

Nanoparticle-Based Photorefractive Polymers

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Photorefractivity has attracted intense attention owing to its ability to spatially modulate the refractive index under non-uniform light illumination. In particular, photorefractive polymers are appealing materials as they enable the high non-linear performance that underpins many areas of photonics. The incorporation of nanoparticles into photorefractive polymers shows an enormous potential owing to the broad spectroscopic tuning range and the high photogeneration efficiency, which are inaccessible to traditional photorefractive materials. This article reviews the recent developments in the field of nanoparticle-doped photorefractive polymers. The merit and functionality of these hybrid materials are summarized and future challenges are discussed. The application of nanoparticle-doped photorefractive polymers under two-photon excitation is also described, which facilitates a promising new area of high-density optical data storage, the third-generation of optical data storage.

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1. Introduction

Years of effort have been spent towards optical devices with a fast response, a high sensitivity, and a high reliability to replace electronic ones. As one of the important optoelectronic materials that are sensitive to light, photorefractive (PR) materials have attracted great interest. Photorefractivity is defined as the reversible spatial modulation of the refractive index as a result

of the non-uniform illumination-induced charge redistribution. It holds a considerable promise for various applications in high-density optical data storage,^[1,2] dynamic image processing,^[3] and waveguides.^[4] Its fusion with polymer science has enormously expanded the impact of the photorefractivity owing to the simple and low cost preparation process. One of the important features of PR polymers is the incorporation of organic



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dyes as charge generators, such that spectrum-selective excitation of the photopolymer becomes possible.^[5] With the advance of nanotechnology, conventional organic dyes can be replaced with nanoparticles (NP), as the optoelectronic properties of NP can be tuned by their size and composition.^[6] NP-dispersed PR polymers have offered lots of unique properties such as a broad spectroscopic tuning range, an increased photogeneration efficiency, and an improved charge mobility. The research field of NP-doped PR polymers has been intensively investigated by incorporating NP of different compositions and structures under both single photon excitation^[7–12] and two-photon (2P) excitation.^[13]

The development of NP-doped PR polymers is still in its infancy. The current primary challenge is to find an appropriate method to disperse NP homogeneously into a polymer matrix. To date, most of the reported experiments that involve NP-dispersed PR polymers have been conducted at low doping concentrations to prevent particle aggregation. Surface capping ligands are widely used to make NP more soluble and to improve their photostability in the polymer matrix. Furthermore, only a few classes of NP have been adopted for generating photorefractivity. In light of these challenges, the novel applications of NP-based PR polymers have motivated extensive research activities. In this article, we discuss the PR effect in NP-dispersed polymers and the methods used to characterize the PR performance. Finally we present some results on NP-doped PR polymers and discuss their potential applications in high-density optical data storage.

2. Photorefractivity in Polymers

The PR effect in polymers was first experimentally demonstrated by Moerner and coworkers in 1990.^[14] A PR polymer is a multifunctional optoelectronic medium that fuses both the photoconductivity and the electro-optic effect into the same material.^[5] Typically it consists of a polymer matrix, a plasticiser, a high concentration of non-linear dye molecules, and a small amount of sensitizer with each component performing a particular role. Figure 1 illustrates the physical view of the photorefractive process. In the first step, sensitizers photogenerate space charges in the ‘bright area’, which results from the spatially inhomogeneous illumination from the two-beam interference. The second physical process of the photorefractivity is to transport the generated charges along the polymer. Generally the mobile charges can drift or diffuse into the ‘dark area’ under an external electric field bias. To drive the transport a component of the external electric field E_0 should exist along the direction of the grating vector K_G . Third, the impurities and defects in the polymer are able to trap the mobile charges for a period of time. As a consequence, the separation of the space charges introduces a sinusoidal internal electric field. Finally, the electro-optic effect of the non-linear optical dye molecules introduces a refractive index change through both the linear Pockels effect and the non-linear Kerr orientation effect.^[15–17]

The most important feature of the photorefractivity in the two beam interference geometry is the $\pi/2$ phase shift between the incident spatial light intensity grating and the resultant refractive index grating as depicted in Fig. 1. The non-local property originates from the large-scale transport of the space charges driven by an external electric field. This phase shift between the refractive index grating and the spatial intensity distribution makes this PR effect distinct from other refractive index change mechanisms, such as photochromic, photothermal, and so forth.^[14,17] Another important feature of the PR effect is

