

Preparation, characterization, and electro-optic properties of nonlinear optical nanohybrid

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The polyimide-silica nonlinear optical (NLO) hybrid materials with covalent links between the inorganic and the organic networks were synthesized by the sol-gel method. The prepared hybrids were characterized by IR, TGA, XRD, SEM, TEM and can be easily spin-coated, ensuring long-term alignment stability at elevated temperatures. These devices exhibit large electro-optic coefficients at 832 nm. The experimental results suggest that the hybrid thin films have potential applications as passive films for optical devices.

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Nonlinear optical (NLO) materials are key elements for future photonic technologies^[1]. A variety of materials have been investigated for their nonlinear optical properties, e.g., inorganic materials, organometallic compounds, liquid crystals, organic molecules, and polymer. Inorganic crystals, such as lithium niobate, have been used as NLO materials for several and electro-optic devices. However, these crystals have several drawbacks: high quality single crystals are difficult to grow, expensive, and not easy to incorporate into electronic devices. Compared with inorganic crystal, organic polymers are better for use in NLO applications. A lot of organic chromophores exhibit extremely high and fast nonlinearities, much better than those observed in inorganic crystals. In addition, due to the versatility of organic synthesis their nonlinear optical properties can be custom-tailored depending on the desired application. But most of the polymeric materials have either low Tg or exhibit poor reproducibility of optical quality including high optical loss, which limit their applications as optical devices^[2]. Such problems can be alleviated by either doping or incorporating NLO-active organic chromophores into an inorganic matrix yielding organic-inorganic hybrid materials via sol-gel processing^[3-7].

We synthesized nanohybrid from 3,3',4,4'-biphenyltetracarboxylic (BPDA), 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FHP), NLO chromophore NBDPA, 3-amino-propyltriethoxysilane (APTES), and TEOS. The TEOS content is 0, 5, 10, and 15, 22.5 wt.-% respectively. The nanohybrid molecu-

lar structure was shown in Fig. 1.

IR spectra of the prepared thin films were obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer. It is noted that the peaks of the characteristic imide absorption were at 726, 1380, 1725, 1780 cm^{-1} . The absorption band around 1050–1150 cm^{-1} gradually increases intensity with increasing the silica content, consisted with the formation of the three-dimensional Si–O–Si network in the hybrid film. The broad absorption around 3100–3300 cm^{-1} was assigned to the Si–OH residue, formed in the hydrolysis of alkoxy groups of TEOS. Besides, the FT-IR spectrum consists of some peaks located at 1520 (ν_{as} , –N=N–), 1250, 1520 (ν_{s} , –NO₂), 1148 (C=S), and 1728 cm^{-1} (ν_{as} , –C=O), indicating that the silica xerogel networks were composed of Si–O–Si backbones.

The fracture surfaces of hybrid thin films were examined on the SIRION scanning electron microscope (SEM). HITACHI H-600 transmission electron microscope (TEM) measured the particle sizes. In SEM photograph, no phase separation could be observed. That was, covalent bonding (Si–O–Si) between the organic and inorganic components enhanced miscibility. From TEM photograph of 10 wt.-% TEOS sample (Fig. 2), we could find the silica particle size was 60 nm. These micrographs showed the fine interconnected or co-continuous phases morphology, which improved the efficiency of stress transfer mechanisms between the two components.

An attempt for homogeneity was made to estimate the crystallinity of hybrids by the power X-ray diffraction

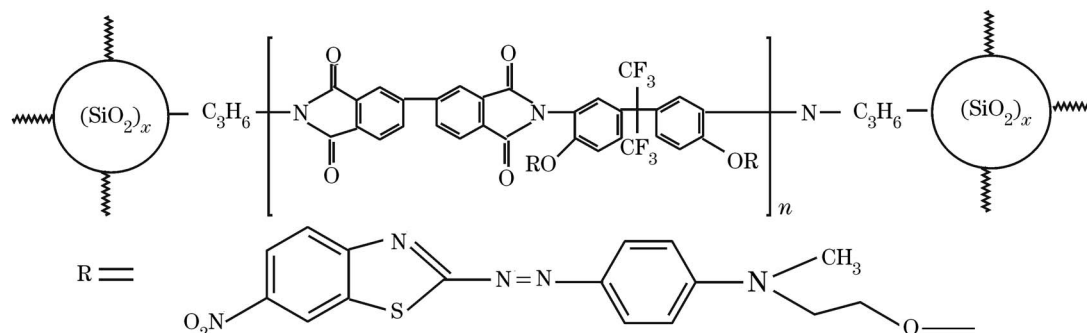


Fig. 1. Chemical structure of the nanohybrid.

