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Localized polymerization using single photon photoinitiators in two-photon process for fabricating subwavelength structures

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ABSTRACT

Localized polymerization in subwavelength volumes using two photon dyes has now become a well-established method for fabrication of nano structures. Unfortunately, the two photon absorption dyes used in such process are not only expensive but also proprietary. Lucirin TPO-L is an inexpensive, easily available single photon photoinitiator and has been used extensively for single photon absorption of *UV* light for polymerization. These polymerization volumes however are not localized and extend to micron size resolution having limited applications. We have exploited high quantum yield of radicals of Lucirin TPO-L for absorption of two photons to achieve localized polymerization in subwavelength volumes, much below the diffraction limit. Critical concentration (10 wt%) of Lucirin TPO-L in acrylate (Sartomer) was found optimal to achieve subwavelength localized polymerization and has been demonstrated by fabricating 2D/3D complex nanostructures and functional devices such as variable polymeric gratings using two photon processes. Systematic studies on influence of Lucirin TPO-L concentration on two photon polymerization of Sartomer show that resolution of the fabricated structures critically depends on loading of Lucirin TPO-L. This is expected to unleash the true potential of two photon polymerization for fabrication of complex polymeric nano devices at a larger scale.

1. Introduction

The developments in the field of polymers for over a century has enabled their applications ranging from high tech devices to simple polyethylene carry bags used by a common man. Polymerization involves reaction of monomeric units to form large networks, involving external stimulants such as catalyst, plasma, photons and the like. Photo-polymerization is one such technique for synthesizing polymers and in general is a chain growth polymerization. In this process polymerization is initiated by absorption of photons either directly by the reactant monomer or by energy transfer through absorption of energy by a photosensitizer. Two photon polymerization (TPP) involves absorption of two photons simultaneously through a virtual state for excitation of a molecule. It has emerged as an extremely powerful tool of triggering chemical and physical processes with high spatial resolution for fabrication of 2D/3D nanostructures via a single step, which is scalable, comparatively inexpensive and a vacuum less approach [1–7]. The quadratic dependence of the two photon process confines the absorption of photons at the focal point within a volume of the order λ^3enabling sub-wavelength structures to be fabricated. This process has been of particular interest to fabricate complex micro/nano-structures for optical circuitry, optical data storage, biology and micro-fabrication technologies and photonic crystals [4,8–11].

An essential requirement for a material to be used as a two photon photoinitiator is its optical transparency to wavelength of ultra-short pulse laser, which typically lies in the region between 600 and 800 nm. This ensures minimization of linear absorption by the photointiator/chromophore which may occur during TPP. The two photon absorption (TPA) cross section is generally used as a metric for comparison of two photon absorption activities of different dye/photoinitiators [12]. Typically two photon absorption dyes are used for this purpose. A highly sensitive and efficient dye can lead to very low threshold and short exposure time, which would lower the volume where radicals are initially generated and decrease the amount of radicals formed and diffusion of the same

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[13]. Various strategies used to design a good TPP initiator include a chromophore group with a large δ_{TPA}, such as a D-π-D structure, chemical functionality that has a high efficiency of initiation and mechanisms by which excitation of the chromophore leads to activation of an electron-transfer process [14]. Efforts have been made to synthesize several linear and cyclic benylidene ketone based TPP initiators containing double bonds and dialkylamino groups in a single step using aldol condensation reactions. Quantum chemical calculations and experimental tests conducted to determine the structural – activity relationships proved that the size of the central ring of the TPP initiators significantly impacted the TPP initiation efficiency [15]. The lateral spatial resolution (LSR) in two-photon induced polymerization was improved to 80 nm by using an anthracene derivative 9,10-bis-pentyloxy-2,7-bis2-4-dimethylamino-phenyl-vinylanthracene BPDPA as a highly sensitive and efficient photo-initiator. Though a lot of molecules with very high TPA cross sections have been developed, their toxicity and commercial unavailability limits the applicability [16].

