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Enhanced all-optical photorefractive effect of bi-functional polymer on sub-wavelength plasmonic substrate

F. GENG[a,b,*], S. F. CHEN[a], X. YE[a], B. L. CHEN[a], F. R. WANG[a]
[a]*Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900, China*
[b]*Science and Technology on Plasma Physics Laboratory, Research Center of Laser Fusion, Mianyang 621900, China*

In this paper, we have prepared bi-functional photorefractive polymer film on sub-wavelength structured substrate with thin gold film deposited on it. The introduction of nano-structured gold film with localized surface plasmon resonance can be used to enhance the all-optical photorefractive properties of polymer at room temperature which is confirmed by two-beam coupling experiment. Such enhancement is suggested to origin from both exciton-plasmon coupling and longitudinal local field intensity gradient along the optical path that existed in the sample.

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1. Introduction

Photorefractive (PR) materials have attracted great interest due to their potential applications in optical data storage and information processing [1-3]. To exhibit PR effect, the material should contain photosensitizer, charger transporter and nonlinear optical chromophore. Among various PR materials, polymers are more attractive for their additional intrinsic features such as low cost and flexibility. The essential functional species contributing to PR effect was proposed to be incorporated in single fully functional photorefractive polymer which can minimize phase separation that usually exists in composite materials [4]. However, preparing such fully functional polymer is not easy due to complex synthesis routes and tough linkage of low-content photosensitizer. A feasible semi-fully functional polymer called bi-functional polymer was thus designed with both photoconductivity and electro-optic effect [5-7], in which the nonlinear chromophore with weak optical absorption can also act as photocharge generator.

During the past years, efforts have been made to enhance the PR effect and increase the speed of PR response, such as choosing appropriate sensitizers to enhance photocharge generation or employing materials that contribute good photoconductive performance [8-11]. Another practical strategy proposed is doping metal nanoparticles into polymer composite to improve the PR performance [12]. Recently, metal nanoparticles with local surface plasmons have been applied to enhance various optical processes such as fluorescence emission, Raman scattering, light harvesting as well as some nonlinear processes [13-17]. As expected, plasmon enhanced PR effect have also been explored recently. Gu et al has shown that gold nanoparticles doped in quantum-dot sensitized polymer could not only enhance charge separation process but also reduce recombination probability of free charge and thereby improve the PR performance [18]. Later then, Choi et al demonstrated a similar result also showing plasmon enhanced PR performance of polymetric composites by gold nanoparticles [19]. In both of their studies, plasmon-exciton coupling plays an important role in processes of charge generation and transport. However, there is still little report of plasmon enhanced all-optical PR effect at zero biased electric field. In this paper, we prepared a bi-functional polymer film on a plasmonic substrate based on reactive ion etched (RIE) sub-wavelength structure. Properties of the sample such as structure, optical spectroscopy and two-beam coupling were investigated. Our result shows that the presence of the plasmonic structure could effectively improve all-optical PR effect of the bi-functional polymer.

2. Experiment

2.1. Sample preparation

The sub-wavelength structure on transparent fused silica substrate was prepared by one-step, maskless RIE method described in our previous report [20]. Before etching, the substrate was firstly cleaned and transferred to the RIE chamber. The cleaned substrate was then etched for 20 minutes with gas reactants of trifluoromethane (CHF_3), sulfur hexafluoride (SF_6), and helium (He). After etching, the substrate was further cleaned by oxygen plasma for 5 minutes to remove the RIE residuals on the surface. Later then, thin gold film was deposited onto the etched substrate by magnetron sputtering to obtain plasmonic substrate. The gold film thickness was around 30 nm which was controlled by sputtering time. Since we had prepared plasmonic substrate, the synthetic bi-functional photorefractive polymer was coated onto the substrate by drop-casting method. The bi-functional carbazole-based PR polyphosphazene containing nitro azo chromophore moieties was prepared according to our previous work [21]. The structure schematic diagram of polymer is shown in Fig. 1. The polymer was dissolved in tetrahydrofuran solvent and then about 50 μL solution was dripped onto the plasmonic substrate to form a very thin polymer film.