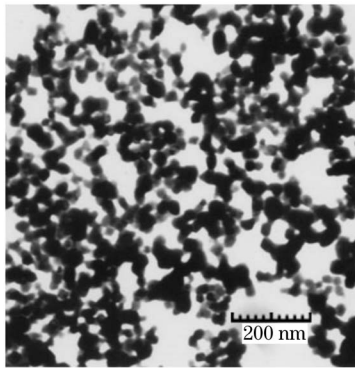


Fig. 2. TEM photograph of nanohybrid.

(XRD) measurement. XRD patterns of SiO_2 were obtained with a $\text{CuK}\alpha$ X-ray source and a step of 0.02 (2θ) and ran from $2\theta=6^\circ$ – 80° at room temperature. It was only broad amorphous halos at $2\theta=22.13^\circ$ (10 wt.-% TEOS sample), deriving from homogeneously silica matrix. This result also indicated that covalent bonding (Si–O–Si) between the organic and inorganic components enhanced miscibility. To study the thermal stability, thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA449C. The pure polyimide (0 wt.-% TEOS sample) thermal decomposition temperature (T_d) was 387°C , but its nanohybrids were 511 to 523°C for 5 to 22.5 wt.-% TEOS. The degradation temperature (T_d) of hybrid materials increased with the increase of TEOS contents. The enhanced thermal stability of hybrid materials was due to the formation of network of polyimide and the inorganic moieties, which resulted from the restriction of polymer chain mobility and became more intertwined with the rigid silica network. From DSC experiments, the pure polyimide (0 wt.-% TEOS sample) T_g was 238°C , but its nanohybrids were 358 to 363°C for 5 to 22.5 wt.-% TEOS. This indicated that the nanohybrid had higher T_g , because of the intimate mixing of organic and inorganic components in the hybrid material. The large-scale cooperative movement of the polymer chain segments (i.e., glass transition) was highly restricted by the crosslinking points as generated from the formation of covalent bonding between the polymer chains and the silica network and by steric hindrance of the rigid silica (hydrolysis and condensation of TEOS) framework. With the increase of the TEOS contents, a higher silica content resulted in a greater number of polymer-silicate bonds and more restriction of the polymer chain movement-giving rise to a higher T_g value. It is estimated that these materials would be pretty good for the practical application.

High-quality films could be easily prepared from the nanohybrid solutions in NMP by spin coating on ITO glass or other substrates. In our experiment, the poling

temperature ramping technique was used to select the optimal temperature (T_{opt}) in order to get the largest second order NLO response. As the set poling temperature increased step by step, the second harmonic generation (SHG) signal was detected at a different temperature after the temperature was held for 10–15 min. The electrooptic (EO) coefficient measurements of our nanohybrid was performed at a wavelength of 832 nm with an experimental setup similar to that described by Jiang *et al.*^[8]. The test sample consisted of a high-index prism, a thin silver film, a poled material layer, a buffer layer, and a base silver film. The silver film was thermally evaporated onto the hypotenuse face of a high-index prism as the first electrode. The thickness of the film was about 55 nm. A nanohybrid film was spin coated onto the silver substrate to a thickness of 1 – $2\ \mu\text{m}$, which can support four or five surface-plasmon modes with TE or TM polarization. A polymer buffer layer was then coated onto the polyimide film to a thickness of 3 – $5\ \mu\text{m}$ or so. Corona discharge poling was performed by alignment of the chromophore dipoles in a high static electric field while the polyimide was heated to high mobility close to its glass transition temperature. The poling voltage was 1500 V. Finally, another silver film was deposited onto the buffer layer as the second electrode. The γ_{33} values were 42, 36, 33 pm/V for 0, 5, 15 wt.-% TEOS respectively and the values retained $> 95.3\%$ at 210°C for more than 500 min.

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