

# High refractive index polyimide–nanocrystalline-titania hybrid optical materials†

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In this study, a new synthetic route was developed to prepare polyimide–nanocrystalline-titania hybrid materials with a relatively high titania content (up to 90 wt%). A soluble polyimide with carboxylic acid end groups (6FDA–6FpDA–COOH) was first synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA), and 4-aminobenzoic acid (4ABA). Such end groups could undergo an esterification reaction with titanium butoxide and provide organic–inorganic bonding. A homogeneous hybrid solution was obtained through the mole ratio of titanium butoxide/carboxylic acid, water/acid content, and a mixed solvent system. HRTEM and XRD results indicated the formation of nanocrystalline-titania domains of around 3–4 nm in the hybrid films. The spin-coated hybrid films had relatively good surface planarity, high thermal stability, tunable refractive index ( $1.571 < n < 1.993$ ), and optical transparency in the visible range. The achieved refractive index of 1.943 is the highest among the polymer–titania based hybrid materials as far as we know. A three-layer anti-reflection coating based on the prepared hybrid films was designed and possessed a reflectance of less than 0.5% in the visible range. Our study demonstrates a new route for preparing high refractive index polyimide–nanocrystalline-titania hybrid materials for potential optical applications.

## Introduction

Organic–inorganic hybrid materials have been recognized as a new class of advanced materials because of their versatile synthetic approaches and molecular tailoring properties.<sup>1–5</sup> We are particularly interested in the hybrid materials for optical applications, such as high refractive index materials, optical waveguides, anti-reflective films, *etc.*<sup>4</sup> For such applications, the inorganic domains must be well controlled, less than 40 nm, to avoid scattering loss and retain the optical transparency.<sup>1c</sup>

Polymer–titania hybrid materials have been extensively studied as high refractive index materials, including poly(methyl methacrylate) (PMMA),<sup>6–8</sup> polyimide,<sup>9</sup> polysilsesquioxanes,<sup>10</sup> and others.<sup>11</sup> For controlling the titania domain size, a combination of *in situ* sol–gel processing with polymer molecular weight control, a coupling or chelating agent is commonly employed to prepare hybrid materials.<sup>6,7,9</sup> Our laboratory has successfully prepared trialkoxysilane-capped poly(methyl methacrylate) (PMMA)–titania hybrid optical films with their refractive index in the range 1.505–1.876.<sup>7a,b</sup> Later, such materials were treated by a hydrothermal process to produce nanocrystalline-titania hybrids with an ultra-fast nonlinear optical response.<sup>6</sup> Although

the PMMA–titania hybrid optical materials were successfully prepared, the poor thermal stability of the PMMA moiety limited their device applications, which might be resolved using thermally stable polyimide as the organic moiety.

Several polyimide–titania hybrid materials have been explored in the literature.<sup>9</sup> The homogeneous hybrid materials prepared by chelating poly(amic acid) (PAA) and titanium alkoxide monomer could control the titania size to around 1.5 nm but only up to 12 wt% titania.<sup>9a</sup> The highly electronegative OR groups of titanium alkoxide are very susceptible to nucleophilic attack by PAA and result in uncontrolled gelation or a relatively large titania domain (100 nm–1  $\mu$ m) in the hybrid materials. By using a chelating agent (such as acetylacetone) or a coupling agent (such as 3-aminopropyl trimethoxysilane), the titania content in the homogeneous films was further enhanced to be around 40–59 wt%.<sup>9</sup> However, additional coupling or chelating agent remaining in the hybrid materials might affect important thermal/mechanical/optical properties. Also, the refractive indices of such hybrid materials are limited to be only around 1.80, which is only slightly higher than recently developed high refractive index organic polymers.<sup>12</sup> Hence, the development of polyimide–titania hybrid optical materials with a higher titania content than 60 wt% is necessary.

