PHOTOPOLYMERIZATION

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Abstract

Photopolymerization is a process, where monomer molecules polymerize under exposure of light. It is one of the most important types of photochemical reactions that have been used for laser fabrication of microstructures. This is because the material used in the photopolymerization process undergoes a phase transition, from liquid to solid, and non-polymerized liquid is easily removed so that solidified 3D structures stand out. By using two-photon induced photopolymerization, it is possible to polymerize structures with sub-micron features, implying a more diverse use of the technology. This seminar will focus mostly on two-photon photopolymerization and will present its (potential) use in fields such as photonics, optoelectronics, biology and micromachines.
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Introduction

Photopolymerization or photoinitiated polymerization is a process of formation of crosslinked higher molecular weight materials (polymers) from monomer or oligomer molecules under exposure of laser light, usually of wavelengths in the ultraviolet spectrum. The reactive materials that are most commonly used are low molecular weight unsaturated acrylate or methacrylate monomers that can be made to crosslink with the use of a radical generating photoinitiator.

Photopolymerization is the basis for most of the commercial applications of photopolymer technology. In the last few decades we have seen rapid progress in high-performance ultraviolet photopolymerization systems, which have resulted in a growing number of industrial applications, including paints, optical adhesives, medical applications, coatings, graphic arts, microelectronics, optics, manufacturing, and so on. It is estimated that the world consumption of UV curable products in the year 2000 was around 200,000 tons [1], which corresponds to a two billion dollar market.

Besides the above mentioned applications, laser rapid prototyping, is a new and expanding technology. It converts complex-shaped three-dimensional objects from designs into real products. The material used for fabrication is polymerized and solidified at the spot exposed to UV laser, we talk about single-photon photopolymerization. Commercial laser rapid prototyping machines have a fabrication precision greater than 10 µm [1]. However, this accuracy can no longer fully satisfy the modern requirements for device multifunctionalization and miniaturization that demand sub-micron feature sizes. The emergence of a new technology, two-photon photopolymerization, has overcome these limits. As indicated by the name, the material is polymerized not by absorbing one UV photon, but by simultaneously absorbing two photons at longer wavelength, usually in the infrared spectrum. Besides the improved accuracy of about 100 nm [2], the process has other various advantages which will be discussed in the seminar. Two-photon polymerization enables manufacturing that is otherwise not accessible and brings new scientific possibilities to nano-research.
Theoretical background

In order to produce a lasting effect on a material, photons must first be absorbed. The energy and momentum are exchanged between the electro-magnetic field and molecules through absorption and emission. In such a process, the imaginary part of nonlinear susceptibility represents the energy transfer from the light field to a medium. The light-matter energy change per unit time and unit volume is:

\[ \frac{dW}{dt} = \langle \vec{E} \cdot \hat{P} \rangle, \]

where \( \vec{E} \) is the electric field vector and the brackets denote time average. The value of material polarization \( \hat{P} \) is:

\[ P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots, \]

where the quantities of \( \chi^{(1)} \), \( \chi^{(2)} \), \( \chi^{(3)} \) are second-, third-, and fourth-rank tensors, representing linear, second-order and third-order optical susceptibilities. Instead of one, the molecule can also absorb two photons simultaneously, although the probability for this process is significantly smaller. Two photon absorption (from now on referred to as TPA), is the absorption of two photons of identical or different frequencies in order to excite a molecule from one state (usually the ground state) to a higher energy electronic state. The energy difference between the involved lower and upper states of the molecule is equal to the sum of the energies of the two photons. Two-photon absorption is a second-order process several orders of magnitude weaker than linear absorption. It differs from linear absorption in that the strength of absorption depends on the square of the light intensity, thus it is a nonlinear optical process. For degenerate two-photon absorption, that is, the process of photons of identical energy being simultaneously absorbed, the energy absorption rate is given by:

\[ \frac{dW}{dt} = \frac{8 \pi^2 \omega}{c^2 n^2} I^2 \text{Im}\chi^{(3)}, \]

where \( \omega \) is a frequency corresponding to the photon’s energy, \( n \) is a refractive index of the material, \( c \) a speed of light, and \( I \) is the light intensity. It is seen that the TPA rate is proportional to the square of the light intensity, which is an important mechanism to improve the spatial resolution in two-photon fabrication. A high capability of materials to absorb photons through TPA is desired and that is described by TPA’s cross-section \( \delta \), defined by:

\[ \frac{dn_p}{dt} = \delta N I^2, \]
where $N$ and $n_p$ are the number density of absorbing molecules and number of absorbed photons, respectively, and $F = I / h \nu$ denotes flux of photons. The TPA cross-section is therefore:

$$\delta = \frac{8 \pi^2 h \nu^2}{c^2 n^2 N} \text{Im}[\chi^{(3)}]$$

Molecules with large TPA cross-section have a TPA cross-section larger than $100 \cdot 10^{-50} \text{ cm}^4 \text{s(photons)}^{-1}$, which is up to $10^{25}$ times less than the cross-section for one photon absorption [3].

**Photoinitiation and Photopolymerization**

As already mentioned in the introduction, photopolymerization refers to the process of using light as an energy source to induce the conversion of small unsaturated molecules in the liquid state to solid macromolecules through polymerization reactions. Although other radiations, including X-ray, $\gamma$-ray and even electron and ion beams can induce similar curing reactions, photopolymerization deals with those that are induced by light in the ultraviolet, visible spectral region. The basic components of the starting liquid material are monomers and oligomers. Let’s take a look at the basic scheme of a reaction:

$$M \rightarrow M_2 \rightarrow M_3 \ldots M_{n-1} \rightarrow M_n,$$

here $M$ is the monomer or oligomer unit, and $M_n$, the macromolecule containing $n$ monomer units. For practical photopolymer systems, more components are included, most importantly photoinitiators and photosensitizers. In order to increase the polymerization efficiency, one or several molecules that are more sensitive to light irradiation are added. They form initiating species of radicals or cations by absorbing photons. Such small molecules are called photoinitiators. The production of such molecules, a process called photoinitiation, is the most important step in photopolymerization. Let’s take a look at the example of radical photoinitiator, with the following initiation step:

$$I \rightarrow R^* \rightarrow R^* + M \rightarrow R^* M \rightarrow R^* M M \rightarrow \ldots \rightarrow R^* M_n$$

where symbols denote photoinitiator I, radical $R^*$ and $I^*$, an intermediate state of the photoinitiator after absorbing a photon. Therefore the polymerization process is more precisely described by the following equation:

$$R^* + M \rightarrow R^* M \rightarrow R^* M M \rightarrow \ldots \rightarrow R^* M_n$$

The photoproduced radicals react with monomers or oligomers, producing monomer radicals, which combine with new monomers, and so on; so the monomer radicals expand
in a chain reaction, until two radicals meet with each other. This chain propagation stops in either of the following channels:

\[ RM_n \cdot + RM_m \cdot \rightarrow RM_{m+n} R \text{ or} \]

\[ RM_n \cdot + RM_m \cdot \rightarrow RM_n + RM_m \]

Therefore the polymerization process consists of several steps: photoinitiation, chain propagation and termination. We can see from the above description that a good photoinitiator should be easily reduced to an initiating species upon light irradiation and provide photoproduced radicals or cations active enough to react with monomers or oligomers.

Besides photoinitiator, a molecule called photo-sensitizer is commonly involved in the process of polymerization. A photo-sensitizer is a molecule that absorbs light and then transfers the energy to a photoinitiator. With such a scheme, the photoinitiation process is expressed as:

\[ \text{hv} \]

\[ S \rightarrow S^* \rightarrow I^* \rightarrow R \cdot \]

where S is the photosensitizer. A coinitiator itself doesn’t absorb light, but it is involved in the production of radical species.

A common chemical used in the polymerization process is acrylate. Acrylate is activated by a photoiniciated radical which binds itself to the acrylate (Figure 1) and breaks the double bond. This enables another acrylate to bind to the structure and the chain reaction can propagate.

\[ \text{Figure 1: Photoinitiator binds itself to the monomer molecule (acrylate) [3].} \]
Two-Photon Absorption