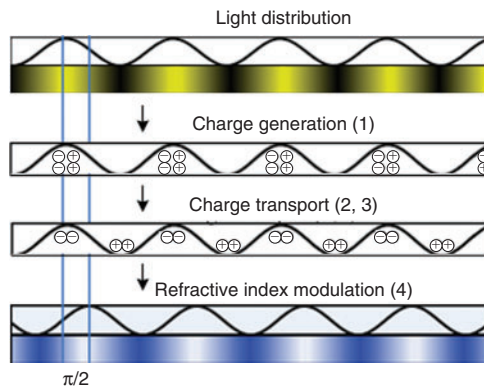


Fig. 1. Physical view of a photorefractive process in polymers. (1) Generation of space charges, (2) transporting and trapping of mobile charges, (3) resulting electric field, and (4) refractive index modulation.

its complete reversibility. The trapped charges can be released back by exposing the material to homogeneous UV irradiation or heat. The trapped space charges recombine and the space charge field becomes neutralized. Subsequently the refractive index modulation disappears.

3. Characterization of Photorefractivity

The ability to write and erase the refractive index gratings in polymers is not sufficient enough to confirm the presence of the photorefractivity. Two main characterization methods widely used to confirm the PR effect are four wave mixing (FWM) and two-beam coupling (2BC).^[16–18] The asymmetrical energy transfer from one beam to the other takes place as predicted by the non-local property when two incident beams interfere inside PR polymers. This mechanism unambiguously distinguishes the PR effect from other refractive index change mechanisms.

A typical experimental configuration for a 2BC measurement is illustrated in Fig. 2a. A sample consisting of poly(*N*-vinyl carbazole) (PVK):9-ethylcarbazole (ECZ):2,5-dimethyl-4-*p*-nitrophenylazo anisole (DMNPAA):2,4,7-trinitro-9-fluorenone (TNF) at a weight concentration ratio of 53:16:30:1 is prepared. An inspection of the transmission intensity of the two incident beams as a function of time under an external electric bias in Fig. 2b reveals that one beam gains the energy while the other beam loses its energy. Chopping either of the two incident beams causes the other beam to recover to its original intensity level. As the 2BC gain is given by $\Gamma \propto \Delta n \times \sin\Phi$, where Δn is the refractive index modulation and Φ is the phase shift of the index grating,^[17] 2BC has been used to confirm the presence of the PR effect and characterize the capability of the refractive index modulation of the material. It is clear that the asymmetrical energy transfer can be a maximum as the phase shift is close to $\pi/2$, whereas no energy coupling occurs for in-phase gratings. The gain coefficient can be experimentally determined using $\Gamma = \frac{1}{L} \ln[(I_{2(\text{in})} \times I_{1(\text{out})}) / (I_{2(\text{out})} \times I_{1(\text{in})})]$, where L is the optical length of the amplified beam, $I_{(\text{in})}$ and $I_{(\text{out})}$ are the incident and transmitted beam intensity, respectively.^[17,18] The energy transfer direction can be reversed by either changing the polarization state of the two writing beams or switching the direction of the electric field.^[18]

A typical FWM experimental configuration is shown in Fig. 2c. FWM is quite similar to 2BC except that a separate probe beam propagating in the opposite direction to either of

