
Originally published in the Australian Journal of Chemistry, 60(7), 484-495.

Available from:
http://dx.doi.org/10.1071/CH06484

Copyright © 2007 CSIRO.

This is the author's version of the work. It is posted here with the permission of the publisher for your personal use. No further distribution is permitted. If your library has a subscription to this journal, you may also be able to access the published version via the library catalogue.

Accessed from Swinburne Research Bank: http://hdl.handle.net/1959.3/39119
Two-Photon Polymerization for Three-Dimensional Photonic Devices in Polymers and Nanocomposites

Baohua Jia, Jiafang Li, Min Gu

Fabrication of micro- or nano-scale photonic devices in polymer materials to control and manipulate light propagation represents a hot topic nowadays. Compared with conventional semiconductor materials, polymers are easy to prepare and have the flexibility of incorporating active materials to realise various functionalities. As one of the most powerful tools in micro-optical fabrication, the two-photon polymerization technique has been widely employed recently to produce multifarious photonic devices, particularly the photonic crystals, which are promising candidates for integrated optical devices. In this article the recent advances in the fabrication of three-dimensional photonic devices such as diffractive optical elements, photonic crystals, and superprisms in polymer materials using the two-photon polymerization technique are reviewed. In particular, the fabrication of photonic crystals in nanocomposite polymers, which are formed by incorporating nanocrystal quantum dots into polymer materials, is demonstrated, providing an interesting physical platform for the investigation into new types of active micro-devices.

1. Introduction

Over the past few years a great deal of research effort has been focussed towards micro-fabrication using a femtosecond laser, aiming to miniaturize optical systems and achieve high resolution, speed, and portability.[1–11] As a kind of versatile material, polymers have been widely employed in optoelectronic and photonic devices due to the simplicity in structure design and processing and the capability of incorporating novel materials. For example, nano-particles or non-linear materials can be doped into a liquid-phase resin to realize various functionalities.[1–11]
Upon light exposure, liquid-phase photosensitive resin can be converted into polymer through a photochemical reaction called photopolymerization. Among all the photopolymerization techniques, two-photon polymerization (2PP) has been demonstrated to be one of the most promising tools in micro-optical-fabrication due to its intrinsic capability of achieving arbitrary three-dimensional structures with sub-wavelength spatial resolution.\textsuperscript{[3-7,9-11]} Unlike the single-photon case, in 2PP the resin is illuminated by a tightly focused ultrafast laser beam at a wavelength beyond the single-photon absorption band of the resin. The high photon density in the highly localized focal region triggers the non-linear effect of the resin and leads to the absorption of two photons simultaneously, providing sufficient energy to initiate the photochemical reaction. Due to a quadratic dependence on the laser intensity and a threshold effect of 2PP only the resin in close vicinity of the laser focal spot can be polymerized, leading to a high spatial resolution of 100 nm or less.\textsuperscript{[5]}

Due to its high precision and simplicity,\textsuperscript{[4-7,9-11]} this powerful method has enabled the synthesis of many novel microstructures and photonic devices, in particular the three-dimensional photonic crystals (PCs) and diffractive optical elements (DOEs), which are capable of controlling and manipulating the light propagation and thus are considered promising candidates for miniaturized optical devices.

To explore the advanced functionalities of three-dimensional PCs such as the superprism effect, the cavity effect, the negative refraction and self-collimation effect, novel materials possessing special linear or non-linear optical properties are required to be incorporated into a resin. To this end, nanocrystal quantum dots (QDs) have been demonstrated to be an ideal candidate because of their size-controlled emission spectral tunability covering both the visible and NIR wavelength region.\textsuperscript{[12,13]}

In this article the recent progress on the fabrication of three-dimensional photonic devices, including DOEs and woodpile PCs, in polymer materials using the 2PP technique is reviewed. The principle of the 2PP technique and its application in micro-fabrication are introduced. In particular, the influence of photo-initiators (PIs) and material properties of the resins are discussed. Recent advances related to the development of initiators and resins for 2PP are summarized. Chemical processes, preparation procedures, and post-processing of common resins (including commercial and customer-made ones) for micro-fabrication applications are also summarized. Micro-photonic structures including three-dimensional DOEs, woodpile PCs, and superprisms fabricated by the 2PP technique in various resins are reviewed. Three-dimensional PCs fabricated in a QD-doped polymer are briefly described.

