[12] They observed how the CNTs not only promote and accelerate the allylic polymerization of the monomers but also increased the refractive index modulation of the holograms which generated high diffraction efficiencies (>96%). In addition, CNTs improved the mechanical properties of the holograms without compromising their flexibility. Chen et al. studied the effect of the addition of graphene oxide sheets in a methyl methacrylate (MMA) mixture.[13] The fabricated holograms with this mixture proved how the graphene oxide contributed positively to the enhancement of the diffraction efficiency by promoting the polymerization of MMA. The experimental results also showed that the graphene oxide was grafted to the polymers chains which could benefit the refractive index modulation of the photosensitive material.

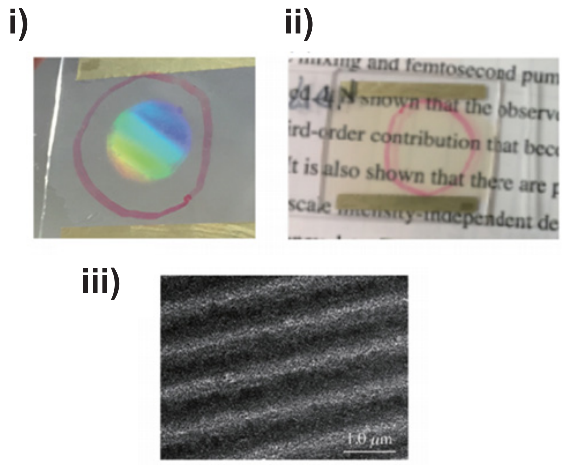


**Figure 5.** Hologram fabricated with photopolymers doped with nanodiamonds by Tomita et al. i) Photograph of the hologram under illumination with white-light, ii) Photogram of the same hologram viewed from the top and iii) from a fluorescent lamp and iii) TEM image of the cross section of the grating. Reprinted (adapted) with permission from *Phys. Rev. Appl.* **2020**, *14* (4), 1. Copyright © 2020, American Physical Society.

### Carbon nanomaterials as additives in holographic PDLC

Carbon nanomaterials have been added to H-PDLC mainly to improve the electrical conductivity of the holograms and, thus, to decrease the voltage needed to perturb their optical responses. Fullerenes were introduced into PDLC by Kim[14] to increase the electrical conductivity of polymer matrixes and hence the local electric field on LC droplet. This led to a decrease in the droplet size of the LC, with increased droplet density, that was translated into an augmented diffraction efficiency while the operating voltage was reduced. Later, same authors studied the doping of PDLC with multi-walled carbon nanotubes observing that the diffraction efficiency was increased due to the induced local electric field of the polymer but also to the delay in the nucleation of LC during the periodic modulation. Interestingly, they carried out the experiments with pristine and vinyl-modified CNTs, observing better performance of the functionalized ones ascribed to their finer dispersion. Surprisingly, larger LC droplets were observed with the functionalized CNTs.[15] A different group observed that CNTs play the same role when they were incorporated in different polymer matrixes (Figure 6).[16,17]