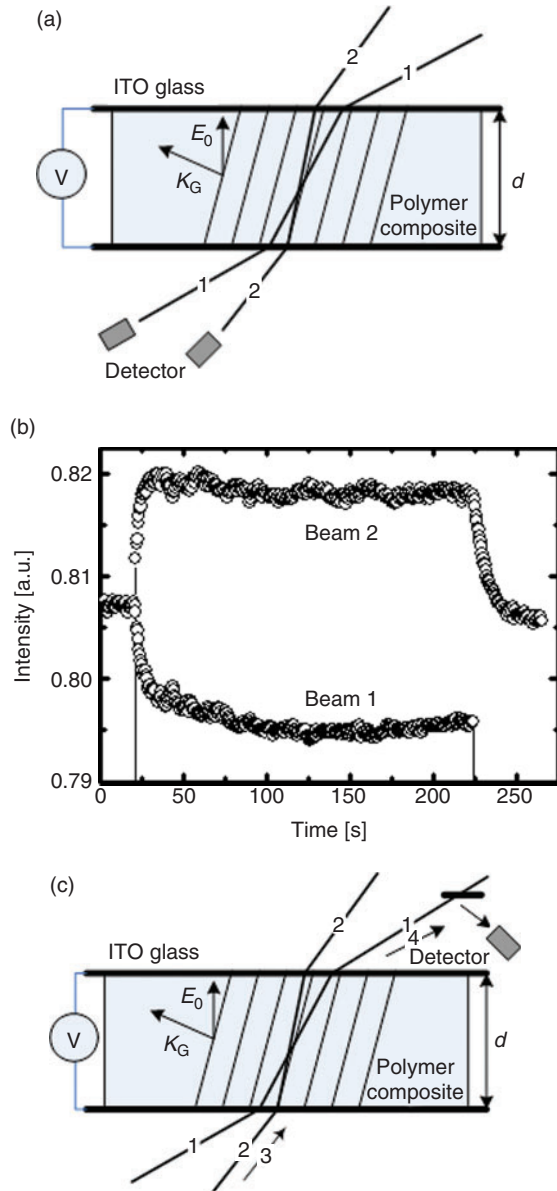


Fig. 2. (a) Experimental geometry of 2BC. The grating is written by the interference between beam 1 and beam 2. (b) 2BC experiment for PVK:ECZ:DMNPAA:TNF at 633 nm with $E_0 = 30 \text{ V } \mu\text{m}^{-1}$. The intensity of beam 2 is monitored as beam 1 is switched on at $t = 20 \text{ s}$ and off at $t = 225 \text{ s}$. (c) Geometry of FWM is similar to 2BC except that a separate probe beam 3 is required.

the two writing beams is also required. Usually, the two writing beams are s-polarized and the probe beam is p-polarized with an intensity much weaker than that of the writing beams. The benefit of such a configuration is that less energy transfer between writing beams occurs, which reduces undesirable deconstructive reading. The diffraction efficiency is experimentally given as $\eta = I_4/I_3$, where I_4 is the transmitted intensity of the probe beam I_3 .^[17] As η is square sinusoidally dependent on Δn , it can be used as a way to characterize the refractive index change. A standard FWM experiment involves the measurement of the diffraction efficiency as a function of the electric field bias or time. $1/\tau_w$ is another important parameter to characterize the response rate of the PR effect in the material, where τ_w is the characteristic growth time for the diffraction efficiency to reach the steady-state.^[17] FWM has been widely used as an

indispensable tool for temporal investigation into the formation or the erasure rate of refractive index gratings.

4. NP-Dispersed PR Polymers

Among all available organic sensitizers, C60^[19] and TNF^[20] are the most frequently utilized photocharge generators in high performance PR polymers. However, these sensitizers, as with most organic sensitizers, suffer from a narrow spectroscopic tuning range. Organic photosensitizing in the infrared (IR) range is generally unstable.^[21] In particular, not many organic sensitizers are available at the telecommunication wavelengths of 1.3 and 1.55 μm . Second, they are less efficient in photocharge generation.^[22] Furthermore, photobleaching under intense light irradiation limits their applications in devices.

NP or quantum dots (QD) are appealing materials because of their electronic and optical properties. For example, the position of the absorption edge of NP is strongly size, composition, and shape dependent, which can be tuned during the growth process.^[6,23] By an appropriate choice of their composition and size, a spectroscopic tuning range of the absorption edge from the visible to telecommunication wavelengths can be achieved. Since the first demonstration of the PR effect in a QD-dispersed PR polymer in 1999,^[7] a variety of hybrid PR polymers that contained various NP with different compositions and structures have been intensely investigated. A summary of these studies in terms of the NP concentration, the PR response rate, the 2BC gain, and the diffraction efficiency is presented in Table 1, while the advantages of NP-dispersed polymers are shown in Table 2.

QD are appealing photosensitizers primarily because of their broad spectroscopic tunability and high photogeneration efficiency.^[7–10] By judiciously designing the size and composition of QD one can tune the optical response of PR polymers ideally to a desirable wavelength range. CdS, CdSe, and CdTe QD,^[7,9,25,27–36] as well as clay nano-particles^[37] have been widely studied to achieve the PR sensitivity in the visible wavelength range, whereas PbS and PbSe QD^[8,24,26] have been incorporated in the PR polymers in the telecommunication wavelength range between 1.3 and 1.5 μm .

