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A Survey on Multiphoton Lithography for Fabricating Optical Microdevices

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Multiphoton lithography is a promising microfabrication technique to produce complex microstructures. Besides the ability to make 3D structures with very few constrains, this technique provides sub-micrometric resolution and high fabrication speed. Furthermore, it also allows for incorporating a variety of organic and/or inorganic dopants into the polymeric matrix, leading to functional structures with tailored properties. It is therefore possible to produce microdevices for a wide range of applications. In this review we show a series of recent advances regarding methods to introduce different types of material into the microstructures and ways to characterize those microdevices. The fabrication of doped samples using multiphoton lithography allows for the exploration of the unique properties from metallic and semiconductor nanoparticles, as well as a variety of organic compounds. Here we emphasize the production of optically-active samples exhibiting variable or broadband emission spectra, which are suitable for applications in electronic and photonic devices.

Keywords: two-photon polymerization, multiphoton lithography, doped microstructures, optically active devices, metallic nanoparticles, fluorescent microstructures, functional devices

1. INTRODUCTION

Driven by the need for the miniaturization of devices required in many technological areas, from microelectronics to biology [1-3], several meth-

ods have been explored for the fabrication of micro/nano structures [4-8]. Among these methods, the use of ultrashort laser pulses to microstructure materials stands out due to the high resolution and three-dimensionality it provides. In this context, multi-photon lithography (MPL) [9] can be highlighted as a method that allows for sub-micrometric resolution, high fabrication speed, and the production of complex 3D microstructures with only few geometrical constraints. Furthermore, such a method permits incorporating dopants into the polymeric matrix, which can lead to structures with enhanced properties.

The first experimental demonstration of two-photon absorption (2PA) was realized in 1961, by observing the two-photon excited fluorescence in CaF_2:Eu^{+2} [10], although it was theoretically predicted by Maria Goeppert-Mayer in 1931 [11]. In such a process, the electronic transition is undergone by the simultaneous absorption of two photons in a single quantum event. Albeit the 2PA probability is too low to be measured by conventional light excitation [12], 2PA can be observed when intense laser light, such as that from femtosecond laser pulses, is used. Because the rate of 2PA scales with the square of the light intensity, the polymerization induced by two-photon absorption, known as two-photo polymerization (2PP), is confined to the focal region, providing high spatial selectivity and resolution to this fabrication method.

In two-photon polymerization (2PP), the radicals responsible for starting the polymerization are produced by two-photon excitation of an initiator molecule (photo initiator). Since 2PA is confined to the focus, radical formation and consequently polymerization occurs only in the proximity of the focal region. This feature allows 2PP to be used as a method for fabricating micro and nanodevices [13-17].

From the experimental point of view, 2PP can be accomplished by optical systems that scan the sample stage three-dimensionally, or by using an approach in which a pair of scanning mirrors is responsible for the *x*-*y* movement of the laser beam, while the movement in the *z* axis is carried out by a translation stage. Figure 1 illustrates the fabrication setup using the scanning mirror configuration. As excitation source for 2PP, fs-laser pulses, in general provided by Ti:sapphire laser oscillator system ($\lambda \sim 800$ nm and MHz repetition rate), are employed. After being deflected by the scanning mirrors (*x*-*y* directions), the laser beam is focused into the sample with a microscope objective. The sample (unpolymerized resin) is positioned on the axial stage that is responsible for the vertical scanning. The fabrication process is accompanied with the aid of a CCD camera. When the fabrication of the desired microstructure is finished, the samples are immersed in a suitable solvent, given the specific polymer used, to eliminate unsolidified resin, leaving on the glass substrate only the polymerized microstructure.

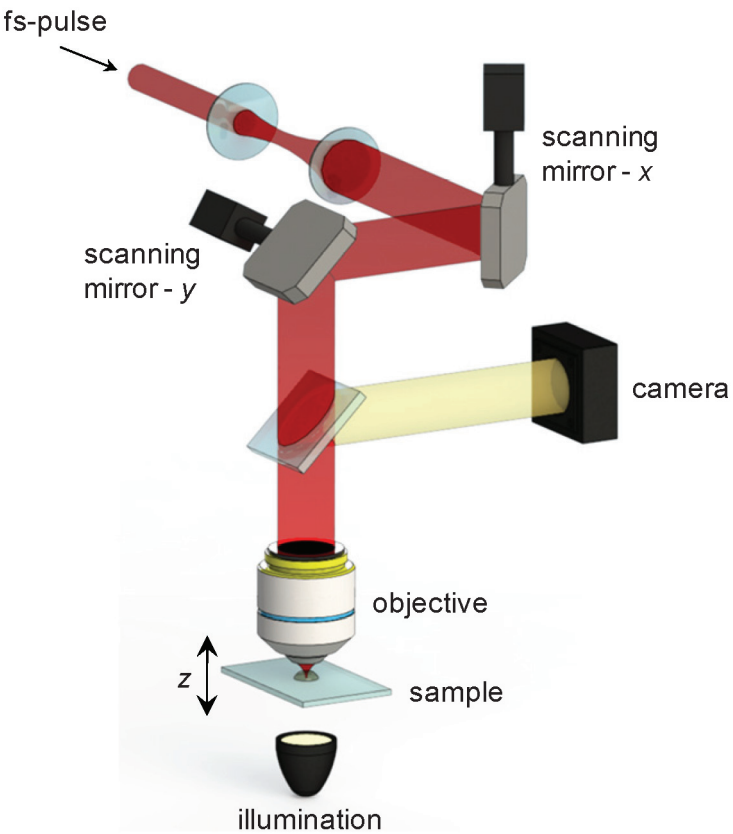

FIGURE 1
Illustration of the experimental setup used for the fabrication of three-dimensional microstructures by two-photon polymerization