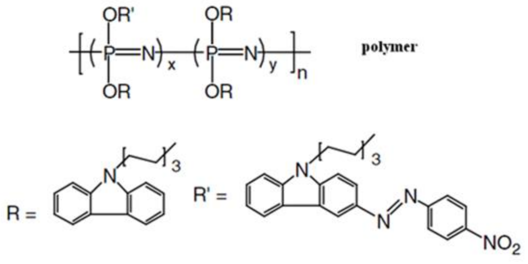

Fig. 1. The structure schematic diagram of carbazole-based polyphosphazene polymer

2.2. Characterization

Surface structure of plasmonic substrate was analyzed by scanning electron microscopy (SEM). The average thickness of the polymer film on the substrate was about 1 μm which was measured by a film-thickness meter. Optical spectral properties of the plasmonic substrate and PR polymer samples were measured using a PerkinElmer spectrophotometer. To characterize the all-optical PR performance, two-beam coupling measurement at zero biased electric filed was performed with configuration similar as the setup reported [22]. He-Ne laser (633 nm) was used as the light source split to two coherent beams that overlapped in the thin polymer film. The incident angles of beam 1 and beam 2 were about 35 degree and 38 degree with respect to the surface normal. The laser power of transmitted beams was measured and recorded simultaneously by two power-meters (Coherent Inc.).

3. Results and discussion

The one-step, maskless RIE processed substrate was revealed to have a grass-like structure with random nanocones on substrate surface in our precious study [20]. The height of the nanocone was about 300 nm, while the average lateral space between adjacent nonacones was about 100 nm. By depositing thin gold film on such surface, rough plasmonic film with grain assembly formed. In order to ensure the transmittance of the substrate, the coated gold film was controlled with thickness less than 50 nm (typically 30 nm). Each formed grain was considered to have silica nanocone covered with a thin gold shell. SEM image of the morphology of such plasmonic surface was shown in Fig. 2(a). The average size of the core-shell grain was about 120 nm. Fig. 2(b) shows the UV-Vis absorption of the plasmonic substrate. The substrate exhibits an obvious broad absorption band with peak at 535 nm. Such absorption is attributed to arise from the localized surface plasmon resonance of gold nanostructures on the surface.

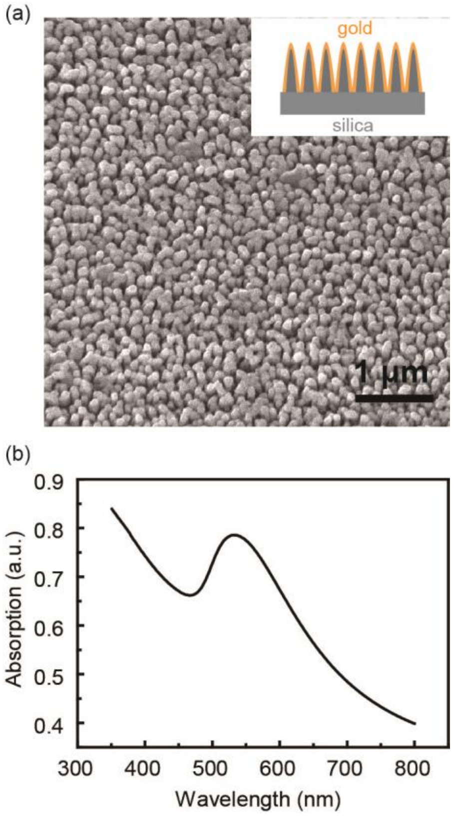

Fig. 2. (a) SEM image of the prepared plasmonic structure surface. Inset: schematic illustration of prepared plasmonic structure. (b) Optical absorption spectrum of the plasmonic substrate

In order to investigate the PR effect of polymer influenced by the plasmonic substrate, we prepared polymer film on plasmonic substrate and bare fused silica substrate respectively. Optical absorption spectra of the samples are shown in Fig. 3. Polymer on bare fused silica shows an absorption band with peak at ~440 nm, which corresponds to the absorption band of the azo group. For polymer on the plasmonic substrate, an absorption peak at 542 nm was observed red-shifted by about 7 nm in comparison with the absorption peak of clean plasmonic substrate, due to the modification of the interface by polymer near the gold nanostructure which introduces a dielectric redshift [23]. A shoulder at ~438 nm was also observed indicating the absorption of azo group in the polymer film.