At a given weight percentage, QD are more efficient in photocharge generation than organic sensitizers. In general, a strong dependence of the charge generation efficiency on the external electric field is an important feature of polymer materials. Under an electric field the photocharge generation efficiency of the CdS-dispersed PVK-based PR material is one order of magnitude higher than that in the material sensitized by C60.^[22] The barrier to the charge transfer between the QD and the surrounding polymer matrix can be reduced by a careful choice of surface capping. Small molecules attached to the surface of QD generally constitute only a thin barrier to the charge transfer between the QD and the surrounding polymer matrix. The mobile charges more easily escape through the capping layers into the polymer matrix, thus facilitating a high efficiency of the charge generation as well as a fast grating build-up response.^[9,29] A high PR performance has also been observed in the material containing core/shell QD where a shell of wide-bandgap materials is grown on the surface of the core particles.^[28,30,31] This improvement has been attributed to the wide-bandgap shell acting as an effective potential barrier to the recombination for holes immobilized on the particle surface. A population of the charge traps in the ‘dark regions’, which are the destination of the mobile charges, is crucial for a stable space-charge electric field as well as the refractive index modulation. The negatively

Table 1. Merits of reported QD-dispersed PR polymers to date
PR, photorefractive; QD, quantum dots

Material	C [wt.-%]	Size [nm]	$1/\tau_w$ [s^{-1}]	$\Delta n \times 10^{-3}$	η [%]	λ [nm]	G [cm^{-1}]	Ref.
PVK:TCP:NPP:CdS	0.191	<2.2	0.137	–	8	514	59.5	[7]
PVK:TCP:NPP:PbS (HgS)	0.99	50(10)	0.05	–	–	1310	30.9(4.3)	[24]
PMMA:TL202:ECZ:CdS	2	<14	>0.02	–	72	514	30	[25]
PVK:ECZ:DEANST:PbS	2	6	0.5	–	–	1340	185	[8]
PVK:ECZ:DEANST:PbSe	10	5.2	–	3.1	40	1550	86.4	[26]
PVK:EHDNPB:CdSe	0.44	4	0.04	0.18	0.15	633	–	[27]
PVK:EHDNPB:CdSe/CdS	0.1	–	0.06	0.35	1.3	633	–	[28]
PVK:EHDNPB:CdSe-HPA	0.4	4.6	0.077	0.912	9.3	633	13.2	[29]
PVK:EHDNPB:CdSe/ZnS	0.4	4.4	0.04	0.3	4.21	633	30.6	[30]
PVK:EHDNPB:CdSe/ZnS	1	–	0.02–0.1	0.09	0.23	633	7.2	[31]
PVK:AODCST:ECZ:CdTe	1.15	4.04	5	0.45	20	633	25	[32]
P-PMEH-PPV:DPP:DO3:CdSe	1	4–10	0.5	–	–	633	48.3	[33]
PVK/CdSe:ECZ:DO3	0.2	5–10	–	–	–	633	35	[34]
PVK:ECZ:DO3:CdS	1	6	>0.1	–	4.4	633	78.4	[35]
PVNPAAK-15-CdS	1:32 (mol)	5	–	–	–	633	–	[36]
PVK:7DCST:DBDC:BBP:CdSe	1	–	10	–	20	633	–	[9]
ECYENPA:Alq ₃	2	–	0.035	–	–	633	424	[11]
E7:PK-802(clay)	1	100	0.02	1.9	12	514	–	[37]
PVK:DMNPAA:ECZ:LiNbO ₃	0.1	20	15	–	–	633	35	[12]

Table 2. Several uses of QD in PR polymers and their corresponding advantages

HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; NP, nanoparticles; PR, photorefractive; QD, quantum dots

Use	Scheme of NP function	Properties	Advantage
As charge generators		Photogeneration efficiency	Broad spectra tunability over size. High photogeneration efficiency compared with organic sensitizer
To improve charge mobility		Photoconductivity	Controllable in charge mobility by tuning doping concentration
To improve trap efficiency		Electron affinity	Tunable trap density by careful choosing energy level and concentration of NP

charged NP, formed after holes from photogenerated excitons escape out of particles, fulfill the roles of traps. With a barrier formed by the wide-bandgap shells on the surface, the NP are less likely to be neutralized when encountered by mobile holes, which therefore leads to a stable trap density and an enhanced index modulation.^[28,30,31]

