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Highly Transparent and Flexible Polyimide/ZrO₂ Nanocomposite Optical Films with Tunable Refractive Index and Abbe Number

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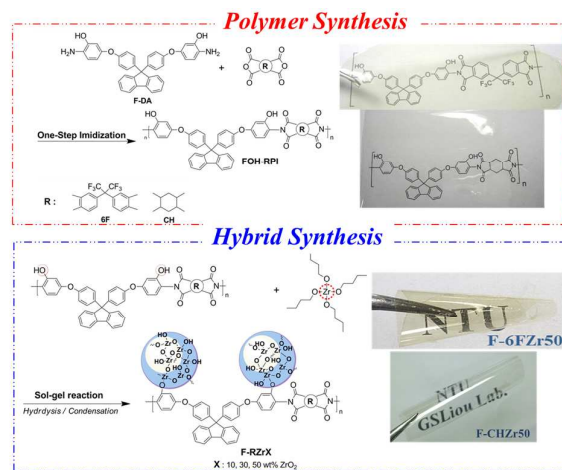
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In this study, novel thermally stable zirconia-containing polyimides (PI/ZrO₂) with excellent optical properties have been prepared successfully. The obtained flexible PI/ZrO₂ hybrid films revealed excellent optical transparency, tunable refractive index and Abbe number up to 1.804 and 32.18, respectively, which are crucial for optical devices. In addition, the PI/ZrO₂ hybrid films also exhibit higher Abbe number and transparency in visible light region due to larger energy band gap of ZrO₂ than the corresponding PI/TiO₂ system.

High refractive index polymers have been widely proposed in recent years for the advanced optoelectronic applications. In addition to the basic parameter of the refractive index, other properties such as birefringence, Abbe number, optical transparency, processability, and thermal stability are also important and have to take into consideration for practical optical applications. Therefore, it is a crucial and on-going issue to achieve the requirements mentioned above.¹ Polyimides (PIs) are the most promising candidates for optical device applications owing to their excellent thermal stability, chemical resistance, and outstanding mechanical properties. In addition, by molecular architecture design and synthesis, polyimides with good processability and well-balanced optical properties could be simultaneously obtained, making the polyimide optical materials an intensively investigated research area.² Fluorene and its derivatives with bulky and rigid structure are well-known candidates as optical materials when incorporated into polymer backbone, and could reduce the intermolecular interaction and packing density of the PI chains to enhance the transparency and processability of the corresponding PIs.³

Recently, polymer-inorganic hybrid materials have attracted a great deal of attentions owing to the outstanding combinations of mechanical, thermal, magnetic, optical, electronic, and optoelectronic properties when compared with individual polymer

or inorganic components.⁴⁻⁶ For optical material applications, the inorganic domains must be controlled lesser than 40 nm in diameter for reducing scattering loss and maintaining the optical transparency.⁷ Chemical bonding approaches based on in-situ sol-gel reaction made it possible to overcome the agglomeration phenomenon of inorganic nanoparticles by manipulating the organic/inorganic interactions at various molecular and nanometer length scales, and the polyimide/titania (PI/TiO₂) hybrids with high refractive index could be achieved by increasing TiO₂ content in our previous studies.⁸ However, the optical transparency of the obtained PI/TiO₂ hybrid films reduced dramatically at wavelength around 400 nm attributed to the low band gap of TiO₂ (3.2 eV), resulting in pale yellow color of the hybrid films. Besides, Abbe number of the PI/TiO₂ hybrid films also decreased with increasing TiO₂ content. Thus, by choosing species of inorganic materials in the hybrid system for enhancing the refractive index without sacrificing Abbe number and optical transparency in visible light region is an important issue.



Scheme 1. Synthesis and structures of the poly(*o*-hydroxy-imide)s and Preparation of PI/zirconia hybrids.

Zirconia (ZrO₂) has excellent combination of optical properties, such as high refraction index, Abbe number, and transparency on a broad spectral range due to the large band gap of ZrO₂ in the range 5.0-5.85 eV.⁹⁻¹¹ Therefore, a facile in-situ sol-gel approach for

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† Electronic Supplementary Information (ESI) available: Experimental section.

Table: basic properties. Figure: basic properties of hybrids. See DOI: 10.1039/b000000x/

obtaining optically transparent polyimide/zirconia (PI/ZrO₂) hybrids was used in this study. The pendent hydroxyl groups in PI chains could provide the organic-inorganic bonding sites with zirconium butoxide (Zr(OBu)₄) to obtain, PI/ZrO₂ hybrid films with different ZrO₂ contents for advanced optical applications.

