Electric-Field-Induced Layer-by-Layer Fabrication of Second-Order Nonlinear Optical Films with High Thermal Stability

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A promising modality for fabricating highly thermally stable organic second-order nonlinear optical (NLO) thin films containing low molecular weight chromophoric (LMWC) molecules was sustained by electric-field-induced layer-by-layer assembly. The new LMWC molecule but-2-enedic acid monol-[(4-4-(2-carboxy-2-cyano-vinyl)-phenylazo-phenyl)-methyl-amino]-ethyl ester (BCPE) was first designed and synthesized successfully, which possesses two negative groups at both ends and still retains the molecular polarity after ionization. Under a dc electric field, the density of the oriented chromophores BCPE deposited on the substrate is increased largely, and upon UV irradiation, accompanied with the transition of the ionic bonds between the layers to covalent bonds, the resulting NLO films possess excellent environmental stability and high thermal stability (the resulting films can retain 92% of the polar order up to 200 °C), which may rival the properties of the latest poled polymer films for electro-optic devices.

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Recently, various novel and high-performance second-order nonlinear optical (NLO) thin films containing low molecular weight chromophoric (LMWC) molecules was sustained by electric-field-induced layer-by-layer assembly. The new LMWC molecule but-2-enedic acid monol-[(4-4-(2-carboxy-2-cyano-vinyl)-phenylazo-phenyl)-methyl-amino]-ethyl ester (BCPE) was first designed and synthesized successfully, which possesses two negative groups at both ends and still retains the molecular polarity after ionization. Under a dc electric field, the density of the oriented chromophores BCPE deposited on the substrate is increased largely, and upon UV irradiation, accompanied with the transition of the ionic bonds between the layers to covalent bonds, the resulting NLO films possess excellent environmental stability and high thermal stability (the resulting films can retain 92% of the polar order up to 200 °C), which may rival the properties of the latest poled polymer films for electro-optic devices.

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6 Highly ordered arrangements of LMWC molecules can be obtained by Langmuir–Blodgett (LB) techniques and LMWC molecules can be ordered by self-assembly, through selective ionic interaction, hydrogen bonds, complexation, and so forth, with the layer-by-layer (LBL) technique.4 However, LB film materials are restricted in the application of nonlinear optics because of their poor mechanical stability. In turn, when the LBL technique is used for LMWC molecule organization, the self-ordered degree, density, and stability of LMWC molecules in LB films still need to be improved effectively due to the weak driving force for assembly and instable molecular interaction between layers.2 Accordingly, it is hitherto still considered to be a challenge for researchers to find a constructive combination of LMWC molecules and polyelectrolytes that could be used to improve the deposition density of LMWC molecules and construct stable NLO films with high performance for E-O devices.6

In this study, the authors clarify a new strategy that first introduces the electric-field-induced LBL assembly technique to the preparation of stable NLO multilayer films. Using this method, a new LMWC molecule (see the Supporting Information) and the polyelectrolytediazoerin

are effectively combined under a dc electric field (EF). Owing to the inducing influence of the EF in the assembly process, the oriented deposition of chromophores becomes easier and the deposition density of oriented chromophores is notably increased which accordingly results in the control of the thickness of NLO films. In addition, upon postirradiation with ultraviolet (UV) radiation, the diazonium and carboxyl groups in the neighboring layers can undergo a reaction to form carboxyl ester in this system. Accompanied with the transition of the ionic bonds between the layers to covalent bonds, the stability of the NLO films is improved greatly.