In addition to the high charge generation efficiency, an increasing hole mobility has been observed in a QD-doped PVK-based material, an enhancement not shown in organic-dye-doped polymers.^[38,39] The carrier mobility is dependent on the sample thickness as well as the QD concentration. By increasing the QD doping concentration, an enhanced hole mobility has been

previously observed.^[38,39] This feature has been attributed to the active participation of QD in the carrier transport process by absorbing and re-ejecting the mobile carriers. In a random distribution of QD, mobile carriers drifting through the polymer sample may easily encounter QD. Because of a potential difference across a QD under the influence of an external electric field, it is quite possible for a carrier to gain a considerable acceleration after re-ejection from the QD, as the carrier mobility in a semiconductor is much higher than that of the polymer matrix.^[38,39]

It is well known that introducing a trapping layer into PR materials can enhance the PR effect.^[40] An improved PR performance can also be achieved by incorporating NP into PR polymers as electron trappers rather than sensitizers.^[11] By a judicious choice of the NP type, such that the valence band lies below the lowest unoccupied molecular orbitals of the sensitizing molecules, a small amount of NP doping can efficiently trap the photo-generated electrons as a result of the electron affinity gradient while mobile holes remain mobile. The benefit is that the charge separation is much easier, which shortens the growth time of the gratings. As long as the NP doping concentration is high enough, trapped electrons may hop among the neighbouring NP through a pathway created by the network of NP. As electrons and holes transport and recombine simultaneously, the space-charge electric field is reduced. A small amount of NP doping will enhance the PR performance while a high concentration of NP will tend to degrade their PR performance.

5. Two-Photon Excitation in a QD-Doped PR Polymer for High Density Optical Data Storage

PR polymers have been widely used in photonic devices.^[41] Some of the photonic applications of a PR polymer are not based on the formation of a long-range refractive-index grating but rather on localized refractive-index changes in the absence of an external field. Although in defining and characterizing the PR effect an external electric field is generally required to facilitate space charge hopping through the matrix, it may not be necessary for the presence of an external electric field to introduce the charge separation and the resultant refractive index modulation in a short range.^[42] It has been demonstrated that 2P excitation can be applied to achieve a large electric field gradient within the focus of a high numerical-aperture objective. As a result, a localized refractive index change can be introduced for three-dimensional (3D) optical data storage in both PR crystals and polymers without the use of an external electric field.^[43,44] The feasibility of 2P excitation in a PR polymer has also been demonstrated through a 2BC experiment.^[45]

Because of the large 2P absorption cross-section of QD (two orders of magnitude higher than organic sensitizers)^[46] 2P excitation can greatly expand the impact of QD-dispersed PR polymers for 3D optical data storage.^[13] For the 2P experiment outlined here a small amount of CdS QD was incorporated into 4-diethylaminobenzylidene-malononitrile (DABM)-doped PVK polymers as 2P sensitizers. A Ti:sapphire ultrashort pulsed laser beam of pulse width 100 fs (Spectra-Physics Tsunami) at a wavelength of 780 nm was employed as a 2P excitation source and focussed by an objective (NA = 0.7; 20 \times) into the PR medium. Differential interference contrast microscopy was used to readout the refractive index change of the recorded bits introduced by 2P excitation. The readout contrast of the recorded bits is plotted as a function of the writing power, as shown in Fig. 3. An enhanced refractive index change is evident from

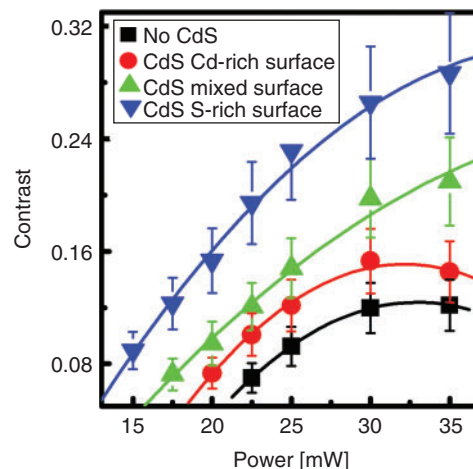


Fig. 3. Readout contrast of the refractive index change for various CdS QD with different surface stoichiometry properties.