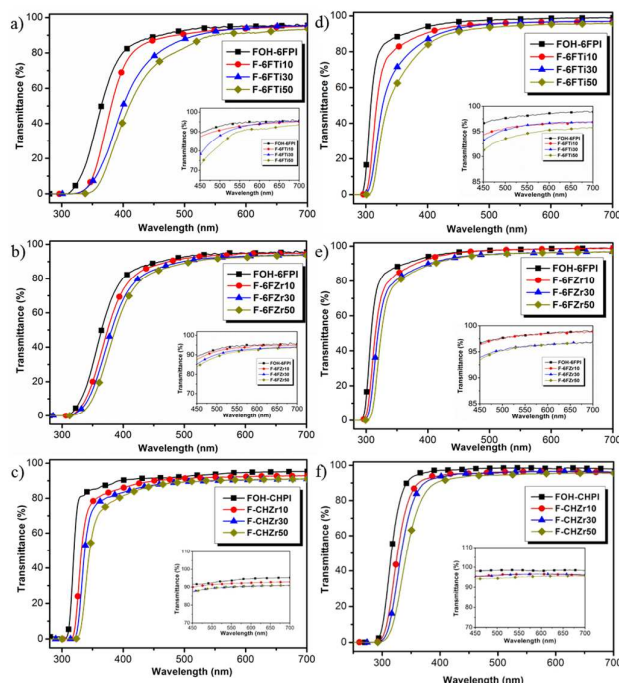


Figure 1. Optical transmission spectra of **F-6FTiX**, **F-6FzrX** and **F-CHzrX** hybrid thick films (a), (b), (c) (thickness: 19±3 μm); and thin films (d), (e), (f) (thickness: 500-600 nm).

FOH-6FPI and **FOH-CHPI** synthesized by the one-step polycondensation starting from hydroxyl-substituted diamine monomers **F-DA** and aromatic tetracarboxylic dianhydrides **6FDA** and alicyclic dianhydrides **CHDA** in the presence of a catalytic amount of isoquinoline at 170-180 °C, and the fabrication procedure of hybrid films from **FOH-6FPI**, **FOH-CHPI** and zirconia precursor are depicted in Scheme 1, respectively. The flexible, transparent, and homogeneous PI-nano-zirconia hybrid optical films with different zirconia contents (up to 50 wt%) could be successfully prepared, and which are also shown in Scheme 1. The detailed synthetic procedure and basic properties are described in the ESI†

Thermal behaviors of the obtained PI/ZrO₂ (**F-6FzrX** and **F-CHzrX**) and PI/TiO₂ (**F-6FTiX**) hybrids evaluated by TGA and TMA are summarized in Table S2. The typical TGA curves (Figure S3) of **F-6FzrX** revealed excellent thermal stability up to 400 °C both in nitrogen and air, and carbonized residue (char yield) increased with increasing zirconia content. The zirconia contents in the hybrid materials estimated based on the char yields under air flow matched with the theoretical calculation and ensured successfully incorporation of the zirconia. The typical TMA thermograms for **FOH-6FPI** and the corresponding hybrid materials revealed that the glass transition temperature increased from 257 °C to 358 °C with increasing zirconia content (Figure S4). Meanwhile, the coefficient of thermal expansion (CTE) of the pure PIs, PI/ZrO₂, and PI/TiO₂

hybrid films summarized in Table S2, and the reinforced hybrids revealed much lower CTE values than pristine PIs, and decreased with increasing the volume fraction of inorganic reinforcement.

The UV-Visible (UV-Vis) transmission spectra of the TiO₂ and ZrO₂ hybrid thick (thickness: 19±3 μm) and thin (thickness: 500-600 nm) films were investigated, and the results are summarized in Figure 1 and Table 1. These well-dispersed PI/ZrO₂ thin hybrid films revealed excellent optical transparency with lower cutoff wavelengths in the UV region. The cutoff wavelength of the PI/TiO₂ hybrid materials red-shifted with increasing the titania content, and the transparency decreased significantly at 400 nm of wavelength even when the titania domain size is less than 10 nm.¹²