The chromophoric molecule but-2-enedioic acid mono-[2-{4-[4-(2-carboxy-2-cyano-vinyl)-phenylazo]-phenyl}-methyl-amino]-ethyl ester (BCPE) was first designed and synthesized by the author’s group (Scheme 1); this molecule possesses two negative groups at both ends and still retains the molecular polarity after ionization. The DAR and BCPE were dissolved and ionized (0.5 mg mL\(^{-1}\)), respectively. The assembly process (Scheme 2) was recorded and monitored using an UV–vis scanning spectrophotometer. The absorption at 375 nm is due to the \(\pi-\pi^*\) transition of the diazonium group of DAR, and the absorption at 470 nm is attributed to the azo group of BCPE. From the UV–vis absorption spectra (Figure 1a) and the atomic force microscopy (AFM) images of the single bilayer films assembled under different dc voltage EFs, we found that when the applied dc voltage was lower than 0.5 V, the effects of the external EF involving enhanced deposition density of chromophores and so forth were not displayed since their UV–vis absorption spectra were similar to that without using the EF. Conversely, when a dc voltage higher than 5 V was applied, the resulting films were no longer homogeneous and some granular domains emerged in the surface. It is shown in the inset of Figure 1a that the maximum absorption of 375 and 445 nm in transmission through the films assembled under the satisfactory 1 V dc voltage is linear as a function of the number of bilayers. It reveals that the assembly induced under the dc EF is still a uniform deposition process even though the deposition density of the oriented chromophores is increased considerably. Compared with that (470 nm) of the films self-assembled without the EF, which is very weak because of the lower deposition density of chromophores (Figure 1a), the maximum absorption of the films assembled under the 1 V dc voltage is blue-shifted to 445 nm, indicating the H-aggregates of the chromophores occurred on the substrate evidently.

It is believed that the asymmetry of the influence on the two ends of the BCPE molecule resulting from the EF exists because the intensity of the electron cloud of the end comprising cyano is much larger than that of the other end of the molecule. By reasons of the synergetic effect of the asymmetry and the driving force from the EF, it is considered that the ionized polar molecules are driven toward the anode and deposited in aslant orientation on the substrate so as to form a macroscopically noncentrosymmetric structure. That is a probable explanation for the achievement of the relatively large second harmonic generation (SHG) intensity. The oriented phenomenon is primarily proved using in situ angle-dependent transmission SHG measurement. It is illustrated that the SHG intensity reaches the largest value when the incident angle of the laser is 55° perpendicular to the normal of the films.

Using a computer-controlled oven to ramp the temperature at 5 °C min\(^{-1}\) in air, the thermal stability of the SHG intensity of the films assembled under a 1 V dc EF was investigated before and after irradiation, respectively. Figure 2c indicates that a five-bilayer NLO film of DAR and BCPE on one side of indium-tin oxide (ITO) glass after irradiation retains 92% of the polar order up to 200 °C. However, only 60% of the polar order is retained just at 140 °C in the one without irradiation (Figure 2a). The AFM image in Figure 2b indicates that the oriented arrays of chromophores or their aggregates are destroyed in the surface of the nonirradiated film. In contrast, Figure 2d reveals the retention of the ordered arrangement in the surface of the irradiated film albeit the film was heated to 200 °C. So, it is believed that the ordered orientation of the chromophores in the irradiated films is substantially stabilized. The probable explanation for that is as follows: first, upon the UV irradiation, the diazonium and carboxyl groups in the neighboring layers undergo a reaction to form carboxyl ester; consequently, the ionic bonds between the layers convert to covalent bonds, which overcome the disadvantage of the weaker strength of the ionic bonds or hydrogen bonds. Here, it should be emphasized that the photoreaction changes the interactions from ionic to covalent not only between the neighboring layers but also between the first layer of DAR and the modified substrate, which is also responsible for the improvement of the stability of the irradiated films. Second, the chains of the polyelectrolyte DAR are cross-linked to a certain extent in the multilayer after irradiation, which constrains sterically the movement of the chromophoric molecules and further prohibits the chromophoric orientation from relaxing. Furthermore, to investigate the environmental stability of the assembled films after irradiation, the films were immersed into a duplicate mixture of H\(_2\)O – DMF (2:1, v/v). Compared with a decrease exceeding 80% for nonirradiated films, the absorption values at 445 nm wavelength of the irradiated films just decreased <10% of their original value after the films were immersed in the etching mixture for 30 min (Figure 1b), which will contribute to device operation, too.

Further research involving the microstructurally oriented electrophoresis behavior of the dinegative polar molecules in an EF will be undertaken next to provide optimal physical properties for the E-O materials.

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**Supporting Information Available:** Details of BCPE synthesis, film growth, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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