The microscope objective used in the 2PP setup imposes a physical limit to the laser beam waist at the focus, given by the diffraction limit [18]. Due to the nonlinear nature of the process, 2PP allows to overcome the diffraction limit, which enables polymerization with high resolution. Furthermore, if the energy used for 2PP is close enough to the minimal one required for polymerization (threshold), it is possible to diminish the size of the volumetric pixel (voxel), which further enhances the resolution of 2PP [13].

Among several applications of 2PP, its use as a method to fabricate doped microstructures for devices has received special attention in the last few years. Hence, in this paper we present some advances on methods, characterization and properties of 2PP microstructures containing different dopant materials.

2. PROGRESS ON DOPED MICROSTRUCTURES AND APPLICATIONS

2.1 Initial demonstrations of doped microstructures

Due to the rising need and interest for photonic and microelectronic devices, microstructures tailored by femtosecond laser gained great attention. One important initial step for producing functional doped microstructures was made by Kawata's group [19]. In the early 2000's, they attained the production of microstructures doped with a fluorescent dye via 2PP [19]. By adding a laser dye, which was predominantly composed by Rhodamine B, as a dopant into the resin, laser microfabrication was not compromised. However, the dye could promote undesired polymerization due to induced two-photon fluorescence, leading to a lower spatial resolution [19]. Two-photon fluorescence confocal microscopy images of the produced microstructures show that structural integrity and dye fluorescence were preserved, and the dopant was observed homogenously distributed through all the polymer volume. Figure 2 presents fluorescence images of such a 3D doped structure [19].

The authors also highlighted that the lateral resolution obtained was down to 120 nm, which can be achieved when large numerical aperture microscope objectives are employed. Such high resolution is an advantage that 2PP offers over traditional lithography techniques in producing complex structures [14]. These results added to the possibility of producing microsized structures for active media devices.

Later, in 2006, Farsari *et al.* [20] demonstrated the fabrication of 3D microstructures followed by doping, aiming at biological applications. They employed *three*-photon polymerization, which yields even higher spatial resolution for designing microstructures. Before the microstructures were doped, their surfaces were functionalized in order to provide the attachment of streptavidin, a fluorescent compound [20]. To ensure that doping was achieved, polymerized structures were imaged by fluorescence microscopy.

2.2 Fabrication of microstructures with distinct inorganic and organic dopants

In 2007 Mendonça and coworkers [21] reported on polymeric microstructures doped with another type of organic material, an azo-aromatic dye. The dopant provided birefringent samples. By adding an azochromophore to the base resin, the resulting microstructures presented optically induced birefringence, a property explored in applications such as optical storage [22]. Birefringence of produced microstructures was observed using polarization microscopy. Therefore, by doping the resin used in 2PP, one widens the range of possibilities for fabricating doped microstructures.

However, not only organic compounds can be added to polymer microstructures. Hybrid materials have great potential for applications in functional

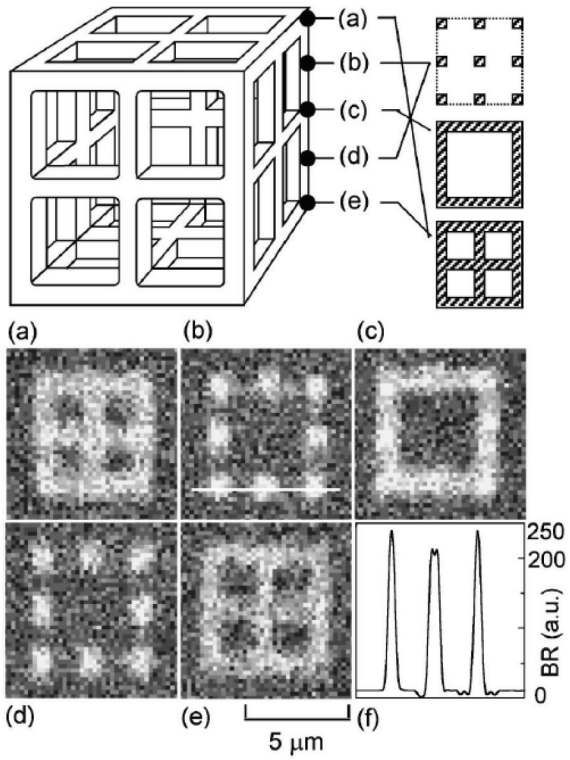

FIGURE 2
Fluorescence images of a dye-doping polymerized cubic cage (a)–(e), of which a schematic is illustrated by the top line drawing. The heights are (a) 0.0, (b) 1.35, (c) 2.7, (d) 4.05, and (e) 5.4 mm, respectively. A fluorescence intensity distribution was extracted from (b) and given by (f). BR: brightness. Reprinted with permission from (Sun, H.B. et al., 2001). Copyright (2014), AIP Publishing LLC.