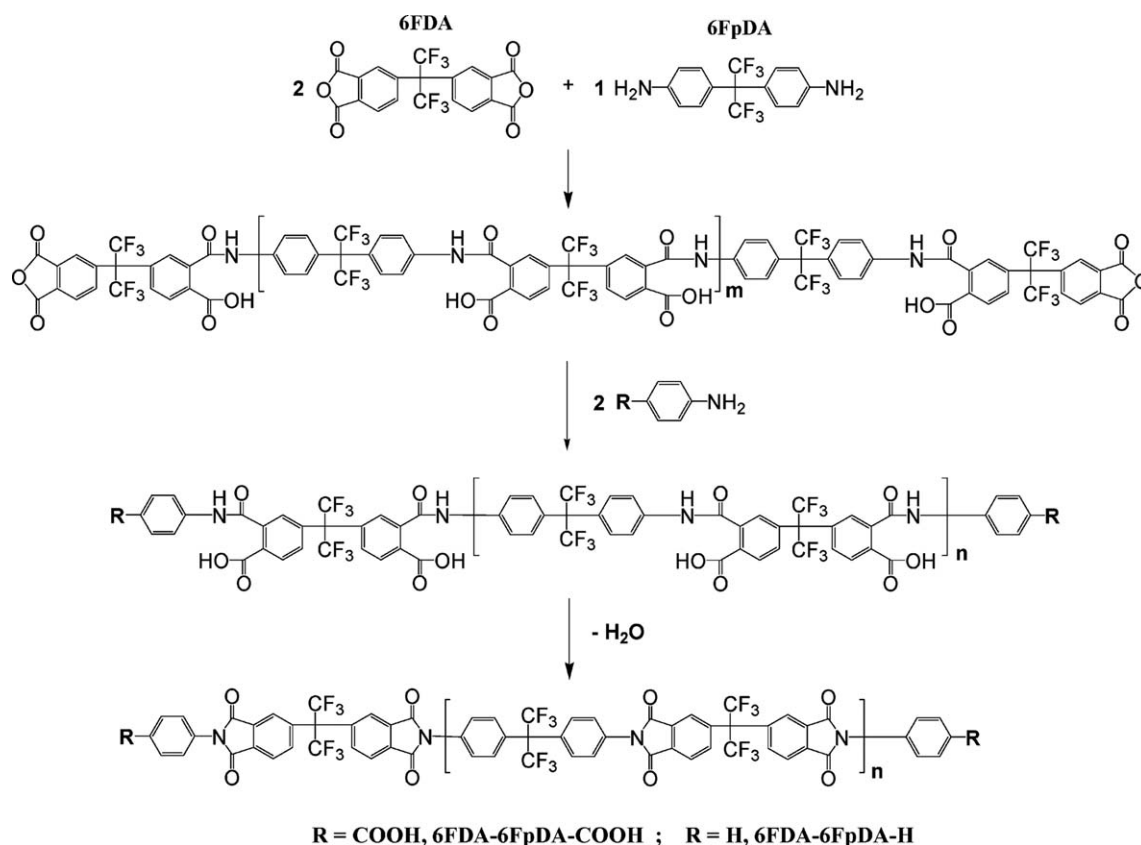
In this study, a new synthetic route was developed to prepare polyimide–nanocrystalline-titania hybrid materials with a relatively high titania content (up to 90 wt%), which led to a refractive index of around 1.943. Instead of using poly(amic acid) to prepare the titania hybrid materials, a soluble polyimide with carboxylic acid end groups (6FDA–6FpDA–COOH) was synthesized from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-(hexafluoroisopropylidene)dianiline

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**Scheme 1** Synthesis of organo-soluble polyimides, 6FDA-6FpDA-COOH and 6FDA-6FpDA-H.

(6FpDA), and 4-aminobenzoic acid (4ABA), as shown in Scheme 1. The carboxylic acid end groups could have an esterification reaction with titanium butoxide [ $\text{Ti}(\text{OBu})_4$ ] and provide organic-inorganic bonding. Thus, no additional coupling agents or chelating ligands were used in the preparation of the hybrid materials. By using a molar ratio where  $\text{Ti}/\text{COOH}$  is greater than 1, a stable sol with an isolated monodentate structure of carboxylate ligands with titanium tetraalkoxide was formed in the case of methacrylic acid.<sup>8</sup> In the present study, a mole ratio of  $\text{Ti}/\text{COOH}$  higher than 3 was used to obtain the stable sol. In the following, an appropriate amount of water and acid were added drop-wise for the hydrolysis-condensation reaction of  $\text{Ti}(\text{OBu})_4$  in the mixed solvent of *n*-butyl alcohol and *N,N'*-dimethylacetamide to proceed. Highly homogeneous hybrid films with different titania contents were thus obtained using spin-coating and thermal curing. AFM, SEM, HRTEM, and XRD were used to characterize the morphologies of the prepared hybrid materials. The thermal properties, optical absorption, and refractive index dispersion of the prepared hybrid films were studied.

## Experimental

### Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%) and 4,4'-(hexafluoroisopropylidene)dianiline (6FpDA, 99%) were obtained from Chriskev (Lenexa, USA). 4-Aminobenzoic acid (4ABA, 99%), aniline (99.5%), and titanium *n*-butoxide [ $\text{Ti}(\text{OBu})_4$ , 99%] were obtained from ACROS (Geel, Belgium).