2. Fundamentals of Two-Photon Polymerization

2.1 Single-Photon Polymerization

Liquid materials can be converted into solid phase upon light exposure either by photo-cross-linking or by photopolymerization. The former relates to the formation of cross-links between two macromolecule chains, while the latter is usually concerned with creation of a polymer through a chain reaction initiated by light. When a monomer molecule contains more than one reactive function, both procedures may occur simultaneously.

Since most monomers and oligomers commonly employed do not possess initiating species with a sufficient quantum yield upon light exposure, it is necessary to introduce low-molecular-weight molecules called PIs that start polymerization.\textsuperscript{[14]} Light absorption by a PI requires the overlapping of the emission line from a light source and an absorption band of the PI. The energy of a photon is transferred to the electron of the PI molecule, and the PI can convert this light energy into chemical energy in the form of reactive intermediates, such as free radicals (R\textsuperscript*\textsuperscript{)} or reactive cations (R\textsuperscript{+\textsuperscript{)}, which subsequently initiate polymerization of monomers and oligomers.\textsuperscript{[15]} Electronic transition energy for most initiator molecules corresponds to the UV spectral range. The initiator only absorbs one UV photon through linear absorption, which occurs anywhere along the beam path as shown in Fig. 1 (see Fig. 1a).

A normal single-photon polymerization (1PP) process consists of the following steps:

\[
\text{hv} \text{UV} + \text{initiator} \rightarrow \text{R}^* \text{or R}^+ \\
\text{R}^* \text{or R}^+ + \text{monomers} \rightarrow \text{free radical or cationic polymerization (Reaction 2-1)}
\]

Upon exposure to UV light, the PI is photolyzed to produce free radicals via molecular bond cleavage. The bond must have a dissociation energy lower than the excitation energy of the reactive excited state. Fig. 2 shows various pathways of deactivation and activation for an excited commercial initiator (Irgacure 369). After absorbing energy from UV light, the initiator transfers from the ground state to an excited singlet state and then to a triplet state. Part of the absorbed energy may be lost due to the internal conversion from the excited state into the ground state, and some reactive intermediates can be quenched by oxygen, monomer (inefficient energy or electron transfer), and the recombination of intermediates. Some of the excited initiators can abstract hydrogen from a hydrogen donor and undergo a photo-induced electron transfer and fragmentation process to produce efficient reactive intermediates. Hydrogen abstraction is a typical reaction of triplet-excited diaryl ketones. The triplet energy is high enough to overcome the bond energy of a carbon-hydrogen bond which makes it broken from an activated position (\(\alpha\)- or \(\beta\)-cleavage). The reactive intermediates interact with monomer and trigger a polymerization chain reaction. Other initiators may...
directly undergo a fragmentation process without abstracting hydrogen from donors.\textsuperscript{[15,16]}

The polymerization rate depends on the intensity of the light source, the concentration of the PIs, the presence of oxygen and additives, the quantum yield of the radical generation, and the initiation efficiency of the generated radicals. Generally, the rate increases with the incident light intensity, but not with the initiator concentration. Different concentrations of initiators can lead to different molecular weight and molecular weight distributions, resulting in polymers with various mechanical properties. Therefore, the concentration of initiator should be selected carefully to obtain optimized performance of a micro-structure. An ideal initiator should have a high molar absorption coefficient and a well adapted absorption spectral range. It should also be able to produce intermediates with excellent reactivity and photolysis by-products with low toxicity. Moreover it should be compatible with monomer and oligomers, and should be dispersed in the monomer uniformly before photo-polymerization.

In Table 1 some commercialized UV initiators from Ciba Specialty Chemicals (CAS) are listed. These initiators may also be available in other chemical suppliers. The CAS numbers provided here are the universal reference numbers for the same chemical product.

There are a variety of well known applications of 1PP like UV-photolithography or stereolithography, where a single UV photon is required to initiate the polymerization process near the surface of a photosensitive resin as shown in Fig. 3 (see Fig. 3a). Depending on the concentration of PI in the optionally added absorber molecules, the UV light is absorbed by the resin within the first few micrometers. Thus, 1PP is a planar process restricted to the surface of the resin.