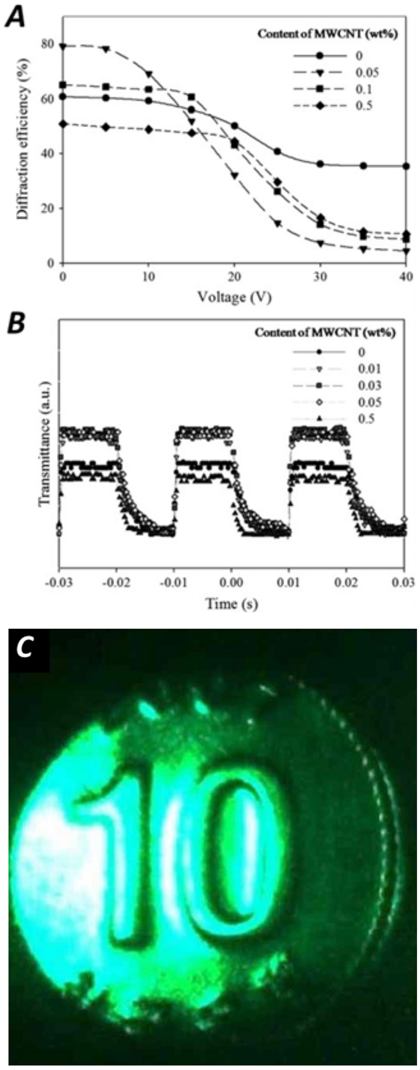


**Figure 6.** Electro-optical properties of the H-PDLC obtained by Kim et al. using a polyurethane-based matrix doped with various MWCNT contents at 40 wt% LC: **A)** driving voltage and **B)** response time at 50 Hz, 30 V**. C)** Photograph showing a reconstructed virtual image of a coin recorded using a H-PDLC obtained at 40 wt% LC with 0.05 wt% MWCNTs. Reprinted (adapted) with permission from *Polym. Int.* **2010**, *59* (9), 1289–1295. Copyright © 2010, John Wiley and Sons.

In a posterior study, similar results were observed with graphene as it improved the local electric field and the diffraction efficiencies of PDLC.[18] However, while polymer conductivity increased linearly with the increasing graphene content, excessive quantities of graphene (higher than 0.10 %) produced undesired augmented viscosity and aggregation processes detrimental of the diffraction efficiency. The same studies performed with allyl-modified graphene oxide confirmed the role of the graphene in the viscosity, the grating kinetics and morphology, the diffraction efficiency (DE), and the electro-optical properties of holographic PDLC.[19] The group of Fontecchio also doped the PDLC with oxidized multi-walled carbon nanotubes observing a decrease of the LC droplet sizes and improved electro-optical response of the holographic material leading to increased diffraction efficiencies.[20,21] In an interesting study, multiwalled carbon nanotube were covalently functionalized with liquid crystal chains and subsequently used to dope PDLCs.[22] The functionalization improved dispersion of the CNTs in the medium which yielded holograms with enhanced electro-optical properties in terms of voltage requirements. In the last study found about this topic, Liu et al. doped PDLCs with multiwalled carbon nanotubes and carried out theoretical simulations to analyse and predict the effect of the CNTs on the electro-optical properties of the holograms.[23]a model developed for establishing the lowest possible driving voltage of Holographic polymer-dispersed liquid crystal (H-PDLC They showed how the CNTs improved the phase separation of LC and polymer regions and accumulated in the LC region, thus improving the diffraction efficiency of the holograms. CNTs also modified the LC droplet sizes and decreased the dielectric permittivity of the gratings that improved their electro-optical response. One of the problems of holograms fabricated with liquid crystal is that they are not temporally stable. However, Abbasov et al. proved that the doping with carbon nanotubes could not only improve the diffraction efficiency of liquid crystal-based holograms but also improve their stability over time (over two years).[24] Gao et al. also doped liquid crystal films with carbon dots observing good diffraction efficiencies with low voltages.[25] What is more, they acquired real-time dynamic holographic display videos with these films which might be potentially applied in future true 3D TV display.

### Fabrication of holograms by the laser ablation of carbon nanomaterials

Holograms have also been generated by the direct photoreduction of graphene oxide.[26] Li et al. dispersed graphene oxide into polyvinyl alcohol binder and spin coated the solution over a glass slide to create a thin film. By the application of fs-pulsed laser beam at the wavelength of 800 nm, they were able to reduce the graphene oxide and thus, create holographic gratings. What is more, they observed that they could modulate the phase of the materials by changing the pulse fluence of the laser beam. The large dynamic range of the phase modulation opened the door to the fabrication of holograms of high diffraction efficiency able to generate three-dimensional holographic images with a wide viewing angle.

