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Near-IR Two-Photon Photoinitiated Polymerization Using a Fluorone/Amine Initiating System

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Emerging device technologies such as microelectromechanical systems and integrated sensors are placing increased demands on the development of materials processing and fabrication techniques.[1,2] In response, the characteristic three-dimensional (3-D) spatial resolution of the simultaneous two-photon absorption (2PA) process is being harnessed for 3-D photoinitiated polymerization and microlithography. This is facilitated by the unique properties associated with simultaneous absorption of two-photons relative to single-photon mediated processes. There have been a limited number of reports of two-photon photopolymerization of commercial acrylate monomer systems, pre-formulated with UV photoinitiators.[3−6] Efficient two-photon absorbing compounds based on phenylethenyl constructs bearing electron-donating and/or electron-withdrawing moieties have been reported.[7] Among these are electron-rich derivatives that have been found to undergo a presumed two-photon induced electron transfer to acrylate monomers[8] or proposed fluorescence energy transfer to a photoinitiator,[9] initiating polymerization. The reportedly efficient two-photon photoinitiators, although more photosensitive than previously studied UV photoinitiators, are not commercially available and require rather involved syntheses. Thus, the practicality of their broader use is questionable. Herein, we report the near-IR two-photon induced polymerization of (meth)acrylate monomers using a commercially available photoinitiator system based on a visible light-absorbing dye.

Multiphoton absorption has been defined as simultaneous absorption of two or more photons via virtual states in a medium.[10] The process requires high peak power, which is available from pulsed lasers. A major feature that distinguishes single-photon absorption from two-photon absorption is the rate of energy (light) absorption as a function of incident intensity. In single or one-photon absorption, the rate of light absorption is directly proportional to the incident intensity ($\mathrm{d}w/\mathrm{d}t \ \alpha\ I$), while in 2PA, the rate of light absorption is proportional to the square of the incident intensity ($\mathrm{d}w/\mathrm{d}t \ \alpha\ I^2$).[10,11]

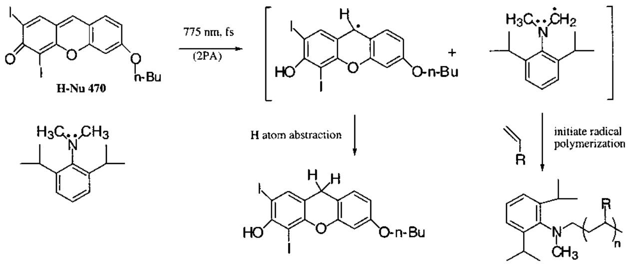

Figure 1. Direct two-photon photoinitiated polymerization at 775 nm using a fluorone 2PA photoinitiator adapted from the single-photon mechanism.[16]

The quadratic, or nonlinear, dependence of two-photon absorption as a function of light intensity has substantial implications. For example, in a medium containing one-photon absorbing chromophores, significant absorption occurs all along the path of a focused beam of suitable wavelength light, leading to out-of-focus absorption and associated processes. In a two-photon process, however, negligible absorption occurs except in the immediate vicinity of the focal point of a light beam of appropriate energy. This allows spatial resolution about the beam axis, as well as radially, and is the principle basis for two-photon fluorescence imaging.[12]

In 2PA, the final state reached has the same parity as the initial state, while in single-photon absorption the parity is opposite as given by dipole selection rules. However, in most solids and complicated molecules, the parity can become mixed in “bands”. In such molecules (such as the fluorone dye used in this report) two near-IR photons achieve essentially the same electronically excited singlet state as would be obtained via resonant single-photon absorption at or near $\lambda_{\max}$. These molecules are expected to display identical photochemical and photophysical behavior when excited by one or 2PA. If such species return to the ground state via emission, fluorescence results with the energy of emission greater than the energy of the individual photons involved in the 2PA excitation.

It is widely believed that a “revolution” in miniaturization, particularly in the field of microelectromechanical systems (MEMS), is underway. It is projected that the design and manufacturing technology that will be developed for MEMS may rival, or even surpass, the far-reaching impact of ICs on society and the world’s economy. At the forefront of techniques being explored for 3-D spatially resolved materials imaging and processing are methods based on 2PA. The use of longer wavelength light as the excitation source leads to deeper penetration depths than possible with conventional UV or visible excitation techniques. Since the absorption/excitation is confined to the focal volume in the 2PA process, there will be virtually no out-of-focus excitation/reaction, facilitating 3-D spatial control of the process.

We conducted two-photon initiated polymerization at 775 nm via direct excitation of a commercially available dye (5,7-diiodo-3-butoxy-6-fluorone, H-Nu 470) in the presence of an arylamine,

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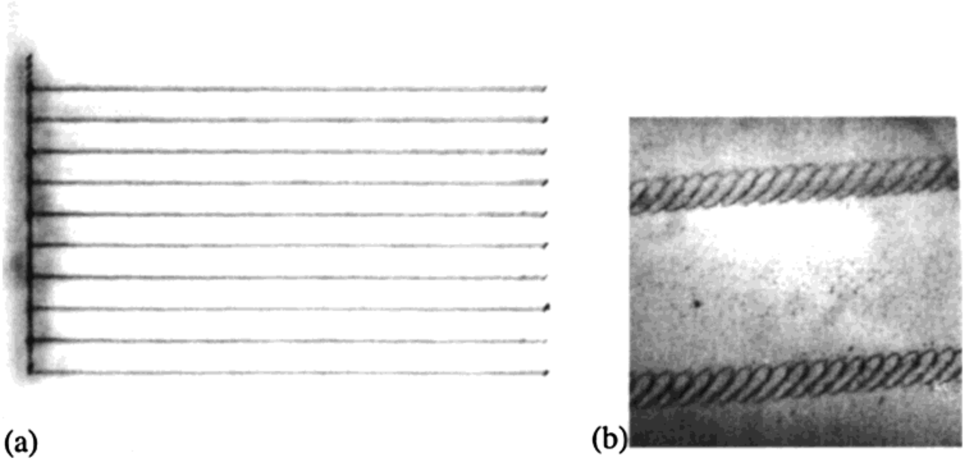