### 2.2 Two-Photon Polymerization

For a 2PP process, the first step of the reaction is different from that in the 1PP process:

\[
2\nu_{\text{NIR}} + \text{initiator} \rightarrow \text{R}^- \text{ or R}^+ \text{(Reaction 2-2)}
\]

An initiator absorbs two NIR photons simultaneously with a long wavelength through a non-linear absorption process called two-photon absorption (2PA), which is a radiation–matter interaction that occurs in the excitation of an atom or a molecule from a lower quantum state to an excited state of the same parity as the low state in a single step.\textsuperscript{[17]} 2PA is the fundamental process making 2PP possible. It is a third order, optically non-linear process and involves the interaction of a medium with two photons without any excited intermediate state (of resonance). Very high intensity is required for 2PA since two photons have to be

---

**Table 1. Examples of commercialized UV initiators supplied by Ciba Specialty Chemicals**

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Chemical name</th>
<th>CAS number</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRGACURE\textsuperscript{®} 369</td>
<td>2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one</td>
<td>119313-12-1</td>
<td>366.5</td>
</tr>
<tr>
<td>IRGACURE\textsuperscript{®} 184</td>
<td>1-Hydroxycyclohexyl phenyl ketone</td>
<td>947-19-3</td>
<td>204.3</td>
</tr>
<tr>
<td>IRGACURE\textsuperscript{®} 819</td>
<td>Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide</td>
<td>162881-26-7</td>
<td>418.5</td>
</tr>
<tr>
<td>DAROCUR\textsuperscript{®} 1173</td>
<td>2-Hydroxy-2-methylpropophenone</td>
<td>7473-98-5</td>
<td>164.3</td>
</tr>
<tr>
<td>IRGACURE\textsuperscript{®} 1000</td>
<td>80% DAEOCUR\textsuperscript{®} 1173; 20% IRGACUR\textsuperscript{®} 184</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** (a) In a 1PP process, UV light is absorbed at the surface of a photosensitive polymer and can only be used to fabricate planar structures. (b) In a 2PP process, NIR light can be focussed into the volume of the UV-sensitive resin and can therefore be used for truly three-dimensional structuring.
absorbed simultaneously, which means that 2PA is proportional to the square of light intensity. Thus to observe 2PA, a tightly focussed laser beam with a high peak intensity is required. In this case, the maximum absorption wavelength of the initiator is required to be shorter than the wavelength of the fabrication laser.

2PA is an important tool in laser spectroscopy since transitions between two states that cannot be connected by dipole transitions can be observed. One of the most common applications of 2PA is two-photon confocal microscopy,[18] where the fluorescence of a dye molecule is observed inside a medium with high spatial resolution due to the fact that 2PA can be initialized anywhere in the volume of a transparent medium with a high spatial confinement as shown in Fig. 1b.[19] For example, if using a standard oil immersion objective with a numerical aperture (NA) of 1.4, a lateral resolution in the order of 100 nm and an axial resolution of 500 nm can be achieved.[20]

The enormous applications of 2PA can be extended to the area of three-dimensional fluorescence microscopy, three-dimensional micro-fabrication, and optical data storage. Due to the last-mentioned area, it is important to design and synthesize highly active organic two-photon chromophores. Up to now, fully understanding the relationship of the molecular structure and property with varied structural parameters and precisely reproducing characteristics of two-photon properties are still challenging. But the major design concept is based on the relationship between the molecular two-photon cross section and the imaginary components of the third-order non-linear susceptibility.[21-24]

A typical structure of the two-photon initiator is the \( \pi \)-conjugation bridge chromophore with high planarity substituents of electron donor (D) or electron acceptor (A). Type I structures are symmetrical, such as \( D-\pi-A \), \( D-\pi-\pi-A \), \( A-\pi-D-\pi-A \) molecules. Type II molecular structures are asymmetrical, like \( D-\pi-A \) molecules. There is a series of strategies to increase the cross section of molecules:[25,26]

1. Extending the \( \pi \)-conjugation length;
2. Increasing the planarity of the chromophore by using a fused aromatic ring \( \pi \)-bridge;
3. Increasing the strength of donors and acceptors.

For a normal UV initiator, the two-photon cross section is very small (< \( 10 \times 10^{-50} \) cm\(^4\) s/photon). By using molecules with the above-mentioned structures, the two-photon cross section can be increased to \( 1000 \times 10^{-50} \) cm\(^4\) s/photon.[23,24]

For a two-photon initiator, the molecules should not only have a large two-photon absorption cross section, but also have high efficiency to produce reactive intermediate radicals or cations, just like normal UV initiators. The intermediates can efficiently activate the chemical functionality. By using a two-photon initiator, the photo-sensitivity of the whole system can be increased leading to a lower polymerization threshold. As a result, the laser-writing window can become broader, and the possibility of damaging the structure due to high fabrication intensity and long exposure time associated with commercial UV initiators can be reduced. In some cases, two-photon initiators can increase the polymerization rate. In spite of the advantages mentioned above, the current two-photon initiators are still only applied in scientific laboratories for fundamental research purposes.