microdevices. Another key step towards fluorescent and luminescent microstructures produced by 2PP was carried out by Kawata's group in 2008. Sun *et al.* were the first to incorporate nanoparticles into polymeric micrometer-sized structures [23]. One of the biggest challenges was to dissolve the nanoparticles homogenously into the resin, avoiding agglomeration and, consequently, preventing the sample from becoming opaque. They overcame those issues by performing an *in situ* synthesis of the nanoparticles after the laser irradiation. The authors also managed to explore a feature of foremost importance in semiconductor nanoparticles; *viz.* the tunability of emission due to quantum size effects. This feature enables production of highly efficient luminescent devices, which could be of great use in photonics applications and colored displays.

Samples composed of a precursor of CdS nanoparticles (cadmium methacrylate), monomers, oligomers, photoinitiator and photosensitizer were photo-polymerized and immersed in hydrogen sulfide gas for in situ synthesis. Different amounts of the oligomer Dipentearythritol hexaacrylate (DPE-6A), used as crosslinker, mixed to the monomer methyl methacrylate, led to distinct CdS nanoparticle absorption spectra. High-resolution transmission electron microscopy confirmed that the average size of the *in situ* synthesized nanoparticles decreased (from 6 to 2.6 nm) as the crosslinker content increased (from 0 to 48.7 weight percent), which explains the observed fluorescence peak change from 466 to 528 nm for each designed resin. This strategy was successfully applied to microstructures produced via 2PP. Figure 3 shows scanning electron and fluorescence microscopy images of micro-bulls and micro-lizards fabricated using the mentioned approach [23].

Also in 2008, Farsari et al. [24] contributed to the development of new materials with tunable properties for optically active devices in microphoton-

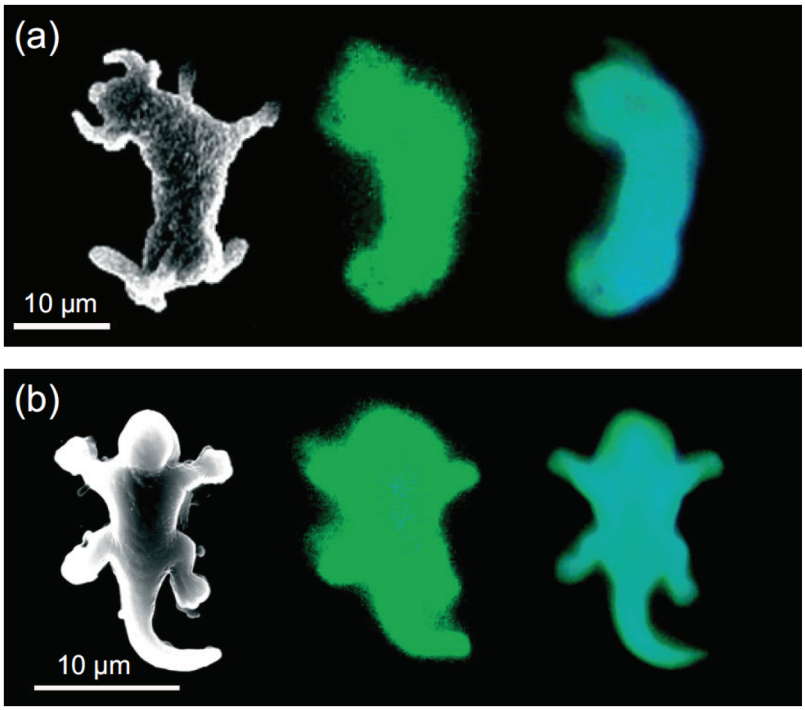

FIGURE 3
Scanning Electron Microscope (left) and Fluorescence Microscopy images of three-dimensional (a) microbull and (b) lizard fabricated from different resins (center and right). Reprinted with permission from (Sun, Z.B. et al., 2008). Copyright (2014), John Wiley and Sons, Copyright Clearance Center.

ics and microelectronics. They managed to synthesize a nonlinear optical active sol-gel chromophore, which they employed to fabricate photonic crystals having stop-gaps in the near infrared. Sol-gel was shown to be an interesting matrix to fabricated microstructures, in addition to exhibiting high nonlinearities, and stable alignment of the chromophores [25-26]. The insertion of nonlinear chromophores into sol-gels produced electro-optical active materials that could be used in many types of active devices [27]. In this case, the chromophore used as dopant was Disperse Red 1 that even when combined with the sol-gel is completely transparent in the near infrared, which is an advantage for photonic crystals at telecommunication wavelengths [24]. The fabrication of the photonic crystal was based on a woodpile structure, conducted by stacking layers of one-dimensional rods. Each layer of rods was shifted by half of their separation and rotated 90º yielding complex structures. The fabricated photonic crystals presented bright red color due to the presence of Disperse Red 1 in their composition. Fourier Transform Infrared Spectroscopy was used to characterize the photonic crystals transmission spectra, for microstructures with rod distances within the layers ranging from 1.4 to 1.8 um. Stop-gaps at expected frequencies were observed, shifting to shorter wavelengths as rods got closer.