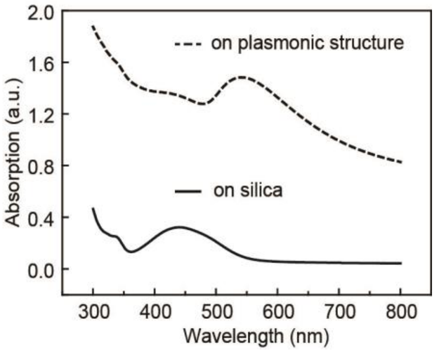

Fig. 3. Optical absorption spectra of the prepared samples

We then measured the photoluminescence (PL) of the two samples. The excitation wavelength was chosen as 450 nm, corresponding to the n-π^* transition of the azo group which was expected as photocharge generator. The results are illustrated in Fig. 4. Photoluminescence of polymer on bare fused silica shows a weak and broad emission band with peak at about 527 nm. This band is suggested from the emission of the azo group [24]. On the plasmonic substrate, the PL emission is heavily quenched. Such emission quenching indicates effective electron transfer from the polymer to the gold nanostructure because of the directly attachment between polymer and the plasmonic substrate, which consequently suppresses the radiative processes in the polymer [25].

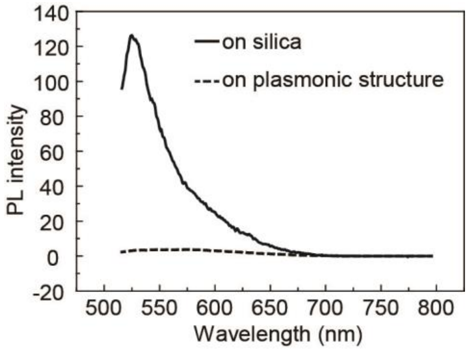

Fig. 4. Photoluminescence of polymer on silica (solid curve) and plasmonic structure (dashed curve)

The all-optical PR performance of the sample is characterized by two-beam coupling method (TBC), noting that there is no electric field applied on the sample (Fig. 5a). TBC results of the two prepared samples are shown in Fig. 5. For polymer on silica without gold nanostructure, no obvious TBC signal was observed because the coated polymer film was so thin that the PR effect was too week in such an all-optical TBC configuration. Interestingly, as shown in Fig. 5(b), a nonzero TBC signal from polymer on the plasmonic structure can be observed which appeared quickly when the two coherent beams were incident on the sample simultaneously. The normalized intensity of beam 1 and beam 2 oscillate oppositely to enlarge the gap in the first 50 seconds and then tends to be stable in the later 150 seconds. It implies that all-optical PR effect of the polymer could be enhanced by the plasmonic structure. The TBC gain coefficient is calculated by the following formula [26]:

$$\Gamma=1/d\ [\ln(\gamma\beta)-\ln(\beta+1-\gamma)],$$

where d is the thickness of the polymer film, $\beta=I_1/I_2$ is the initio intensity ratio of beam 1 (142 μW) and beam 2 (87 μW), $\gamma=I_{12}/I_1$ is the beam coupling ratio, I_{12} is intensity of beam 1 in the presence of beam 2. For the polymer on plasmonic substrate, the calculated TBC gain coefficient is about 161 cm^{-1}, which is larger than the result of pure thick polymer film reported previously [26, 27].