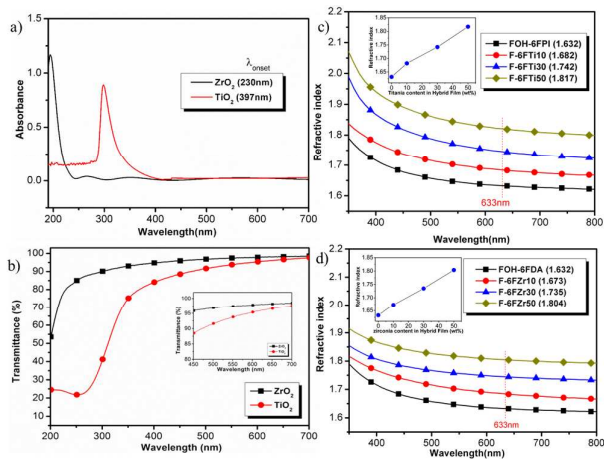


Figure 2. (a) UV-visible absorption spectra of ZrO₂ and TiO₂ (thickness: 200-300 nm), (b) optical transmission spectrum of ZrO₂ and TiO₂ thin films (thickness: 100±15 nm) (100 wt% ZrO₂ and TiO₂ were synthesized from Zr(OBu)₄ and Ti(OBu)₄ by sol-gel reaction heated to 300 °C, respectively); Variation of the refractive index of the (c) **F-6FTiX**, (d) **F-6FzrX** hybrid films with wavelength. The insert figure shows the variation of refractive index at 633 nm with different titania and zirconia content.

In addition, the cutoff wavelength of the PI/ZrO₂ hybrid films also red-shifted with increasing zirconia content. Generally, the overall optical absorbance of a hybrid film could be enhanced by not only its absorption coefficient but also the path length of light within materials. The optical thickness is to scatter incident light, and scattering always occurs when the refractive index of medium is locally perturbed which increases with increasing content of ZrO₂ in the PI matrix. Because of the particle size of ZrO₂ less than 10 nm, the red-shift phenomenon could be ascribed to the slightly variation in particle size with increasing of zirconia amount in the hybrid film

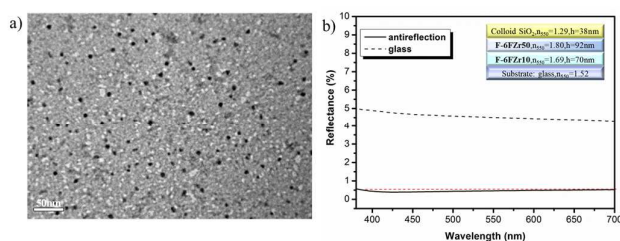


Figure 3. (a) TEM image of the hybrid film of **F-6Fzr50**; (b) Variation of the reflectance of the glass slide with wavelength by three-layer antireflection coating.

Table 1. Optical properties of the hybrid films with ZrO₂ and TiO₂

Index	Optical Properties					
	λ_0 (nm) ^a	T ₄₀₀ (%) ^b	T ₄₅₀ (%) ^b	n^c	Δn^d	V_d^e
FOH-6FPi	292/312	94/83	96/90	1.632	0.0058	19.44
F-6FZr10	295/320	92/80	96/88	1.673	0.0071	20.65
F-6FZr30	298/322	90/76	94/85	1.735	0.0096	28.23
F-6FZr50	303/323	89/72	94/84	1.804	0.0115	32.18
100wt% ZrO₂	-	95 ^f	96 ^f	1.897	0.0278	38.20
F-6FTi10	295/327	90/76	94/87	1.682	0.0073	19.54
F-6FTi30	298/327	87/58	93/79	1.742	0.0092	19.02
F-6FTi50	306/340	83/49	91/73	1.817	0.0108	19.25
100wt% TiO₂	-	84 ^g	89 ^g	1.983	0.0398	18.32
FOH-CHPI	287/308	97/90	97/92	1.635	0.0063	22.70
F-CHZr10	295/316	94/86	95/90	1.679	0.0075	21.43
F-CHZr30	298/319	93/84	95/88	1.727	0.0099	25.73
F-CHZr50	303/321	91/82	93/88	1.795	0.0118	30.28

^aThe cutoff wavelength (λ_0) from the UV-vis transmission spectra of polymer thin films/thick films (Thickness: 500-600nm/19±2μm). ^b Transmittance of polymer thin films/thick films (Thickness: 500-600nm/19±2μm) at 400 and 450nm. ^c Refractive index at 633 nm by ellipsometer. ^d The in-plane/out-of-plane birefringence (Δn) was calculated as $\Delta n = n_{TE} - n_{TM}$ were measured by prism coupler. ^e Abbe's number is given by $V_d = n_{587.56} - 1 / n_{486.1} - n_{656}$. ^f Transmittance of 100wt% ZrO₂ thin films (Thickness: 100±15nm) at 400 and 450nm. ^g Transmittance of 100wt% TiO₂ thin films (Thickness: 100±15nm) at 400 and 450nm. (100 wt% ZrO₂ and TiO₂ were synthesized from Zr(OBu)₄ and Ti(OBu)₄ by sol-gel reaction heated to 300 °C, respectively).