Since the cross section for 2PA is orders of magnitude lower than that for single photon absorption, the intensity of the excitation beam is required to be in the order of TW (Terawatts) cm\(^{-2}\) to generate a sufficiently high density of radicalized starter molecules, especially when using PIs that are not optimized with respect to high 2PA cross section. This explains why a tightly focussing high NA objective and a femtosecond (fs) laser are necessary to trigger the 2PP. For NIR light beyond the single-photon absorption band of the PIs, the used photosensitive resins are transparent, i.e., NIR fs laser pulses can be focussed into the volume of the resin without having any single-photon absorption. 2PA occurs within the focal volume of the objective only when the photon density exceeds a certain threshold value initiating the polymerization process leading to a high spatial resolution. Unlike single-photon absorption, 2PA can be initialized anywhere in the volume of a transparent medium due to the absence of linear absorption, as shown in Figs. 1a and b. When the laser focus is moved three-dimensionally through the volume of the resin, the polymerization process is initiated along the trace of the focus allowing the fabrication of arbitrary three-dimensional micro-structures, as illustrated in Fig. 3b. The three-dimensional movement of the laser focus can be realized by either scanning the laser in the \( x-y \)-plane using a galvo-scanner while moving the sample in the \( z \)-direction or by moving the sample three-dimensionally using a three-dimensional piezo stage.

Obviously, there are several advantages of 2PP compared to 1PP: First, since the polymerization can be initiated within the volume of the resin rather than being restricted to the surface, 2PP is a real three-dimensional process whereas 1PP is a planar process. By applying 1PP, three-dimensional structures can only be fabricated by means of working 2.5-dimensionally, i.e., working layer-by-layer. However, this limits the resolution (as in stereolithography, where the smallest achieved structure sizes are several micrometers) and does not allow for a rapid single-step fabrication process. Second, photopolymerization in contact with oxygen leads to quenching of the radicalized molecules on the surface of the resin and hence to a suppression of the polymerization process. Therefore, high-resolution 1PP processes have to be performed in an inert gas atmosphere. In a 2PP process this will not cause any problem because the fabrication occurs in the volume of the resin rather than at the surface. Third, the two-photon excited spot is smaller than a single-photon excited spot, allowing the precise fabrication of fine structures with high resolution down to 100 nm.[5]

Fig. 4 presents a typical fabrication setup for generating micro-structures using the 2PP approach.[9] NIR fs laser pulses generated in a Ti:Sapphire laser are converted into the visible by means of an optical parametric oscillator (OPO). A neutral-density filter (ND) is introduced into the beam path allowing for adjustments of beam intensity. The telescope arrangement leads to uniform illumination over the back aperture of an oil immersion objective (60 \( \times \) NA = 1.45) used to focus the laser beam. The beam is focussed into a sample to initiate polymerization. The sample, a photo-sensitive liquid resin, is sandwiched between two coverslips and mounted on a three-dimensional piezoelectric scanning stage. The movement of the scanning stage is pre-programmed to form different three-dimensional micro-structures and controlled by a computer. The fabrication process is monitored in real time by a charge-coupled device (CCD). The requirements for photo-sensitive resins are discussed in Section 3. Due to the threshold behaviour of the 2PP process, resolution beyond the diffraction limit can be realized by controlling the laser-pulse energy and the number of applied pulses (see Fig. 5).[27]
They should have a fast curing speed and the polymerized area should be confined to a close vicinity of the focal spot with only little scattering. The highly cross-linked material must have washout resistance and should not swell or be deformed by any solvents used in the washing process, which guarantees the fabricated micro-structure remaining unaffected upon the development process. Photosensitive resins generally show shrinking behaviour during the polymerization process. To obtain high quality micro-structures, the shrinkage and resulted distortion of the structure should be kept as small as possible. The refractive index of the resin before fabrication should be close to that of glass which is approximately 1.5, which allows the beam to be focussed deeply into the resin without aberrations to access a large vertical dimension. After polymerization, the refractive index generally increases slightly, which enhances the contrast of the image in the CCD camera when the fabrication is monitored in real time. The thermal stability of the cross-linked resin is also expected to be good enough to sustain 100–150°C high temperature because later the fabricated micro-structure may be used as a template to be infiltrated with other functional inorganic materials to form high-index photonic structures. Furthermore, the polymerized resins should also have proper mechanical properties, i.e. toughness and hardness, to maintain the structure shape and at the same time sustain the deformation of shrinkage.

