Three-dimensional micronanofabrication via two-photon-excited photoisomerization

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In this letter, laser micronanofabrication via two-photon absorption initiated isomerization was proposed and explored. Experimentally a *cis*-form rich poly[2,5-dihexyloxy-1,4-phenylene] vinylene)-alt-(2,5-diphenyl-1,4-phenylene vinylene)] (DPO-PPV) was used as the precursory material, which underwent pinpoint molecular conformational change upon the near-infrared femtosecond laser irradiation. Due to pronouncedly reduced solubility of trans-configuration molecules, the precipitate at the tiny volumes was implemented as voxels to construct two- and three-dimensional micronanostructures. This mechanism may provide an alternative enabling tool other than two-photon absorption initiated polymerization of resins for designable micronanofabrication of photonic or optoelectronic devices including organic electroluminescent devices, particularly those based on PPV and its derivatives. © 2009 American Institute of Physics.
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Two-photon excitation-induced polymerization (TPP) of resins has been proved a powerful technology for fabrication of micronanodevices of complicated three-dimensional (3D) geometry.[1,2] Compared with other approaches[3] such as chemical self-assembling, nanowriting by various tips (e.g., near-field tips) or by focused electron- or ion-beam, and Si:microelectromechanical systems, the merit of the two-photon method lies in the structural *designability* and *realizability* in 3D space with nanometer accuracy, as embodied by photonic crystals,[4] diffractive lenses,[5] microtweezers,[6] microrotators[7] and oscillators,[8] and microfluidic systems.[9] For device functionalization, active components such as nanoparticles or smart molecules have to be induced beforehand into resins to be used for fabrication by guest-host doping or by copolymerization. For example, Duan et al.[10] increased the refractive index of resin by 10% through in-site chemical synthesis of TiO_2 nanoparticles, Yamada et al.[11] produced electric conductive polypyrrole microstructures from a mixture of pyrrole, lithium tetrafluoroborate, methylviologen and $Ru(bpy)_3^{2+}$, Wang et al.[8] realized remote manipulation of a microoscillator by Fe_3O_4 magnetic nanoparticles incorporation. These works are important for function-designable, controllable, and tunable micronanodevices. However, the low loading concentration of the active ingredients restricts the magnitude of the devices response to external stimuli, leading to a large turning-on threshold and working power. In order to solve this problem, optically, electrically, or magnetically more sensitive dopants or monomers/oligomers are now being synthesized.[12] It is also essential to explore alternative strategies other than photopolymerization, which are expected, on one hand, to retain the 3D and high resolution merits arising from two-photon ab-

sorption, and on the other hand, are capable of introduction of high concentration of active ingredients as the basic building block of functional micronanodevices. We report in this communication femtosecond laser micronanofabrication based on two-photon-excitation induced isomerization (TPI) of poly(p-phenylene vinylene) (PPV) derivative, a class of widely used electroluminescent materials.[13,14] Because of the significantly reduced solubility of the *trans*-PPV, micronanostructures consisting of nearly 100% *trans*-PPV are realized by pinpoint laser exposing and depositing *cis*-PPV-riched precursory.

Shown in Fig. 1(a) is the molecular structures of the *cis* and *trans* poly[2,5-dihexyloxy-1,4-phenylene]vinylene)-alt-(2,5-diphenyl-1,4-phenylene vinylene)] (DPO-PPV) derivatives, which were synthesized by Witting reaction.[14] The content of *cis*-olefins of the as synthesized DPO-PPV may reach as high as 87%, and fall to less than 0.05% after fully exposed by UV-visible light, for instance, under a 150 W mercury lamp for 10 min. With the proceeding of the exposure, the color of the solution pronouncedly alters from the original green to yellow, and loosen floccus deposition appeared. In the meantime, the absorption peaks of the solution gradually shifted from 390 to 436 nm [Fig. 1(b)]. The above phenomena are naturally interpreted by the occurrence of photoisomerization of DPO-PPV: each molecule of the *cis*-olefin absorbed a UV-visible photon, undergoing the molecular configuration change from *cis*-form to *trans*-form with rotational motions of the double bonds. The *cis*-form is readily soluble in common organic solvents such as chloroform, tetrahydrofuran, and even cyclohexane because of the twisting configuration of the *cis*-vinylene segments, while solubility of *trans*-form become worse due to the stronger intermolecular attractions arising from the more-coplanar molecule conformation. The difference of solubility between the *cis* and *trans* forms indicates the feasibility of micro-