### Patterns of carbon nanomaterials with applications in holography

Butt and others have used carbon nanomaterials to fabricated diffractive elements useful as holograms in processes alternative to holography. They fabricated uniform patterns of nanomaterials onto transparent support via electron-beam technologies in such an ordered way that they could diffract light as holograms do (Figure 7). The most interesting property of these diffractive elements is that, due to the nanoscale dimension of nanomaterials, they can generate diffraction images of high contrast and with very large field of view. Carbon nanotubes have been the main carbon nanomaterial employed for the fabrication of these kind of diffractive elements[27–31] but they have also used graphene obtaining very good results.[32] Although the technique developed by Butt and co-workers awaken interest in holography, it will not be deeply discussed here as their technology would deserve a different perspective of analysis as it is not holography in terms of using beam interference.

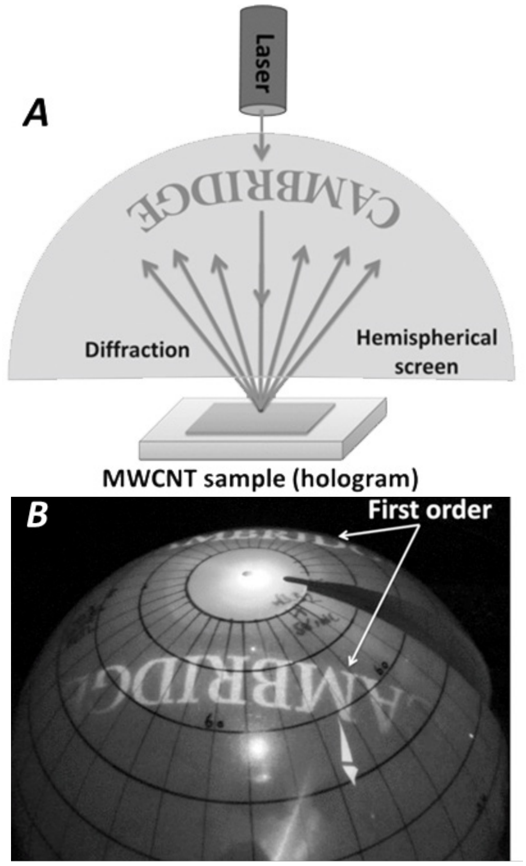


**Figure 7.** Experimental setup and measured diffraction pattern results of the holograms fabricated by Butt and colleagues. **A)** The schematic diagram of the experimental setup employed to capture the diffraction pattern. **B)** The pattern was obtained on a semitransparent hemispherical screen of radius 15 cm by shining a green (532 nm) laser perpendicular to the plane of the CNT array. A clear CAMBRIDGE image was observed in the first order of the diffraction pattern.

### Future perspectives

Holography is an advanced technology useful in multiple fields. The laser interference warrants an accurate control of the fabrication processes in terms of holograms dimensions. However, to exploit all its potentials, the improvement of the holographic materials is still needed. This review has summarized the use of carbon nanomaterials to improve the performance of the photosensitive materials used for the recording of holograms. In addition, it has presented the fabrication of diffractive patterns of carbon nanomaterials that could be used as holograms using alternative technologies. The studies here presented show how holography benefits from the excellent properties of the carbon nanomaterials in many ways, such as improvement of mechanical and elecro-optical properties of the gratings or enhancements in their diffraction efficiencies. Nonetheless, despite all the efforts, there is still room for improvement in this research area.

For example, a total control over the functionalization of the carbon nanomaterials to improve the viscosity and conductivity of the photopolymers seems to be absolutely needed. This could imply using different functional groups and methodologies to increase the length of the organic chains attached to the nanomaterials. In addition, it should be noticed that carbon nanomaterials are presented in multiple formats (size and shapes) and not all of them have been studied. New studies about the anchoring of the nanostructured to the photopolymers would also be beneficial for understanding the mechanisms of the grating formations.

### Acknowledgements

This work was financially supported by the E.U. FEDER, the Spanish Ministry of Economy and Competitiveness MINECO (AdBiHol-PID2019-110713RB-I00) Generalitat Valenciana (PROMETEO/2020/094). M. I. Lucío acknowledges MINECO for her Juan de la Cierva-incorporación grant (IJC2018-035355-I).

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