Several resins, as summarized in Table 2, have been employed for micro-fabrication, some of which have been commercialized. Regarding to the chemical process, only the resin SU-8 has a two-step cross-linking procedure. In the first step a strong acid is induced within the focal spots during the exposure process followed by an acid-initiated, thermally driven epoxy cross-linking in the post-exposure bake step. As a commercialized product, SU-8 is supplied as a liquid consisting of an epoxy resin, a solvent, and a photo-acid generator. Before fabrication, the resin is required to be coated on a substrate using a spinner to form a thin film with different thickness, which can be controlled by the spinning speed and depends on the viscosity of the resin. Alternatively, pure liquid resin without solvent can also be sandwiched into two coverslips with a thin spacer to form a thin film with fixed thickness. Upon exposure to a light beam, a strong acid is generated, which allows the epoxy resin to network with a high cross-linking density if it is heated above a critical temperature in the post-exposure bake. The unexposed material is then removed with a solvent in the developing process. Because it is a two-step procedure, while the formation of the micro-structures occurs in the second step, the fabrication process cannot be monitored in real time. In the post-exposure bake step, the fabrication parameters, i.e. exposure time and intensity, process can be monitored and optimized in real time by adjusting the fabrication parameters, i.e. exposure time and intensity. Although polymerization is a single-step procedure, the light treatment for a sample can be varied according to different

---

**3. Photosensitive Polymer Materials for Two-Photon Polymerization**

Resins used in micro-fabrication are functionalized oligomers as polymer binders, which by polymerizing will constitute the backbone of the polymer network, or multi-functional monomers, which act as reactive diluents, with PIs added through a solvent-mixing process. A pulsed laser beam excites the initiator to produce radicals or cations, and then they interact with the surrounding monomers to trigger a polymerization chain reaction as shown in Reactions 2-1 or 2-2. Multi-functional monomers can form a cross-linked network within the focal volume of the laser beam, which cannot be dissolved by any solvent. By moving the laser focus three-dimensionally, the resin is solidified along the pathway of the light beam. The non-cross-linked monomers maintain good solubility in certain solvents and can be washed away after the 2PP process, leaving a three-dimensional micro-structure which is an exact replica of the pathway of the laser focus.

Resins used for fabrication must be transparent in the visible and NIR region to allow the laser pulses to focus into the volume of the resin without any single-photon interaction. They should have a fast curing speed and the polymerized area should be confined to a close vicinity of the focal spot with...
4. Photonic Applications of Two-Photon Polymerization

4.1 Three-Dimensional Microstructures

The non-linear and threshold properties of 2PP allow for the direct fabrication of any arbitrary three-dimensional microstructures with high precision. Such a feature has been intensively demonstrated by the production of three-dimensional artistic structures such as a micro-bull,[5] a micro-Venus,[10] a micro-tower, and interlocking rings[7] and the ‘world smallest’ Sydney Opera House[32] with resolution of hundreds of nanometers. Fig. 6a presents a three-dimensional pacman-like cone structure and a three-dimensional kangaroo constructed by an outline scan algorithm, which traces only the border of the structure leaving its unsolidified interior to be UV-cured afterwards.[36] A human hair is also presented in this figure to demonstrate the scale. Fig. 6b and c show a micro-scale model (64 × 38 × 41 μm³) of the Sydney Opera House that was fabricated by means of 2PP in resin IPG.[32] The 2PP technique can also be applied to produce micro-devices such as gear wheels[4] and light driven rotors.[8] Table 2 summarizes the common resins used for micro-fabrication, the preparation and post-processing methods, the icon structure of a specific resin, and the achievable minimum size of the structure.

4.2 Diffractive Optical Elements

DOEs refer to modulation devices for light field synthesis. They are key components in miniaturizing optical system to achieve fabrication requirements. For example, resins such as Norpocure 800 need to be pre-exposed to UV light to increase its viscosity.[4]

Although commercial resins are easy to access and have good performance for certain applications, the compositions of the resins are uncertain and unchangeable. In order to meet some special requirements in micro-fabrication, such as high resolution, transparency at certain wavelengths, a high curing speed, and a good thermal stability, the resins have to be customized and tailored with specific components allowing for the adjustment of the mechanical and surface properties of the fabricated structures and mixing of various initiators to be adapted to different laser wavelengths. Furthermore, the concentration of the doped initiator can be optimized to obtain the best structure, and more efficient initiators can be applied to increase the sensitivity of the resin.