Not only chromophores and nanoparticles can be inserted into polymeric microstructures, but also other polymers can also be blended into the base resin, rendering new properties to the device. In 2009, Mendonça et al. [28] explored the fabrication of microstructures containing poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylevevinylene) (MEH-PPV), an electroluminescent polymer. They added MEH-PPV to the resin in order to take advantage of its conductive and luminescent properties [28], and produced a waveguide-like structure. Fluorescent confocal microscopy at different layers height of the fabricated microstructure showed that MEH-PPV was completely dispersed in the structure volume. They also investigated the viability of guiding light throughout a microstructure. In order to achieve that, 100 μm long doped waveguides were illuminated at their center by a focused 532 nm laser beam and fluorescence from the polymer was guided to the ends of the structure. However, guiding in such waveguides was only observed when microstructures were fabricated on top of a low refractive index substrate (porous silica), which avoids light coupling to the substrate.

2.3 New developments on 2PP microfabrication towards device applications

For several applications, including displays, it would be desirable to fabricate structures with two or more distinct dopants. In 2010, Zukauskas et al. [29] demonstrated, for the first time in the literature, the fabrication of optical gratings by 2PP with organic modified silica (ORMOSIL) doped with Rhodamine 6G (R6G) and Fluorescein. Such gratings composed of two different dopants were fabricated on the same substrate by a sequential fabrication

procedure. Initially, horizontal lines were fabricated with ORMOSIL doped with R6G and the sample subsequently rinsed in ethanol to remove the unpolymerized resin. After this step, Fluorescein doped ORMOSIL was drop-casted on free-standing horizontal lines, fabricated in the initial step, and vertical lines were produced. After the publication of this pioneering work, there was an increasing interest on multi-doped microstructures fabrication. The advantage of this methodology is not to limit the shape or the number of microstructures that may be produced.

In addition to all the attention given to the production of functional micro-devices, 2PP can also be used for the production of micro-optical components which can be applied, for instance, in imaging systems. In 2010, Malinauskas and co-workers [30] demonstrated the fabrication of spherical lenses with different radii of curvature in ORMOSIL, by means of 2PP. Figure 4 (a) shows screenshots of real-time fabrication of a lens with 25 μm radius and 8 μm height. The bright spot indicates the laser focus position. Figure 4 (b) shows a SEM image of a microlens with radius of curvature of 15 μm. The sample was scanned laterally (axially relative to the focus) resulting in polymerized rings that form the lens.

The ability to produce lenses in ORMOSIL is associated to its good structuring qualities, low shrinkage [31] and the proximity of its refractive index to that of glass, ($n_{Ormosil}$ = 1.504, n_{Glass} = 1.52), that in general is used as a substrate for microstructures. The refractive index matching of the materials minimizes refraction from the interface between the lens and the glass. Acrylate materials can be used for this purpose as well.

Malinauskas et al. [30] characterized the focal length of the fabricated lenses and demonstrated their imaging capabilities using macroscopic objects. For example, for microlenses with radius of curvature of 25 μm,

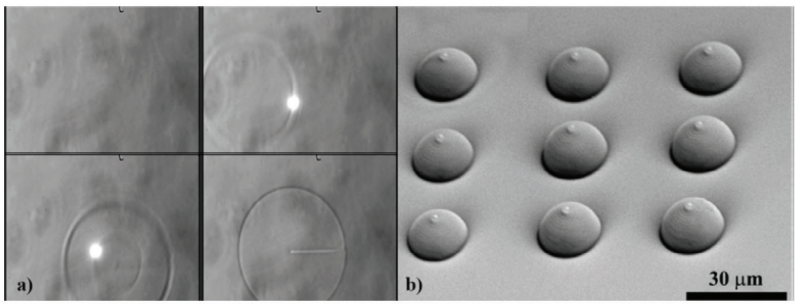

FIGURE 4
(a) Screenshots of the real-time lens fabrication (radius 25 μm, height 8 μm). (b) SEM micrograph of a microlens array with 15 μm diameter. Reprinted with permission from (Malinauskas et al., 2010). Copyright (2014), IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.

the measured focal length was 45 ± 10 μm, in good agreement with the expected value of 50 μm. The surface roughness of the microlenses, determined by atomic force microscopy (AFM), was satisfactory for optical applications. These lenses allowed imaging of millimetric objects; by using a lens with radius of curvature of 92 μm, it was possible to visualize an object with 1.2 mm.