Most resins that polymerize under UV exposure can undergo similar reactions when two photons are absorbed simultaneously. Electron excitations that need absorbance of two-photon energy can occur stepwise or simultaneously. The former relies on the existence of a real intermediate state, from which an excited population is further pumped to a higher energy level by absorbing photons of the same energy as the ground state. Simultaneous TPA is a quantum mechanical process, where an electron absorbs two photons simultaneously to transcend the energy gap in one excitation event. An intuitive physical scenario is, as light passes through a molecule, a virtual state is formed when the first photon is absorbed. It persists for a very short duration (of the order of several femtoseconds as prescribed by Heisenberg’s Uncertainty Principle), which contrasts with the long lifetime of the actual intermediate energy level in stepwise absorption. TPA can result if the second photon arrives before the decay of this virtual state. If the energy of the two photons are identical, the process is referred as degenerate TPA, otherwise, the process is a non-degenerate one. TPA was theoretically predicted in 1931 by a German physicist Maria Göppert-Mayer [1] who was later awarded a Nobel prize, making her the second female Nobel laureate in physics after Marie Curie. TPA was experimentally observed for the first time in 1961 [1].

TPA can be utilized for inducing photopolymerization. The difference between one-photon and two-photon induced photopolymerization lies in how the energy for activating initiators is provided. In the case of TPA photopolymerization, initiators are excited to triplet states by absorbing combined two-photon energy:

\[ I \rightarrow I^* \rightarrow R \cdot \]

or

\[ S \rightarrow S^* \rightarrow I^* \rightarrow R \cdot , \]

where \( v' = v/2 \) denotes photon frequency in the two-photon excitation beam. Frequencies of both absorbed photons are in most cases the same.
Setup

Laser rapid prototyping involves the formation of a 3D object additively, in a layer-by-layer way. Figure 1 shows a practical prototyping system. In fabrication, 3D patterns are extracted into a series of two-dimensional slices corresponding to profiles at different height levels. Starting from the first layer, the lateral dimension is controlled by scanning a laser beam over the surface of the polymer film to form a gelled layer of polymer with desired and fixed depth. After the formation of the first layer that is fixed to the substrate, a new thin layer of polymer is added by casting, by immersing the platform, or by releasing the liquid surface and then solidifying. This process is continued in an additive modeling fashion until the desired object is formed.

![Setup of a laser rapid prototyping system. Writing is accomplished by mirror angle scanning [3].](image)
In the above system, patterning in the two horizontal dimensions is realized from a series of slices, and the longitudinal spatial resolution is controlled by the thickness of newly-added resin film. There are two disadvantages that prevent applying the mechanism for micro-nanosize fabrication. First, it would be difficult to form film of thickness 1 µm or less due to the viscosity and surface tension of the resin, and second the layer-by-layer scanning method sometimes restricts the achievable geometry.

To solve this problem, a two-photon laser rapid prototyping technology was proposed, now known as two-photon photopolymerization. In this scheme the laser was directly focused inside a liquid resin droplet and it polymerized the focal point volume by TPA. This technology firstly eliminates the requirement of thin additive liquid film and controls the longitudinal spatial resolution by focal spot size itself, and secondly, it provides the capability of writing arbitrary 3D patterns within the droplet volume, as can be done in 3D laser writing in solid matrix only if the resin viscosity is reasonably high. From this sense, the laser focus functions as a real 3D laser pen.

**Spatial resolution**

Laser energy distribution directly determines the spatial resolution of fabrication. After spatial filtering and beam expanding, only the central portion of the laser beam is induced into an objective lens. The focal spot size is estimated using the Rayleigh criteria, \( Z_R = (n \pi \omega_0^2 / \lambda) \) along the optical axis, where \( n \) is the refractive index of the medium into which the laser is focused, \( \lambda \) is the vacuum wavelength, and \( \omega_0 = 1.22 \lambda / (n NA) \) is the lateral diffraction limit, if NA is numerical aperture of the objective. It is clear that the objective lens strongly redistributes the beam energy, and the laser intensity distribution at the focal region sensitively depends on numerical aperture. Intensity that triggers TPA is in the order of TW/cm^2, whereas in the single-photon photopolymerization, continuous laser beam is used with intensity in the order of W/cm^2.