as the similar trend of titania hybrid system.¹² Moreover, the obtained zirconia hybrid film exhibit transparency of at 400 nm reduced much slightly, which could be ascribed to the much shorter absorption wavelength edge of ZrO₂ (230 nm) than that of TiO₂ (400 nm) due to energy band gap of ZrO₂ (5.0-5.85 eV) is comparatively larger than TiO₂ (3.2 eV) as shown in Figure 2(a).

In addition, the 100 wt% ZrO₂ thin film also exhibits superior optical transparency (96%) at 450 nm of wavelength than 100 wt% TiO₂ thin film (88%) (Figure 2(b)). Thus, these results demonstrate that PI/ZrO₂ hybrid system is an excellent alternative for high-performance optical materials in terms of transparency.

Furthermore, semi-aromatic PIs derived from alicyclic dianhydride or diamine have higher transparency due to the absence of intra- and inter-molecular charge-transfer (CT) interactions.^{8(c)} Therefore, the incorporation of alicyclic units in **FOH-CHPI** results in higher transparency in the UV-visible region than the corresponding aromatic PI (**FOH-6FPi**), and the zirconia-containing **FOH-CHPI** hybrid films (**F-CHZrX**) exhibited higher transparency than **F-6FZrX** hybrid system, the results are summarize in Figure 1 and Table1.

The refractive index dispersion in the range of 350–800 nm and refractive index at 633 nm of the obtained films with different titania and zirconia contents, respectively are shown in Figure 2(c), 2(d) and the corresponding insert figures, respectively. The refractive index increased linearly with increasing zirconia contents, suggesting that the Zr–OH groups of the hydrolyzed precursors condensed progressively to form the Zr–O–Zr structures and enhance refractive index. Furthermore, the ZrO₂ hybrid system not only could increase the refractive index but also effectively improves the Abbe number, which is attributed to the ZrO₂ with higher Abbe number than TiO₂, and the results are also summarized in Table 1.

Combining the issues of thickness, flexibility, and optical transparency, the PI/ZrO₂ hybrid optical thick film **F-6FZr50** (19±3 μm in thickness) showed higher optical transparency than the corresponding PI/TiO₂ hybrid film.

The TEM image of F-6FZr50 film shown in Figure 3(a), and the black spots uniformly dispersed in the hybrid film are ZrO₂ particles with average domain size about 6nm. The resulted ZrO₂ in hybrid film is amorphous shown in Figure S5 due to annealing temperature only could be applied to 300 °C (the crystallization temperature of ZrO₂ should be higher than 500 °C demonstrated in Figure S6).

The structure of the three layer anti-reflective coating on the glass substrate and the reflectance spectra depicted in Figure 3(b), and the glass substrate exhibited a refractive index ($n = 1.52$) higher than air ($n = 1.0$) and revealed an average reflectance of about 4.5% in the visible light range. The reflectance could be reduced significantly via the three-layer antireflection structure consisting of colloid SiO₂, F-6FZr50, and F-6FZr10 for the first, second, and third layer with the thickness and refractive index of 38 nm (1.29), 92 nm (1.80), and 70 nm (1.69), respectively. The reflectance of the glass substrate with anti-reflection coatings was less than 0.5% in the visible range (400-700 nm), demonstrating the highly transparent PI/ZrO₂ hybrid films great potential for optical applications.

In conclusion, the colorless and flexible polyimides were readily prepared from the fluorene-containing diamine with commercial dianhydrides 6FDA and CHDA, respectively. These polyimides with pendent hydroxyl groups could provide the organic-inorganic bonding sites for the formation of nano-scale zirconia by sol-gel reaction. Refractive index and Abbe number of the resulting PI/ZrO₂ hybrid system are tunable and up to 1.804 and 32.18, respectively, by increasing zirconia content. In addition, these PI/ZrO₂ hybrid films also revealed much higher optical

transparency than the corresponding PI/TiO₂ system due to the large band gap of ZrO₂. Furthermore, three-layer anti-reflective coating based on the hybrid films exhibited reflectance of less than 0.5% in the visible light region, suggesting a great potential of these novel PI/ZrO₂ hybrid films for advanced optical applications.

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