In another paper by Malinauskas and co-workers [32], they demonstrated fabrication of several micro-optical elements (MOE), such as aspherical, Fresnel and solid immersion lenses (SIL). To produce these MOEs, the authors used a hybrid organic–inorganic photopolymer referred to as SZ2080 [33]. For such fabrication, special attention was given to find ways of reducing the structural distortion of the photopolymerized MOEs, as well as to make it a fast and practical method. They characterized all MOEs and experimentally demonstrated some applications. For example, for solid immersion lenses, they obtained an image magnification of approximately 2.4 [32]. In addition, the authors presented MOEs fabricated in the tip of optical fibers, which can increase significantly the coupling efficiency [34]. Micrograting, microlenses and micro-prisms were also fabricated in the tip of optical fibers. These results opened new perspectives in the fields of optical devices and sensors, allowing for the production of new imaging microsystems.

In 2012, Lee et al. [35] created polymeric microstructures doped with three types of nanoparticles: blue emitting CdS/ZnS, red emitting CdSe/ZnSe and green CdSe/ZnS quantum dots. They produced, by means of 2PP, 3D microstructures with the three quantum dots uniformly dispersed throughout the sample bulk. The produced samples were observed in a confocal microscope, and the obtained images are shown in figure 5 [35]. In figure 5 (a) the sample is excited by a 405 nm laser and a 415-480 nm filter is used to collect the sample fluorescence. For the image in figure 5 (b), a laser line at 488 nm was used for excitation along with a 500-525 nm filter, while image (c) was obtained with 532 nm laser excitation in combination with a 550 nm-IR filter. The image in figure 5 (d) was collected without any filter, and all laser lines were shone upon the sample, to show the white emission arising from the combination of red, green and blue fluorescence from the three quantum dots embedded in the microstructure.

Lee's group [35] have also produced films of this quantum dot-doped polymer, which were used for the production of electroluminescent (EL) devices. Thus, the potential of this kind of material for new RGB colored displays was demonstrated.

Later in 2012 Tribuzi and coworkers [36] introduced a new method for incorporating metallic nanoparticles into polymeric matrices in an indirect manner. The direct insertion of nanoparticles in the base resin for the production of microstructures, prior to polymerization, has some potential disadvantages; it requires an additional synthesis process to obtain the desired nanoparticles, and the presence of this material during pulsed laser irradiation

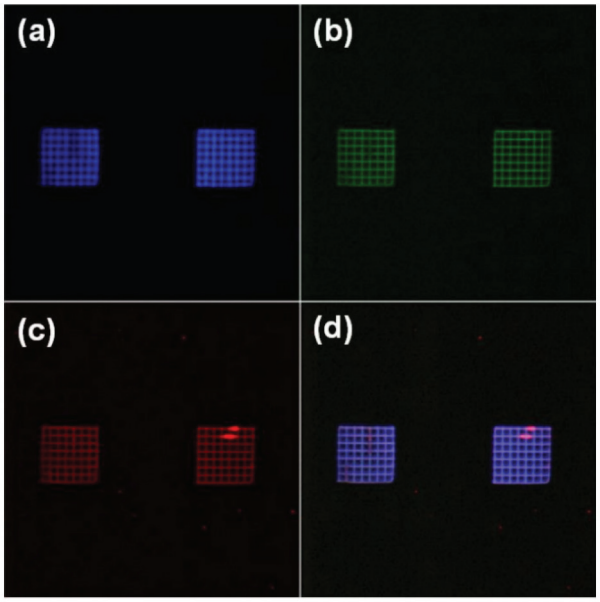

FIGURE 5
Confocal microscope images of 3D structures showing the emission from quantum dots throughout the structure. Reprinted with permission from (Jang et al., 2012). Copyright (2014) The Optical Society (OSA).

might impair polymerization, yielding deformed geometry and loss of resolution. The method proposed in Ref. [36] consists of introducing into the base resin a precursor for the metal nanoparticles. After microstructure fabrication the sample is subjected to thermal treatment, which induces nanoparticle formation into the sample bulk.

The temperature increase plays two roles in this process; it gives the necessary energy to reduce metal ions from the precursor and increases the mobility of those atoms in the polymeric network. In this approach nanoparticles are not formed during laser irradiation, but are produced *in situ* by simply heating the sample, after the fabrication procedure is finished. Therefore, this new method not only prevents inserted nanoparticles from interfering with the 2PP fabrication, but also allows for the use of multiple dopants simultaneously in the same microstructure, since other compounds can be added to the resin along with the precursor. For the indirect insertion of gold nanoparticles, the authors added to the base resin an aqueous solution of $HAuCl_4$ (2 g/l) and mixed it in at a proportion of 1 ml of the solution to 2.5 g of resin. After microstructure fabrication the sample was submitted to a thermal treatment at 185°C for approximately 30 minutes. Gold nanoparticles doped samples presented broadband emission, from approximately 400 nm

to 600 nm, when excited by laser at 325 nm. A comparison between doped and undoped samples suggested that part of the strong fluorescence from the doped samples is a result of local field enhancement; however the excitation wavelength was far from the typical plasmon resonance for these nanoparticles. The strong fluorescence from doped samples, which covers almost the entire visible spectrum, arises from the luminescence of different sized nanoparticles.