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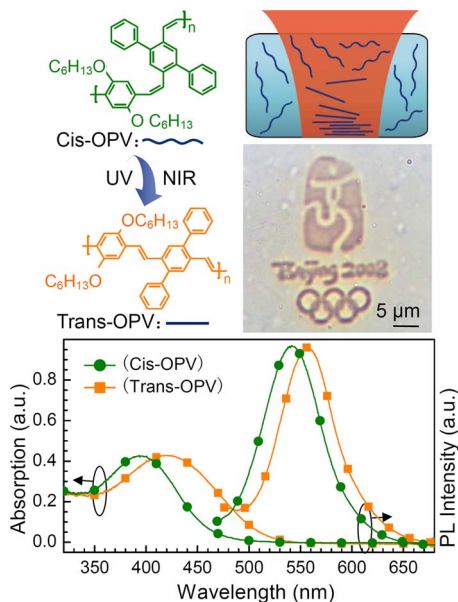
FIG. 1. (Color online) (a) The molecular configuration conversion of DPO-PPV from *cis*-form twisting structure to *trans*-form rigid coplanar structure under UV or near IR light. (b) The absorption and photoluminescence spectra of *cis*-form rich and *trans*-form DPO-PPV. (c) The scheme for isomerization from *cis*-DPO-PPV to *trans*-DPO-PPV, and appearance of *trans*-DPO-PPV deposition in solution upon the femtosecond near-infrared laser irradiation. (d) The pattern of *trans*-DPO-PPV induced by TPI.
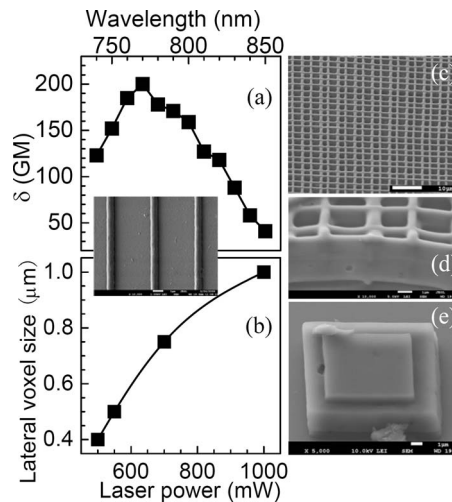

FIG. 2. (a) Two-photon absorption crosssections vs wavelength of *cis*-DPO-PPV rich (87%) DPO-PPV chloroform solution. (b) Lateral voxel size vs laser power in DPO-PPV film under 800-nm femtosecond laser. Insert: The SEM image of lines with the smallest lateral resolution under 500 mW laser power. (c) The upper and (d) tilt SEM images of a logpile photonic crystal. (e) SEM image of a two-stage platform of *trans*-DPO-PPV induced by TPI.

nanofabrication by pinpoint induction of the *cis-trans* isomerization [Fig. 1(c)], a mechanism different from photopolymerization of resins. Depending the laser pulse energy utilized for fabrication, the content of trans form molecules may range from 95% to nearly 100%, sufficiently preventing structures from being deformed in the course of rinsing.

The above idea was experimentally confirmed by irradiating the solution of the *cis*-form DPO-PPV with the second harmonic of 800 nm wavelength, 80 MHz repetition rate, 100 fs pulsewidth laser beam focused by a high numerical aperture (NA ∼ 1.35) objective lens. Scanning of the laser focus relative to the sample in the horizontal plane was realized by steering a Galvano mirror set, while in the vertical direction by a piezo stage with motion accuracy better than 1 nm. A computer programmed pattern was readily created following the scanning locus. Compared with single-photon irradiation, i.e., by 400 nm wavelength light for the current materials, even more interesting is two-photon irradiation induced isomerization for potentially higher spatial resolution and easier actualization of 3D structures. Notice that the linear absorption of the DPO-PPV at red to the near infrared wavelength is negligible, if the two-photon absorption cross-sections (δ_M) of the molecules are sufficiently large, their configuration transition from *cis* to *trans* would be possible by simultaneous absorption of two infrared photons by a molecule. Two-photon absorption cross-section was measured with two-photon-induced fluorescence approach[15] on 87%-*cis*-contained DPO-PPV solution diluted in chloroform [Fig. 2(a)], giving rise to the maximum of $\delta_M = 200$ GM (1 GM$=10^{-50}$ cm^4 s/photon) at $\lambda = 770$ nm, and $\delta_M = 158$ GM at $\lambda = 800$ nm, as is of the same order as the high efficiency two photon initiators.[16] Therefore, 800 nm laser pulses may effectively deposit *trans*-form molecules from chloroform solution by TPI [Fig. 1(d)]. Shown in Fig. 2(b) is the laser power-dependent lateral size of voxels, measured

by the ascending scan method.[2] Lines are used instead of single voxels for the convenience of imaging by scanning electron microscope (SEM). The smallest lateral resolution achieved under 500 mW is 400 nm [Fig. 2(b) and its inset], which is slightly better than those achieved with single-photon, around 620 nm (not shown). Decrease of the laser power leads to weaker adhesion to substrate of loosen structures that are not robust enough to resist developing.