Figure 2. Micrograph of polymerized microstructure (a) 9 μm line width and 50 μm line spacing and (b) higher magnification (a uniform submicrostructure is clearly evident).

and (meth)acrylate monomer,[13] resulting in an electron-transfer free radical initiation process. The excitation wavelength was well beyond the linear absorption spectrum for 5,7-diiodo-3-butoxy-6-fluorone (strong and weak absorption maxima at 330 and 470 nm, respectively). A laser system (CPA-2000 from Clark-MXR with an Er-doped fiber ring oscillator seeding a Ti:sapphire regeneration amplifier, TSRA) was used to generate 775 nm light with 150 fs pulse width at a repetition rate of 200 Hz, and ~3 mW average power (~15 μJ/pulse).[14] The beam width was approximately 10 μm. A computer-controlled motorized *X,Y* step scanner was employed with a scan rate of 1 mm/s. Monomer/initiator films[15] were exposed to the near-IR laser via a variety of scan patterns. Exposed films were scanned and imaged using an Olympus optical light microscope in reflection mode.

According to the mechanism deduced from single-photon photochemical studies of the initiating system (Figure 1),[16] electron transfer from the aromatic amine (*N*,*N*-dimethyl-2,6-diisopropylaniline) to the fluorone derivative, followed by proton transfer from the amine to the fluorone, resulted in formation of an arylamine bearing a free radical localized on the α-methylene carbon. This free radical species then initiated polymerization of (meth)acrylate derivatives. A diaryliodonium salt can be added to accelerate the rate of polymerization but was not necessary in the current work.[16]

A number of control experiments were performed to support a two-photon based excitation process. First, experiments were performed using a Ti:sapphire laser[14] in continuous wave (CW) vs mode-locked (80 fs pulse width). No polymerization was observed in CW mode, while polymerization occurred only when the laser was mode-locked, supporting two-photon absorption since the probability of two-photon absorption is inversely proportional to pulse width. Next, experiments were performed on monomer alone (no initiator). In all cases, with both laser systems, no polymerization was observed upon exposure to near-IR fs radiation. The fluorone/amine co-initiator system worked effectively with both laser systems, in the absence of any iodonium salts. A control experiment was performed with only the monomer and iodonium salt (no other co-initiators). No polymerization occurred upon exposure of this mixture to near-IR fs light. Control experiments were also performed with the fluorone/monomer and the amine/monomer. Likewise, no polymerization was observed for monomer systems in which only individual initiator components were present. Furthermore, an initiator system comprised of isopropylthioxanthone (ITX) and *N*,*N*-dimethyl-2,6-diisopropylaniline (DIDMA) also afforded polymer in the presence of an acrylate monomer under near-IR fs irradiation, attesting to the generality of the electron-transfer polymerization discussed above. Similarly, no polymer was produced when the ITX/DIDMA/acrylate mixture was exposed to the same wavelength in CW mode.

The formation of polymeric microstructures with a variety of dimensions was accomplished. In simple line scans, line widths were reproducibly produced with uniform line widths ranging from 7 to 15 μm, spaced 20−50 μm apart. Microstructures were readily examined by optical reflection microscopy. Figure 2 depicts the microstructure formed in which the line width is 9 μm with relatively uniform 50 μm line spacing. Figure 2b shows the photograph of the same microstructure at higher magnification. Clearly evident in Figure 2b is a relatively uniform nanostructure due largely to the repetition rate and beam profile.

In conclusion, we have demonstrated controlled two-photon induced photopolymerization, employing both commercial monomers and initiator system. Although the efficiency of initiation was not determined quantitatively, qualitatively it was observed that polymerization occurred rapidly, even at higher scan rates and lower power. This paves the way for three-dimensional microfabrication and lithography using readily available materials. Studies are currently under way to characterize the two-photon absorption spectrum and cross section for the fluorone and similar photoinitiators. Additional investigations in our laboratory are focused on control of the nanostructure and extend the polymerization further in three-dimensions in an effort to create a variety of functional microstructures.

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(13) The fluorone dye, 5,7-diiodo-3-butoxy-6-fluorone (H-NU 470) and *N*,*N*-dimethyl-2,6-diisopropylaniline were obtained from Spectra Group Limited, Inc. Acrylate and methacrylate monomers were obtained from Sartomer (ethoxylated bisphenol A dimethacrylate SR349) and Esschem (urethane dimethacrylate X 850, ethoxylated bisphenol A dimethacrylate X 970, bisGMA X 950). Thick films were cast on glass slides from neat mixtures, and thin films were obtained via spin coating from a dioxane solution.

(14) Experiments have also been conducted successfully with a mode-locked Ti:sapphire pumped with a 5 W Millennia laser (Spectra Physics), affording 780 nm light with a 80 fs pulse width, 0.3 W average power, and 88 MHz repetition rate. Polymerization does not occur when operating in continuous wave (cw), only when mode-locked (fs pulses).

(15) A typical monomer film was comprised of a diacrylate monomer (e.g., Sartomer SR 349), fluorone dye initiator (H-Nu 470), and *N*,*N*-dimethyl-2,6-diisopropylaniline in a 1:4.9 × 10^{-4}:4.9 × 10^{-3} ratio, respectively.

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