Recently, we have made significant contributions to this area. A PI has been added into the resin IPG (inorganic polymer glass: RPO, Australia) containing polysiloxane chains with acrylate functional groups attached. The resin has enhanced thermal and optical properties compared with the commercialized ones, and the possibility to perform three-dimensional stereolithography by the IPG resin has been demonstrated.[32] The other resin LN1 containing eight components of different acrylate (Sartomer) has been developed to achieve high resolution down to 200 nm with an increased thermal stability.[16,33] A single-monomer based resin SR348 (also from Sartomer) has also been developed with a simplified preparation procedure without losing the basic properties of LN1.[34]

Resin also possesses the flexibility to be modified into composites to achieve physical functionalities. For example a commercially available nanocomposite called EviComposites (Table 2), formed by doping QDs into an acrylate polymer combined with a colloidal suspension of silica (formed by a sol gel process), has been successfully developed to form an active medium.[35]
integrated circuits. However, it remains a challenge to achieve real continuous grey level three-dimensional DOEs with the conventional semiconductor fabrication approach. It is shown that the multi-level-phase-encoded diffractive optical element fabricated in inorganic–organic hybrid polymer material by the 2PP method facilitates the intensity distribution synthesis with a high diffraction efficiency approaching the theoretical limit. This DOE fabrication method is a mask-free and low-cost single-step fabrication process.

The principle of a DOE is based on the two-dimensional intensity distribution synthesis through the Fresnel diffraction. An original two-dimensional intensity distribution is encoded into phase information by a method called iterative Fourier transform algorithm (IFTA). In Figs 7a and b, the original image, which in this case is a photo of the Sydney Opera House sampled by $128 \times 128$ points, together with the corresponding phase profile, is presented. The DOE structure we fabricated was an exact polymer replica of this phase profile as shown in Fig. 7c. A scanning
electron microscope (SEM) image (Fig. 7d) reveals that in the fabricated DOE each pixel with different heights corresponding to 256 phase levels is well defined.

To characterize the fabricated DOEs, we irradiated the samples with a collimated He–Ne laser beam, as shown in Fig. 8a. A screen was applied to collect the diffraction images. The reconstructed diffraction image of the Sydney Opera House is presented in Fig. 8b. The measured diffraction efficiency of the binary letter image is 84%, which matches well with the theoretical estimation of 86.76% due to the accurate realisation of the designed surface profile with high lateral resolution and 256 fine phase levels.

4.3 Three-Dimensional Photonic Crystals

Recently, the powerful 2PP technique has also been applied to fabricate three-dimensional PCs, which are a promising candidate for the next generation integrated photonic circuits. A PC is a periodical structure caused by the refractive index change at the scale of light wavelength,[29] which possesses band gaps suppressing the light transmission in a certain wavelength range at any angle while allowing other wavelengths to pass freely. A three-dimensional PC has a periodical structure in all three dimensions. The band gap of a PC is determined by the size of the periodicity called lattice constant. Therefore, by varying the periodicity, the band gap of PCs can be engineered.

Although PCs can be generated in a great variety of geometries, this paper is focussed only on the three-dimensional woodpile structure.[9,10] Fig. 9a presents a computer generated sketch of a woodpile structure, which consists of layers of one-dimensional rods with an in-plane period of \( d \) and has a stacking sequence that repeats itself every four layers. The distance between four adjacent layers is denominated by \( c \). Within each layer, the axes of the rods are parallel to each other while rotated by 90° in each adjacent layer. Between every other layer, the rods are shifted relative to each other by \( d/2 \). Generally, the resulting structure has a face-centred-tetragonal (fct) lattice symmetry. For the special case of \( (c/d)^2 = 2 \), the lattice can be derived from a face-centred-cubic (fcc) unit cell with the basis of two rods.[38]

Figs 9b–d show the SEM images of a 40-layer three-dimensional woodpile structure fabricated by the 2PP technique in a homemade photosensitive resin called LN1.[16] The structure was fabricated at a layer spacing of 500 nm and an in-plan rod spacing of 1.5 \( \mu \)m. A structural element size of less than 200 nm has been achieved. It can be seen from the magnified SEM image in Figs 9c and d that the PC structure exhibits a high level of perfection and results in a suppression of the light at wavelength of 2.3 \( \mu \)m (Fig. 9e). The woodpile PC structures have also been demonstrated with other materials including commercially available SU-8, SCR500, Ormocer, SR348, and IPG resins, which are summarized in Table 3 including the suppression rate of IR light transmission (%).