A theoretical simulation shows intensity spread using different numerical apertures. The incident power before the aperture, which has variable size, is assumed to be identical in each case. Using the FWHM as the criterion of resolution, NAs of 1.4, 1.2, 1.0 and 0.8 give rise to FWHMs of 252 nm, 269 nm, 304 nm and 343 nm respectively. It is seen from the Figure 3 that regardless of the absolute intensity level, low NA tends to give larger feature sizes. Therefore, for pursuing high-accuracy nanofabrication, a high-NA objective is preferable.
Figure 3: Theoretical intensity function of different numerical aperture focusing calculated using vectorial Debye method.[3]

Applications

Photonic crystals

Photonic crystals are microstructures with a periodical distribution of refractive indexes. They are the optical analogue of semiconductors, where a bandgap is open due to the electron wave modulation by periodic Coulombic potential. In a photonic crystals, the multiple interference among waves scattered from each primitive unit may lead to a frequency region, called a photonic bandgap, where light propagation in all directions is forbidden. Incident from outside, Photonic crystal is highly reflective at the bandgap wavelength and inside the structure. These features provide a novel scheme for high-efficiency optoelectronic devices such as waveguides with sharp bends and low-threshold lasers, for new nonlinear optical applications such as superprisms, and for the enhancement of nonlinear processes like harmonic generation.

The period of photonic crystals should match the wavelength of interest. For application in the visible and near-infrared communication wave range, the lattice constant is expected to be several hundreds of nanometers. This length scale is not large enough to use mechanical processing like hole drilling.

Two-photon photopolymerization has the intrinsic capability to produce 3D structures of arbitrary lattices, which opens the door to photonic crystal-based polymer optoelectronic devices.

Let’s take a look at an example of photonic crystal fabricated using two-photon polymerization technology. A commercially available resin, Nopcocure 800 (San Nopco) was used, consisting of a radical photoinitiator and acrylic acid ester [4]. The linear
absorption of the resin extends from the UV to around 370 nm. Due to a low TPA cross-section, $10^{-56} \text{cm}^4 \text{s} (\text{photon})^{-1}$ [4], the fabrication was conducted using regeneratively amplified laser pulses. A schematic illustration of the log-pile structure is shown in the Figure 4. It consists of parallel rod layers with a stacking sequence that repeats every fourth layer. Within each layer, the rods are arranged in a simple 2D array with rod spacing $a$. The array in the second neighboring layer is shifted by half the spacing $a$ relative to rods in the first plane in a direction perpendicular to the rods. Unpolymerized part of the liquid was poured away.

Figure 4: Illustration of a photonic crystal structure (a), and optical microscop (b) and SEM (c) image [4]
**Micromechanical Devices**

A variety of micromechanical devices that can be fabricated by the means of photopolymerization are used in experiments involving optical trapping. Let's briefly sum up the basic ideas of optical trapping before continuing with actual devices that take advantage of the mentioned phenomenon.

**Optical trapping**

The technique of optical manipulation has been employed as a unique means of controlling microdynamics of small objects without physical contact since the pioneering works by Arthur Ashkin [5]. For a better understanding of the actuating mechanism, we will briefly introduce where the laser trapping force originates. Assume that a transparent sphere with refractive index higher than its surrounding medium is situated slightly off a laser beam axis.

Most optical traps operate with a Gaussian beam profile intensity. In this case, if the particle is displaced from the center of the beam, as in in the Figure 5, the particle has a net force returning it to the center of the trap because more intense beams impart a larger momentum change towards the center of the trap than less intense beams, which impart a smaller momentum change away from the trap center. The net momentum change, or force, returns the particle to the trap center.

It turns out that whenever the refractive index of the particle is larger than that of the medium, the particle can be stably trapped. The force points always towards the beam focus and is proportional to the gradient of electric field. For small displacements, the force acting on the particle, is proportional to the displacement, which enables easy measurement of the forces.

*Figure 5: Schematic representation of the forces on a beam off (a) and on (b) the axis of the laser beam [5]*
Windmills rotate when facing wind, however a similar rotational phenomenon has been observed in laser-trapped particles. The rotational torque arises from the axial irradiation force as discussed above and from the asymmetrical or rotation-symmetrical shape of the particles. In a micromachine, it is important to design a device structure of helical shape and of proper rotation symmetry so that the structure could be fixed (trapped) at a suitable position and with the desired orientation, for high stability and for minimizing the friction between the rotating parts and its axle. The translation momentum from the light needs to be converted to the spinning momentum of the object. A number of microcomponents satisfying the above requirements have been produced by various microfabrication technologies. In the Figure 6 is a two-photon photopolymerized eight-fold rotary symmetrical rotor. In order to rotate the windmill, a laser beam with rotational asymmetry in intensity profile must be used, such as circular polarized beam or Laguarre beam. Light therefore exchanges angular momentum with the object, which makes the windmill to spin.
Nanospring