Although thin patterns were easy to realize [Fig. 1(d)], TPI of DPO-PPV solution suffers from flow of particles early precipitated into the dilute solution so as that thicker or 3D structures are difficult to produce even if the writing has been managed to start from a glass substrate. In order to solve the problem, we prepare pure DPO-PPV films by multiple cycles of dip coating. In each sequence, the film was kept until complete removal of the chloroform solvent before the next layer is added. The film thickness from one dip-coating is 300 nm in average, meaning that a 3 μm thick film needs ten times dip. By this means, the laser writing may be carried out stably across an entire thick films without external disturbance like floating. TPI did be found to occur in such a thick solid matrix, and laser scanned 3D skeletons survive solvent rinsing, while the unexposed portion was removed. The adhesion of the deposited structures was found greatly improved compared with the case of fabrication in liquid solution. Well-defined structures have been thus achieved, for example, a logpile photonic crystal [Figs. 2(c) and 2(d)] and a two-stage platform [Fig. 2(e)]. The high quality of the fabrication as manifested by the smooth surfaces and the sharp edges of the platform allows for engineering microoptical components with demanded parameters, for example, a Fresnel zone plate (Fig. 3). For a properly operating zone plate, three parameters, the diameter of each ring zones, the refractive index of the lens materials, here the *trans* form DPO-PPV, and the thickness of the plate have to be carefully studied and chosen. The zone plate in Fig. 3 consists concentrically of eight odd zones and seven even zones with the outer radius of the *m*th zone, R_m, determined[5] by $R_m^2 + f^2 = (f + m\lambda/2)^2$, and $R_m = \sqrt{m\lambda f + (m\lambda/2)^2}$, where λ is the
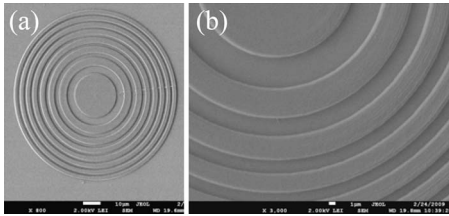
FIG. 3. Fresnel zone plate of DPO-PPV fabricated by TPI. (a) Top-view SEM image and (b), its locally magnified view.

wavelength of light in vacuum and $f=R_1^2/\lambda=294$ μm is the primary focal length for $R_1=12.5$ μm, $\lambda=532$ nm. The refractive index of the *trans* form film was found significantly reduced from 1.722 to 1.687 at $\lambda=532$ nm.[15] The large refractive index reduces the thickness of the step needed to reverse the phase of incident light for a high quality focusing [Fig. 4(a)] and imaging [Fig. 4(d)].

PPV and its derivatives have been widely utilized in polymer electroluminescence devices[13,17] because of their high fluorescence quantum yield, good processability and thermal stability. Accompanied with the molecular configuration change from *cis* to *trans*, the emission peak red shifted from 541 to 557 nm [Fig. 1(b)], and the fluorescent quantum yield jumped from 25% to more than 40%, possibly as result of avoidance of rotational motions of double bands from *cis*-form to *trans*-form competing with the luminescence pro-
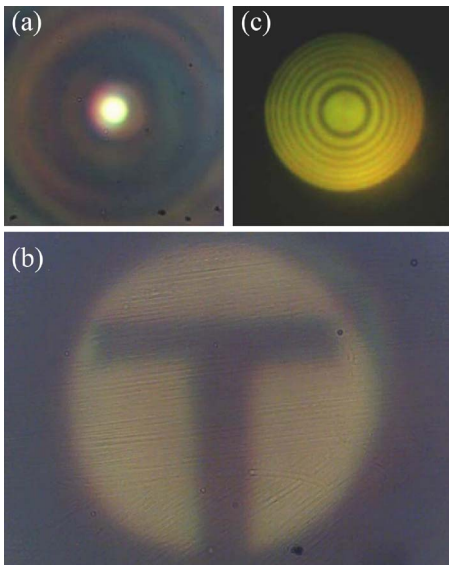

FIG. 4. (Color online) (a) Focusing characteristics of the Fresnel zone plate produced by TPI of DPO-PPV, (b) the same plate under illumination by a Xenon lamp, which exhibits true color of *trans* DPO-PPV, and (c) a letter "T" imaged by the DPO-PPV Fresnel plate.

cess because of near 100% *trans*-form DPO-PPV in the latter case.[15] This implies the possibility of writing pixels that emit different colors by pinpoint addressing TPI by controlled degrees. It is therefore interesting to know whether the fluorescent performance in devices created by the relatively strong femtosecond laser irradiation has been preserved. Judging from yellow fluorescent image of the Fresnel zone plate, it could be preliminarily concluded that the fluorescence characteristics remain in the TPI-created micronanostructures.

In summary, we propose and confirm the concept of TPI-based micronanofabrication. In contrast to the widely used TPP approach, the two-photon isomerization technology features elimination of loading functional components into any matrix, and therefore structures consisting of nearly 100% targeted ingredient, here the *trans* form DPO-PPV, is readily produced. For the particular case of PPV and its derivatives, the high quality fabrication as reflected by a micro-Fresnel phase plate, is strongly indicating an alternative enabling method of microelectroluminescent devices with different structures and functions.

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