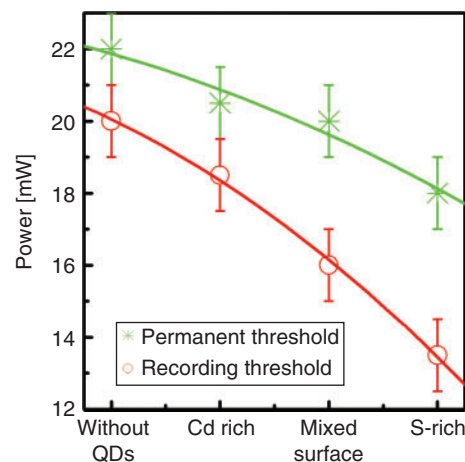


Fig. 4. Dynamic range between permanent recording and recording thresholds for surface engineered CdS QD.

the readout contrast compared with the samples without QD as sensitizers. The refractive index modulation can be further engineered through tuning the surface state of the QD between Cd-rich and S-rich. It is clear from Fig. 3 that the localized refractive index change can be enhanced as the S layer on the surface of QD gradually grows towards a S-rich state.^[13] The enhancement may be attributed to the active participation of unpassivated surface S atoms in charge separation. Dangling bonds of unpassivated S atoms can facilitate the charge separation much easier at the surface of QD by quenching irradiative recombination, which therefore enhances the charge generation efficiency and formation of the space charge electric field.

Not only do QD permit a large refractive index change under 2P excitation, but they also expand the dynamic range of erasable recording thresholds. As noted above, the reversibility is another important feature of PR polymers. The recorded bits introduced by 2P excitation can be erased completely after they are exposed to UV illumination. The margin of the laser power between permanent recording and threshold recording is plotted as a function of surface stoichiometry of CdS QD in Fig. 4. It is clear to see that gradually tuning the surface stoichiometry from Cd-rich to S-rich expands the erasable recording range. The enlarged

Table 3. Main research groups focussed on PR polymers containing QD
NP, nanoparticles; PR, photorefractive; QD, quantum dots

Groups	Nanoparticles	Technique highlight
State University of New York at Buffalo, P N. Prasad	CdS, PbS, HgS, PbSe	Introduce NP into PR polymers PR effect at telecommunication wavelength
University of Manchester, F. Aslam	CdSe, CdSe/CdS, CdSe/ZnS	PR performance of core/shell structure
University of Missouri-Rolla, J. G. Winiarz	CdTe	Enhancement of PR response time
Korea Advanced Institute of Science and Technology, O. O. Park	CdSe	Functional polymer matrix
Wuhan University of Technology, D. S. Jiang	CdS	Full function PR molecules
University of Arizona, B. Kippelen	CdSe	Change surface capping ligand fastest PR response time
Peking University, Q. H. Gong	Alq ₃	Enhancement of PR performance by introducing NP as electron traps
National Tsing Hua University, W. K. Chin	PK-802	Introduce clay NP as charge generator
University of Cologne, E. A. Sliwinka	LiNbO ₃	Introduce LiNbO ₃ NP as charge generator
Swinburne University of Technology, M. Gu	CdS	Engineer surface stoichiometry of NP two-photon excitation technique

rewritable recording power range in QD-dispersed PR polymers is a key parameter for many other applications such as rewritable data storage, dynamic waveguides, photonic crystals, and photonic sensors.

6. Summary and Future

So far various NP with different compositions, passivating ligands, and core/shell structures have been incorporated into the PR system for different functionalities. Table 3 summarizes the developments of NP-dispersed PR polymers as well as their applications, contributed from several groups around the world. It is worth mentioning that the PR polymers sensitized by organic molecules have exhibited a diffraction efficiency close to 100%^[5] and a response time down to 1 ms.^[47] However, the performance of NP-dispersed PR polymers is still inferior to the performance of the PR polymers sensitized by organic molecules in terms of the diffraction efficiency (below 20%) and the response time (slower than 100 ms).

Given the rapid development in NP synthesis, there is a huge potential to further optimize the performance of NP-doped PR polymers, which may exceed the features of PR polymers sensitized with organic molecules. Fully functionalised 'super molecules', individual molecules performing whole PR roles, are also a promising branch.^[34,36] NP sensitizers grafted directly on the polymer backbone may optimize the charge transfer ability and greatly enhance the PR performance. It has been well understood that transforming the shape of NP from sphere to rod, wire, triangle, or others can tailor their optical and electronic properties such as polarization sensitivities.^[48–52] Incorporating such NP into PR polymers can add additional functionalities such as polarization encoding^[53] and spectroscopic encoding.^[54] The combination of these new features coupled with 2P excitation in NP-dispersed PR polymers significantly expands their impact in optical data storage, waveguides, photonic crystals, and photonic devices.^[55–58] In particular, such a unique feature will allow for multi-dimensional optical data storage technologies,^[13,54,59] that break the limit of current 3D optical storage devices.

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