It is already a well-known principle in the aircraft manufacturing industry that real-size systems that are proportionally scaled up from designed models don’t work. This is because the surface area and mass (or volume) of an object do not proportionally increase with dimensions; they follow different laws. The same principle applies when the size of devices are scaled down to micro nanometer sizes. For example, if the feature size of a device is reduced from millimeters to nanometers, the surface-to-mass ratio increases by $10^6$ times. Therefore, in the nano realm, mass and inertia are no longer important, while physical, mechanical and electric characteristics such as stress and tension, thermal transfer, phase transition, fluid phenomena, and achievable field strength abide by rules much different from current experience and would dominate.

Two-photon photopolymerization has been recognized as an important method for producing micromechanical devices. It provides a good opportunity to explore nanodevice mechanics. A nanospring using this technology has been fabricated as shown in Figure 7. Note that the the term “nano” is exaggerated, since the smallest details are only 100 nm big. The spring has a spiral radius of $r_s = 150$ nm, a coil radius of $R_c = 1$ mm, and a pitch of $D = 2 \mu m$ [7]. According to these parameters, the spring constant, $k$, can be calculated according to the relation:

$$k = \frac{G_s r_s^4}{16N R_c^2},$$

where $G_s$ is the shear modulus of the solidified polymer, and $N = 4$ is the number of active coils. $G_s$ was determined from the elastic elongation of a fiber-like sample that was uniformly polymerized under UV exposure. The Young modul was measured to be 0.46 GPa, from here $G_s$ is determined by the formula $E = 2G_s (1 + \nu)$, where $\nu$ is the Poisson ratio. $K$ was calculated to be $4.8 \cdot 10^{-6} N/m$ [7].
In order to measure the spring constant, a microball was polymerized at the open end of the spring, and the other end was fixed to a photopolymerized anchor. Figure 8 shows the system, where the spring was positioned 10 mm above the glass substrate. In operation, the oscillator was kept in ethanol. When the laser focus was carefully adjusted, the bead was three-dimensionally trapped and able to be freely manipulated. The spring was pulled by moving the trapped bead, and then it was released by blocking the laser, initiating an oscillation. The spring was observed to be prolonged from its original length, and restored to its original state after the laser was turned off. Elongations of up to 7 µm over many cycles didn’t cause any elasticity failure, as evidenced by the fact that the spring always returned to its original length. From the bead movement, it is possible to determine the spring constant. The movement is an over-damped oscillation. The viscous friction plays an important role. Since the bead velocity is slow (v = 1.5 mm/s at maximum), it is reasonable to assume the viscous resistance, a non-conservative force that is always opposed to its direction of motion, is proportional to the speed, $F_{\text{vis}} = cv$. In this case the spring oscillation can be described by the following equation:

$$\frac{d^2x}{dt^2} + 2\mu \frac{dx}{dt} + \omega^2 x = 0,$$

where $\mu = c / 2m$ and $\omega = \sqrt{k / m}$ is the circular frequency of the natural vibration of the spring; m is the mass of the bead, and k is the spring constant. The viscous resistance exerted to the bead was assumed to be $F_{\text{vis}} = 6\pi \eta rv$, where $\eta$ is the liquid viscosity. Then by fitting the general solution with the experimental data, the spring constant was derived.
to be \( k = 1 \times 10^{-8} \text{Nm}^{-1} \). Here we see a two-order difference in the measured and calculated spring constants.

The cause of the difference can be in the fact that we ignored the mass of the spring and the viscous resistance between the spring and the liquid. This may be the major source of the negative deviation of two orders.

\[ (a) \text{ Anchor, Laser, Substrate, Objective lens} \]

\[ (b) \text{ Experiment setup (a), photograph of the experiment (b), different phases of oscillation (c), (d), (e), (f) [7]} \]

**Conclusion**

This seminar introduced the technique of photopolymerization, most notably a two-photon photopolymerization, which has opened a variety of possibilities in the filed of microfabrication and is to be further implemented in the fields such as electronic materials, printing materials, optical and electro-optical materials, the fabrication of devices and polymeric materials, adhesives and coating materials and so forth. The technique also allows investigation of properties of nano-sized objects.

In the recent experiments a spatial resolution of \( \lambda/20 \) was achieved [2], which promises further improvements in the technology using photopolymerization.
References