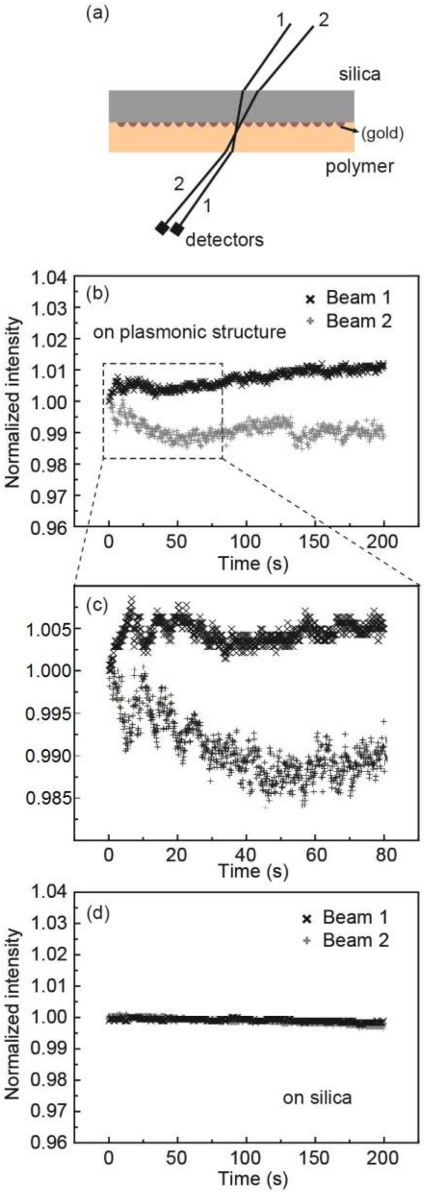

Fig. 5. (a) Schematic two-beam coupling (TBC) configuration at zero electric field. (b) TBC result of PR polymer on plasmonic structure. (c) Enlarged TBC intensity feature of the first 80 seconds shown in Fig.5(b). (d)TBC result of PR polymer on silica

The enhanced all-optical PR effect of polymer on plasmonic substrate can be possibly explained by three reasons. First, photocharge generation in polymer is related to the photon excitation process which is strongly affected by the plasmonic structure. The excitation rate is proportional to $|d{\cdot}E|^2$ where d is the transition dipole and E is the excitation electric field at the location of the dipole. As localized surface plasmon could result in significant field enhancement near the curved metal surface, the excitation of polymer near metal structure can be effectively enhanced by the sub-wavelength plasmonic structure in vicinity. So the photocharge generation process can be consequently enhanced by such exciton-plasmon coupling. Second, due to the presence of the gold nanostructure adjacent to the polymer film, the generated photoelectrons in polymer can be quickly transferred to the gold nanostructure and trapped stably by the nano-grains, which not only improve the PR response speed but also reduce the recombination possibility of the generated carriers, thus resulting in an enhanced PR effect. Third, the plasmonic structure can provide highly localized electric field near the metal surface. In the polymer film, the electric field dramatically decreases from the metal-polymer interface to the polymer-air interface, producing an appreciable longitudinal field intensity gradient along the optical path, which is considered to be an important mechanism responsible for all-optical PR effect [28].

4. Conclusion

In summary, we have prepared thin bi-functional PR polymer film on sub-wavelength structured gold film and investigated the structural and optical properties of the sample. Our results show that the introduction of metal sub-wavelength structures with localized surface plasmon resonance can provide enhanced localized electric field, which promotes photocharge generation and charge separation processes in PR polymer due to exciton-plasmon coupling, and could provide effective longitudinal optical field gradient along the optical path as well. As a result, PR polymer film on plasmonic structure exhibits enhanced all-optical PR effects, which is confirmed by all-optical two-beam coupling experiment at zero field. The calculated TBC gain coefficient is about 161 cm^{-1}, which is larger than the result of pure thick polymer film. Our result provides a prospective method for producing large area PR film with better all-optical PR performance which is valuable for practical application.