Besides the broad emission exhibited by the sample, this doping technique also allows for the exploration of the local field enhancement effect in conjunction with other dopants added to the base resin. Multidoped microstructures, containing metallic nanoparticles and another compound, could represent a class of more efficient active microdevices. Thus, this method opens a path for the study of metal nanoparticles doped microdevices, a field with a wide range of potential applications, such as contrast agents in confocal microscopy, chemical and biological sensors and in the manufacturing of SERS substrates.

Jia et al [37] used a hybrid organic–inorganic polymer containing dispersed PbS quantum dots to fabricate woodpile-shaped photonic crystals with stop gaps in the telecommunications wavelength region. Shukla et al [38] produced metamaterials by designing subwavelength plasmonic structures as small as 150 nm, including optically active planar chiral structures and plasmonic nanostructures. Correa et al. [39] fabricated rhodamine-containing microstructures via 2PP that could be selectively excited by laser light guided by sub-micron silica wires.

In 2012, Otuka et al. [40] presented yet another way to produce samples with RGB-like emission. They fabricated microstructures doped with two and three different organic dyes. These were produced in a multiple step fabrication process, in which the resin containing a different dopant was added to the microstructure at each step. This method limits neither the number of compounds that might be added nor the shape of the fabricated microstructures. To demonstrate this method, the authors used three fluorescent dyes: Rhodamine B, which emits in the red portion of the spectrum, Disodium fluorescein, a green emitting dye, and Stilbene 420, which presents a blue fluorescence. They successfully demonstrated the fabrication of structures with two or three dyes. The emission spectrum of a triple doped microstructure presents three main peaks, centered at 420 nm (blue), 535 nm (green) and 580 nm (red) corresponding, respectively, to fluorescence from Stilbene 420, Disodium Fluorescein and Rhodamine B. Two distinct emission curves were obtained when the excitation beam was directed to different regions of the same sample. When excitation was focused on the Stilbene doped region of the sample, fluorescence shifted to the blue region of the spectrum, while when excitation laser shone upon the Rhodamine-doped region, the emission spectrum was red shifted. Hence, it was possible to select which emission should be collected just by changing the sample

region that was irradiated. This multiple doped sample represents a RGB pixel where the red, green and blue emissions come from adjacent parts of the microstructure, just like a conventional RGB pixel. So the emission can be altered by either changing the excitation wavelength, since each dye has a different absorption spectrum, or by changing the region of the structure being irradiated.

In 2013, five years after the first paper on 3D birefringent microstructures by Mendonça et al., another paper addressed that matter. Tribuzi and co-workers [41] produced birefringent samples using a different dopant, and studied the dynamics of the photoinduced birefringence as a function of the polymeric matrix composition. The compound used to render birefringence to the microstructure was a copolymer having an azo-aromatic chromophore attached as a side group, HEMA-DR13 (2-hydroxyethyl - methacrylate and 4- [N-ethyl-N- (2-methacryloxy-ethil)] -amino-2'-chloro-4'-nitro-azobenezene). The material used in 2PP fabrication process was a blend of this azo-copolymer with a mixture of two acrylic monomers. The two base monomers are used to grant distinct properties to the final polymer. While monomer A (tris (2-hydroxyethyl) isocyanurate triacrylate) rendered hardness to the material, monomer B (ethoxylated(6) trimethylolpropane triacrylate) reduced shrinkage tensions upon polymerization. By using an azocopolymer, the authors were aiming at higher residual molecular orientation (optical storage). The photoinduced birefringence process consists of a series of trans-cis-trans isomerization cycles that result in molecular alignment. Upon irradiation these processes yield an excess of chromophores aligned perpendicular to the laser polarization. A writing laser induces this process, while the transmittance of a reading beam is monitored. When this writing laser is turned off some orientation relaxation takes place. When the azoaromatic group is attached to a larger molecule its freedom of movement is restricted and the molecule is less prone to lose the acquired orientation, which in turn results in larger residual memory. To perform the desired studies, a 532 nm Argon ion laser was used as writing beam, while a 633 He-Ne laser was used as a reading beam. After fabrication, the resulting microstructure was placed between two crossed polarizers, in order to avoid transmission of the reading beam. The experimental apparatus is described schematically in figure 6 [41].

A microscope objective was used to project the microstructure image into a CCD camera. Before irradiation with the writing beam, the image was entirely dark since the polarizer and analyzer were crossed (Figure 6b). After laser exposure, the optically induced birefringence increased (reading laser) transmission, since some of the light going through the sample could be transmitted by the analyzer (Figure 6c). With this setup it was possible to monitor the reading beam transmittance variation with time, thus measuring the dynamics of the process. This photo-induced birefringence dynamics was evaluated for different proportions of monomers A and B (70%/30%, 30%/70% and 50%/50%). Upon using these different proportions one could