Among all these photosensitive resins Ormocer shows outstanding performance with a smallest minimum structure size of 150 nm and comparatively simple process steps, while for other resins the minimum structure sizes are from 200 to 350 nm. The transmission spectrum of a typical PC structure consisting of rods having a width of less than 200 nm and an in-layer rod distance of 800 nm, measured by means of Fourier-transform infrared (FTIR) spectroscopy, is shown in Fig. 10a. A suppression in transmission of \( \sim 70\% \) was found at a wavelength of 1.21 \( \mu \)m which agrees with the calculated result.[39] The drop in transmittance corresponds to the fundamental bandgap between the second and third bands in the stacking (\( \Gamma\rightarrow X\) direction, which is indicated by the shaded area in the band structure.[39]

One of the most useful characteristics of PCs is the highly wavelength dependent dispersion property, which is called the superprism effect. For the band gap property of the three-dimensional PC shown in Fig. 10a, a light source with wavelengths slightly below the band gap of the crystal, where the effective refractive index is most sensitive to the wavelength, was applied.[39] As the wavelength is tuned from 1000 nm (Fig. 10b) to 1020 nm (Fig. 10c), the light inside the crystal changes its direction of propagation by more than 10°. Such a change is two orders of magnitude higher than that in conventional prisms.[40]

With the help of the 2PP method, the superprism shown in Fig. 10 can be integrated with a waveguide.[41] A waveguide-coupled woodpile structure is shown in Figs 11a and b. A tapered waveguide structure with two square facets (13 and 4 \( \mu \)m wide, respectively) was generated for coupling the light into the PCs with a well defined angle.[41] The length of the taper was 140 \( \mu \)m and it was fabricated at a distance of less than 5 \( \mu \)m to the edge of the substrate enabling the light to be coupled into the waveguide with relatively small coupling losses. The rods of the woodpile structure have the same lattice constant and filling ratio as the superprism structure mentioned above; however, they were rotated an angle of 45° with respect to the crystal surface allowing for a maximum dispersion to be explored.

Fig. 11c–e reveal that when a linearly polarized light with a wavelength tuned from 860 to 960 nm is launched into the waveguide, the light inside the PC changes its direction of propagation by \( \sim 60° \). It is interesting to note that at long wavelengths (\( \lambda > 930 \) nm) the structure shows negative refraction: i.e., light is refracted to the opposite direction compared to the direction of incidence (Fig. 11c), as predicted by the theory.[41,42]
Fig. 9. (a) Computer generated sketch of a woodpile structure. (b–d) SEM images of woodpile structures fabricated by means of 2PP. (b) A solid frame was built around the structure to prevent it from shrinking. (c, d) More detailed top and side views of the woodpile structure, respectively. (e) A transmission FTIR spectrum of the PC shown in (b).[16]

<table>
<thead>
<tr>
<th></th>
<th>PCs structure (for shortest wavelength gap one)</th>
<th>Min. structure size [nm]</th>
<th>Shortest wavelength band gap [μm]</th>
<th>Max suppression rate of transmission of light [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8</td>
<td>Woodpile, ( d = 800 \text{ nm}, (c/d)^2 = 2, ) 24 layers</td>
<td>180</td>
<td>1.3</td>
<td>72[29]</td>
</tr>
<tr>
<td>SCR500</td>
<td>Woodpile, ( d = 1500 \text{ nm}, \delta z = 500 \text{ nm}, ) 40 layers</td>
<td>200</td>
<td>1.5</td>
<td>50[9]</td>
</tr>
<tr>
<td>Ormocer</td>
<td>Woodpile, ( d = 700 \text{ nm}, (c/d)^2 = 2 )</td>
<td>150</td>
<td>1.2</td>
<td>70[38]</td>
</tr>
<tr>
<td>IPG</td>
<td>Woodpile, ( d = 1500 \text{ nm}, \delta z = 1000 \text{ nm}, ) 20 layers</td>
<td>350</td>
<td>1.6</td>
<td>20[32]</td>
</tr>
<tr>
<td>LN1</td>
<td>Woodpile, ( d = 1500 \text{ nm}, \delta z = 500 \text{ nm}, ) 40 layers</td>
<td>200</td>
<td>2.3</td>
<td>40[10]</td>
</tr>
<tr>
<td>SR348</td>
<td>Woodpile, ( d = 1500 \text{ nm}, \delta z = 500 \text{ nm}, ) 40 layers</td>
<td>300</td>
<td>1.9</td>
<td>39[34]</td>
</tr>
<tr>
<td>EviComposites</td>
<td>Woodpile, ( d = 1200 \text{ nm}, (c/d)^2 = 2, ) 32 layers</td>
<td>250</td>
<td>1.6</td>
<td>50[35]</td>
</tr>
</tbody>
</table>

### 4.4 Three-Dimensional Photonic Crystals in Nanocomposites

The formation of active PCs in the NIR wavelength range is highly desirable for the purposes of telecommunications. To this end, a resin should be a doped medium consisting of functional species such as non-linear materials or nanocrystal QDs.