Acknowledgments

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References

[1] K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, N. Peyghambarian, Nature **371**, 497 (1994).
[2] W. E. Moerner, S. M. Silence, Chem. Rev. **94**, 127 (1994).
[3] P. A. Blanche, A. Bablumian, R. Voorakaranam, C. Christenson, W. Lin, T. Gu, D. Flores, P. Wang, W. Y. Hsieh, M. Kathaperumal, B. Rachwal, O. Siddiqui, J. Thomas, R. A. Norwood, M. Yamamoto, N. Peyghambarian, Nature **468**, 80 (2010).
[4] Q. Wang, L. M. Wang, L. P. Yu, Macromol. Rapid Commun. **21**(11), 723 (2000).
[5] Y. Chen, Y. He, F. Wang, H. Chen, Q. Gong, Polymer **42**(3), 1101 (2001).
[6] Y. Chen, Z. Chen, Q. Gong, M. Schroers, Material Letters **57**(15), 2271 (2003).
[7] L. Zhang, J. Shi, Z. Yang, M. Huang, Z. Chen, Q. Gong, S. Cao, Polymer **49**(8), 2107 (2008).
[8] Z. H. Peng, A. R. Gharavi, L. P. Yu, J. Am. Chem. Soc. **119**(20), 4622 (1997).
[9] F. Aslam, D. J. Binks, S. Daniels, N. Pickett, P. O'Brien, Chem. Phys. **316**(1-3), 171 (2005).
[10] K. R. Choudhury, Y. Sahoo, S. Jang, P. N. Prasad, Adv. Funct. Mater. **15**(5), 751 (2005).
[11] S. Wang, S. Yang, C. Yang, Z. Li, J. Wang, W. Ge, J. Phys. Chem. B **104**(50), 11853 (2000).
[12] F. Wang, Z. J. Chen, B. Zhang, Q. H. Gong, K. W. Wu, X. S. Wang, B. W. Zhang, F. Q. Tang, Appl. Phys. Lett. **75**, 32434 (1999).
[13] S. Kühn, U. Håkanson, L. Rogobete, V. Sandoghdar, Phys. Rev. Lett. **97**(1-7), 017402 (2006).
[14] K. Kneipp, M. Moskovits, H. Kneipp, Surface-enhanced raman scattering: physics and applications, Springer, New York **103**, 261 (2006).
[15] H. A. Atwater, A. Polman, Nature Mater. **9**, 205 (2010).
[16] S. Linic, P. Christopher, D. B. Ingram, Nature Mater. **10**, 911 (2011).
[17] M. Kauranen, A. V. Zayats, Nature Photon. **6**, 737 (2012).
[18] C. Li, X. Li, L. Cao, G. Jin, M. Gu, Appl. Phys. Lett. **102**, 251115 (2013).
[19] J. Choi, S. H. Ji, C. S. Choi, J. W. Oh, F. S. Kim, N. Kim, Opt. Lett. **39**(15), 4571 (2014).
[20] X. Ye, X. Jiang, J. Huang, F. Geng, L. Sun, X. Zu, W. Wu, W. Zheng, Sci. Rep. **5**, 13023 (2015).
[21] S. F. Chen, L. L. Sun, X. Luo, X. D. Jiang, W. D. Wu, Y. Fang, C. Q. Huang, R. Z. Yang, Q. J. Zhang, Chin. J. Poly. Sci. **32**, 577 (2014).
[22] J. Shi, M. M. Huang, Z. J. Chen, Q. H. Gong, S. K. Cao, J. Mater. Sci. **39**(11), 3783 (2004).
[23] G. Xu, Y. Chen, M. Tazawa, P. Jin, Appl. Phys. Lett. **88**(4), 043114 (2006).
[24] M. Han, D. Ishikawa, E. Muto, M. Hara, J. Lumin. **129**(10), 1163 (2009).
[25] B. Gao, Y. Lin, S. Wei, J. Zeng, Y. Liao, L. Chen, D.

Goldfeld, X. Wang, Y. Luo, Z. Dong, J. Hou, Nano Res. **5**(2), 88 (2012).
[26] L. Zhang, M. Huang, Z. Jiang, Z. Yang, Z. Chen, Q. Gong, S. Cao, React. Funct. Polym. **66**(12), 1404 (2006).
[27] L. Zhang, J. Shi, Z. Yang, M. Huang, Z. Chen, Q. Gong, S. Cao, Polymer **49**(8), 2107 (2008).
[28] M. M. Huang, Z. J. Chen, J. Zhang, Q. Wei, Y. H. Liu, Q. H. Gong, Y. W. Bai, X. F. Chen, X. H. Wan, Q. F. Zhou, Chi. Phys. Lett. **21**(10), 1969 (2004).

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*Corresponding author: gengf0326@sina.com