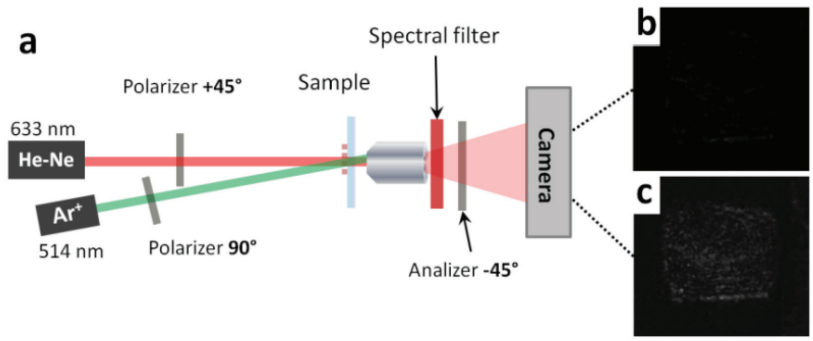

FIGURE 6
(a) Setup used to measure the photoinduced birefringence in microscopic samples. (b) CCD image before the writing beam irradiation and (c) after exposure for one minute. Reprinted with permission from (Tribuzi et al., 2013). Copyright (2014) The Optical Society (OSA).

alter not only the residual memory, but also the rate at which birefringence was induced in the sample (recording speeds).

Despite the fact that monomer A gave hardness to the material, a simple increase of its content in the polymer matrix did not result in higher residual memory. The important feature is actually the free volume available for the azochromophore in the material, which was limited by the monomer to polymer conversion. Furthermore, the use of an azopolymer, as opposed to an azodye, enabled the authors to obtain microstructures with up to 35% of residual memory. This study opened the possibility to improve the development of efficient micro-optical devices for applications in selective polarization, control of light transmittance (optical switching) and optical data storage.

Later in 2013, further investigations of gold nanoparticle doped polymeric microstructures led Almeida et al. [42] to explore this material. Nanoparticle doped microstructures have been shown to possess a broadband fluorescence spectrum when excited by UV (325 nm) laser [42]. However an interesting phenomenon occurred when the excitation wavelength was shifted to the visible spectrum. They found that these microstructures responded with a strong fluorescence not only when excited by UV light, but also by light at the visible part of the electromagnetic spectrum, such as 550nm. Irradiating doped samples with different light wavelengths resulted in a change of the characteristic fluorescence of the microstructure. Fluorescence microscopy images in figure 7 illustrate these results.

In figure 7 the same set of microcubes were excited by light in three wavelengths: 550 nm, 475 nm and 360 nm. As a response to this change in excitation wavelength, in each case the sample emitted with a different color. The blue fluorescence was due to emission from gold nanoparticles themselves.

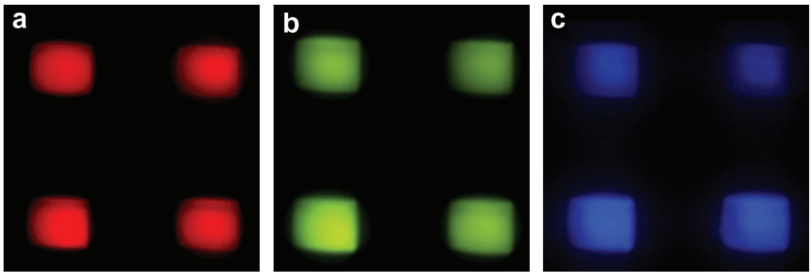

FIGURE 7
Fluorescence images of two-photon polymerized microstructures containing Au nanoparticles, for excitation at (a) 550 nm, (b) 475 nm and (c) 360 nm. Reprinted with permission from (Almeida et al., 2013). Copyright (2014) Elsevier, Copyright Clearance Center.

The green and red emission might be a result of a local field enhancement effect, which increases the fluorescence of the host matrix, since the excitation wavelengths used in these two cases are closer to the typical plasmon resonance of gold nanoparticles (centered at 540 nm). The red, green and blue fluorescence shown in figure 7 revealed that a single microstructure doped with gold nanoparticles could emit in a RGB pattern. These results amount to a demonstration that this approach is promising for applications requiring good emission intensity, such as colored micro displays and other light emitting microdevices.

Early in 2014 another inorganic material was used to produce functional polymeric microstructures. ZnO is a widely known optoelectronic material due to its fluorescent properties [43-44] and wide bandgap (~ 3.3 eV). 2PP fabrication of polymeric structures with zinc oxide (ZnO) nanowires had already been employed [45] to produce fluorescent microstructures, aiming at optical and electronic devices. Fonseca et a [45] produced hybrid organic/inorganic nanocomposites by incorporating ZnO nanowires, in a proportion of 0.5 to 5 wt%, into an uncured resin before laser polymerization. The microstructures [45], when excited by a continuous He-Cd laser operating at 325 nm, showed strong luminescence with a peak centered at 570 nm, typical of ZnO.