QDs refer to crystalline structures whose dimensions are so small (in the order of 1–10 nm) that their electronic states begin to resemble those of atoms or molecules due to the quantum confinement effect rather than those of the bulk crystal.[43] Band gap energies of QDs are strongly size-dependent, so that as the radius of the QDs decreases, the band gap increases. This means by adjusting the QD size within the quantum-confined regime the emission wavelength of the QDs can be accurately tuned. Thus, the size of QDs can be used to directly manipulate their electronic and optical properties to tailor them for specific applications, making them enormously useful in a wide variety of applications including biological labelling, QD lasers, LEDs, photovoltaic devices, sensors/detectors, and optical data storage.[44]

Among all the QD species, colloidal semiconductor nanocrystals...
have attracted particular attention because of the possibility of being integrated into existing micro- and opto-electronic technologies.

Although QDs with emission in the visible wavelength range have been well developed,\(^{45}\) it was not until recently that lead-based QDs (PbS, PbSe, and PbTe) with high optical qualities (high photoluminescence and quantum yields) in the NIR range were developed successfully.\(^{46-48}\) The three-dimensional spatial confinement of charge carries in semiconductor QDs results in size-dependent energies and probabilities of optical transitions. The interplay of electron and photon confinement opens up a pathway to novel light sources with controllable spontaneous emission. The incorporation of QDs with emission in the NIR region into three-dimensional PCs, which are of great importance in terms of telecommunications, has not yet been demonstrated.

In Fig. 12 we show for the first time the three-dimensional woodpile PCs with band gaps in the NIR region fabricated in a commercial QD composite.\(^{35}\) The material we used in this work was a commercial PbSe QD composite operating in the telecommunication wavelengths (Evident Technologies, 1550 nm Java PbSe core shell EviComposites in UV curable sol gel with a concentration of 5 mg mL\(^{-1}\)). Before fabrication, the PbSe QD composite was dropped onto a coverslip and heated in an oven for 10 min at a temperature of 70°C. The pre-baked resin was then fed into the standard 2PP fabrication system (Fig. 4) to form three-dimensional woodpile PCs. An optical parametric oscillator operating at a wavelength of 580 nm, a repetition rate of 90 MHz, and pulse duration of 100 fs was used. The pulses were focussed into the resin with an oil immersion objective (Olympus, NA = 1.4, 100×). The threshold for 2PP with this QD composite was ~3.25 mW before the aperture of the objective and three-dimensional structures can be well developed with an irradiation power above 4.5 mW with a scanning speed of 50 μm s\(^{-1}\). Figs 12a and b present the SEM images of the resulting three-dimensional PC structures and the transmission spectra of the PCs for different lattice constants. For \(d = 1.2 \mu m\) and 1.3 μm, suppression ratios higher than 50% were achieved.
5. Conclusions

The 2PP technique is a versatile tool in real three-dimensional micro-fabrication, and has aroused extensive research interests in the past few years. By using this method high quality, three-dimensional photonic devices, such as DOEs and PCs, which are key elements in integrated photonic circuits, have been realised. In particular, three-dimensional woodpile PCs with band gaps in the telecommunication wavelength region have been successfully fabricated, not only in plain polymers but also in the QD composite. To ultimately generate the next-generation photonic devices such as photonic chips with the 2PP method, it is necessary to develop a highly efficient polymer resin that has a high 2PP cross section, a high emission efficiency, a high effective refractive index, and less shrinkage properties in post-processing.

Acknowledgments

This work was produced with the assistance of the Australian Research Council (ARC) under the Centres of Excellence Program. CUDOS (Centre for Ultrahigh-Bandwidth Devices for Optical Systems) is an ARC Centre of Excellence. The authors thank Dr Martin Straub, Dr Nguyen Le Huong, Dr Shuhui Wu, and Dr Jesper Serbin for their contributions and discussions on this topic.

References