A class of commercially available radical, single photon photoinitiators such as Irgacure 369, Lucirin TPO-L and WLPI have been explored for TPP process [17–20]. These have however resulted in increased line-widths as their two photon absorption coefficient is small (~1 GM) in the IR region (800 nm-1000 nm) compared to IR absorbing dyes (10^3–10^5GM) [13]. In spite of this drawback Lucirin TPO-L an acylphosphine oxide radical photoinitiator is best in this class due to several advantages for two photon induced polymerization. Unlike most radical photoinitiators Lucirin TPO-L is a solid with good solubility and can be mixed with most resins. Although the two photon absorption cross section is small (<1.2 GM), it has been shown that structures with excellent integrity and definition can be fabricated at relatively low laser powers due to the high radical quantum yield of 0.99. This high polymerization efficiency enables for excellent initiation in two photon lithography over broad spectral ranges [21]. The use of Lucirin TPO-L as photoinitiator for TPP by Baldacchini et al. in their Sartomer resin formulation at very low concentrations of (3% weight) gave polymerized features with smallest dimensions of 5 μm[22]. A few more groups have used such formulations for fabrication of polymeric micro-cantilevers, optically active microstructures, gold doped structures and 3D cell migration studies obtaining feature sizes in the order of few microns [23–26]. Very recently branched hollow fiber structures were fabricated with predefined circular pores using Ormocer which is an organic – inorganic hybrid material preloaded with Lucirin TPO-L. Well defined micro structureswere obtained by using average laser power of 105 mW and writing speed of 5 mm/s [27]. However, most of these processes resulted in larger linewidths and were inappropriate for controlled polymerization in smaller focal volume to fabricate finer sub wavelength structures.

In this manuscript we exploit the high quantum yield of radicals of single photon photoinitiator (Lucirin TPO-L) for use as an alternative to two photon dye for fabrication of 2D and 3D structures with sub-wavelength resolution by using a critical loading of such inexpensive single photon photoinitiators. The high quantum yield of the radicals on exposure of Lucirin TPO-L to IR radiation facilitates initiation of the polymerization reactions and makes up for the large two photon absorption coefficient of inefficient two photon dyes. We have further systematically studied the effect of loading concentrations of Lucirin TPO-L on the spatial resolution of the fabricated structures and laser power required for lithography. The structures written were extensively characterized using scanning electron microscopy in order to determine the linewidths. The optimized parameters were used to successfully write complex 2D &3D sturdy structures with sub-wavelength resolution.

Schematic of free radical chain polymerization reaction is shown in Fig. 1, wherein the photoinitiator absorbs incident photons and generates active radicals by chemical decomposition. This usually happens in the triplet state and follows the Norrish type I mechanism. Lucirin TPO-L undergoes bond cleavage and results in the formation of two radicals capable of initiating the polymerization reaction. However, due to the high reactivity of the phosphorous based radical, it is anticipated that larger concentration of polymer contained ethyl phenyl phosphinate at the end of the chain. The radicals generated combine with the monomeric units creating reactive centers. The chain polymerization reaction propagates as the reactive centers further combine with other monomeric units, resulting in increase in molecular weight of the polymer until the

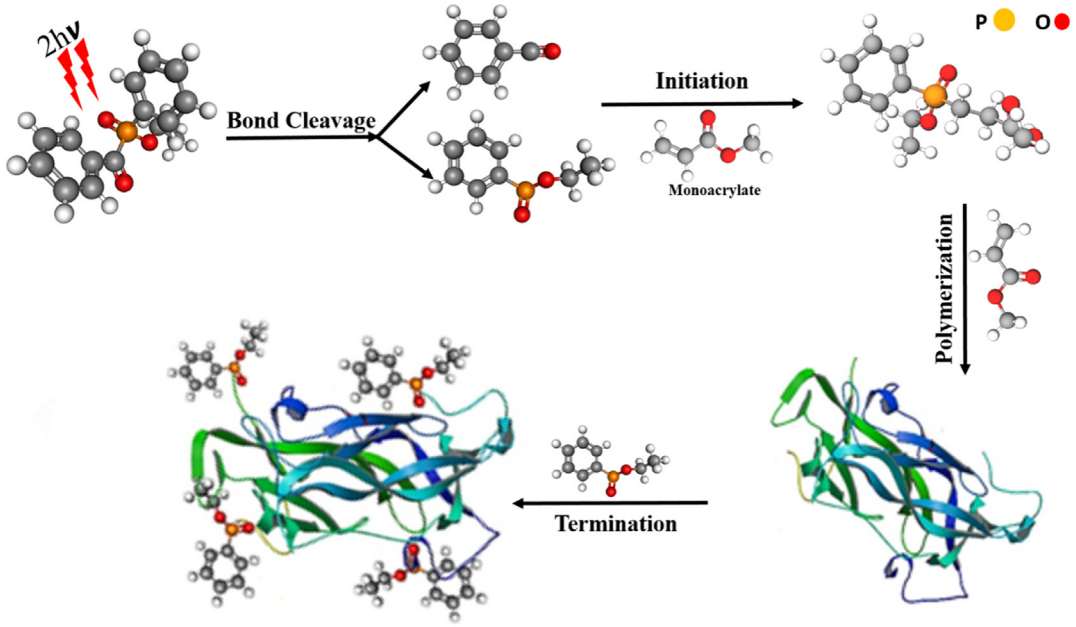

Fig. 1. Schematic of the free radical chain polymerization reaction [28].