Based on the methodology to fabricate multi-doped microstructures [29, 40], Otuka *et al.* [46] produced, as a proof of principle, microstructures which can work like optical micro-cavities. These structures were composed of two concentric cylindrical shells, the inner one doped with Rhodamine B and the outer one constituted only of undoped polymer. To fabricate such kind of structure, they carried out two steps [46]: first, the doped part of the microstructure was fabricated using the doped resin and subsequently, after washing the unpolymerized resin, they produced the second part of the structure, using the undoped resin. Such microstructure was excited using an LED cen-

tered at 450 nm. Although a small scattering was observed in the undoped region, most of the emitted light was confined to the inner cylinder (doped). Therefore, these fabricated microstructures were able to provide light confinement in a given region, which could be used for fabricating optical microcavities.

2.4 Methods to improve 2PP microfabrication

The studies presented so far demonstrate that MPL is promising to engineer novel materials for diverse technological applications. As it happens for all micro- and nanofabrication methods, there is a desire to further improve fabrication resolution, which implies in overcoming the diffraction limit. Alternative methods to achieve very high resolutions have been developed. For instance, in 2009 Linjie Li and co-workers [47] proposed a new way to fabricate microstructures with high resolution. This technique, called Resolution Augmentation Through Photo-Induced Deactivation (RAPID) lithography, allowed them to achieve a resolution around one twentieth of the wavelength used. The basic idea used for RAPID lithography was associated with the stimulated emission depletion (STED) fluorescence microscopy [48-49]. In STED, fluorescent molecules are excited using a short laser pulse. A second laser pulse, tuned to a considerably longer wavelength than the first one, de-excited the molecules through stimulated emission. The de-excited region size depends on the intensity of the depletion beam and the fluorescence is localized in a zone smaller than the excitation wavelength. In RAPID lithography [50], a pulsed laser beam is used to initiate polymerization. A second CW laser beam is used to deactivate the photoinitiator, inhibiting the polymerization process. By spatially shaping the phase of the deactivation beam, features far smaller than the excitation wavelength can be fabricated.

Besides higher resolutions, another key aspect is the fabrication of microstructures at a large production scale. For instance, to apply MPL at an industrial level it is necessary to optimize production time. In 2006, Formanek et al. [51] demonstrated a new methodology to fabricate metallic micro/nanostructures in large scale. They used a commercially available resin (Z7012C, JSR) mixed with styrene (C6H5C2H3) in a 1:1 volume ratio properly modified for such applications. The authors combined 2PP with a microlens array to fabricate several structures simultaneously. The processing efficiency of their technique was demonstrated with fabrication of large samples composed by more than 700 objects written in parallel. At the focal region, 2PP occurs for each individual spot, similarly for a single-beam polymerization.

To produce multiple focus spots for parallel fabrication, they used a 50×50 microlens array [52] covering a total area of 15×15 mm^2. The lenses were 300 μm in diameter and are arranged in a square lattice with a lattice constant of 300 μm. To optimize the fabricated area and to ensure that all lenses would receive the same amount of energy, they expanded the laser beam and only used the central region of the beam to promote the microfab-

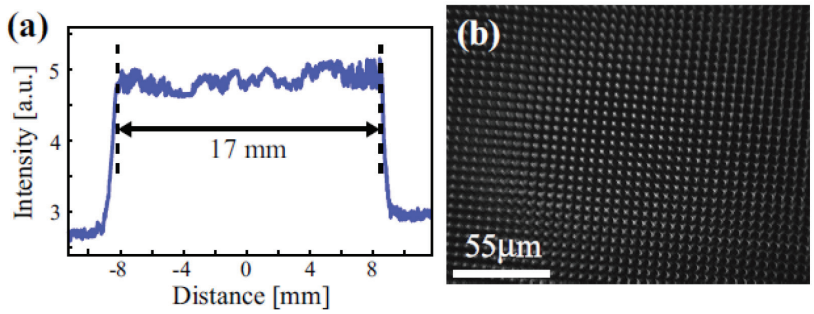

FIGURE 8
(a) Intensity profile of expanded beam measured before the microlens array along the horizontal direction. (b) Optical image of the fluorescence emitted from a PMMA film mixed with coumarin 314 dyes, due to the excitation by the multiple spots after the microlens array. Reprinted with permission from (Formanek et al., 2006). Copyright (2014) The Optical Society (OSA).

rication. Figure 8 (a) shows a profile of the beam intensity (in arbitrary units) recorded along the horizontal direction. In that case, the laser beam had a flat top profile, instead of a Gaussian profile, which is desirable for parallel fabrication.

A major problem in the parallel fabrication is alignment. A small misalignment of the sample can result in microstructures not adhered to the substrate. Figure 8 (b) shows an optical image of the fluorescence pattern recorded with a CCD camera after alignment optimization. Although observing a large number of spots, only part of them is used for the parallel fabrication, due to imperfect focalization.

3. FINAL REMARKS

MPL is a powerful technique for the production of complex functional microdevices, aiming at applications in optical and photonics, such as photonic crystals, micro-waveguides, microlenses, micropixels, etc. Here we presented a survey on results from several research groups around the world, which employed two-photon polymerization to produce micro-optical components and doped microdevices, displaying resolution well beyond the one limited by diffraction. In addition, the relative low cost and ease of operation for two-photon polymerization, combined with the possibility for large-scale parallel fabrication and high resolution, allows for the exploration of new technologies into the micro and nanofabrication world.

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