All monomers were purchased and used without purification. 1-Methyl-2-pyrrolidinone (NMP, 99.9%), 1,3-dichlorobenzene (DCB, 99.9%), *N,N'*-dimethylacetamide (DMAc, 99.5%), and *n*-butyl alcohol (BuOH, 99.9%) were obtained from TEDIA (Fairfield, USA). The acid catalyst of titanium *n*-butoxide, 37.5 wt% HCl, was used as received from Scharlau Chemie (Barcelona, Spain). Synthesis of the PMSSQ precursor and its cured film was according to our previous report.<sup>13</sup>

### Synthesis of organo-soluble polyimide with carboxylic acid end groups (6FDA-6FpDA-COOH)

A solution-imidization technique was employed to synthesize organo-soluble polyimide (6FDA-6FpDA-COOH) with carboxylic acid end groups, as show in Scheme 1. The molecular weight and end group functionality were controlled by the reactant stoichiometry. Firstly, 3.34 g (0.01 mol) of 4,4'-(hexafluoroisopropylidene)dianiline (6FpDA) was added into a 150 ml three-necked round bottom flask and 50 ml of NMP was used to dissolve the reactants. 8.88 g (0.02 mole) of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was then slowly added into the above solution with vigorous stirring under nitrogen purging. The mixture solution was allowed to react for 8 h at room temperature. Secondly, 2.88 g (0.021 mole) of 4-aminobenzoic acid (4ABA) and 15 ml of 1,3-dichlorobenzene were added into the above solution. The 20 wt% of polyamic acid (PAA) solution was thus formed after constantly stirring the reactants for 16 h at room temperature. Then, the PAA

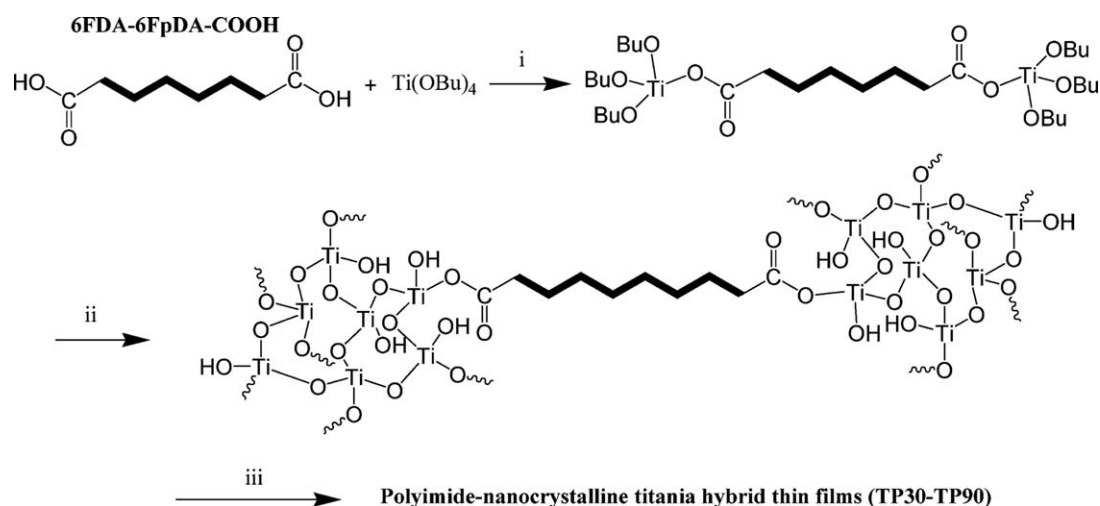
solution was thermally imidized in a 180 °C silicon oil bath for another 12 h and cooled to room temperature. The homogeneous 6FDA-6FpDA-COOH solution was precipitated with 500 ml of methanol and re-dissolved in 30 ml of THF twice. A white-gray precipitate was recovered and subsequently dried in a vacuum oven at 150 °C for 24 h to obtain 4.62 g of 6FDA-6FpDA-COOH (yield: 28.2 %). The acid value of 6FDA-6FpDA-COOH was found to be 40 mg KOH g<sup>-1</sup> using titration. The average molecular weight estimated by the acid value was around 3000. The weight-average molecular weight estimated by GPC was 3670 with a polydispersity index of 1.20. The 6FDA-6FpDA-COOH film was prepared using the following procedure: 0.5 g of 6FDA-6FpDA-COOH was dissolved in 5 ml of DMAc while stirring. The solution was filtered with a 0.2 μm PTFE filter prior to use and spin-coated on to a silicon wafer at 1000 rpm for 20 s. Then, the film was then baked at 60 °C on a hot plate for 10 min and at 150 °C for another 30 min to evaporate the solvent. In order to be compared with the polyimide-titania hybrid films, the cured film of 6FDA-6FpDA-COOH is named TP0. FTIR (cm<sup>-1</sup>): 3434 (COOH), 1788 (CO), 1726 (CO), 1610 (C<sub>6</sub>H<sub>5</sub>), 1517 (C<sub>6</sub>H<sub>5</sub>), 1435 (C<sub>6</sub>H<sub>5</sub>), 1370 (CN).

### Synthesis of organo-soluble polyimide without carboxylic acid end groups (6FDA-6FpDA-H)

The same procedure used to prepare 6FDA-6FpDA-COOH was followed to prepare 6FDA-6FpDA-H, except that 1.96 g (0.021 mole) of aniline was used in place of 2.88 g (0.021 mole) 4ABA. The yield of 6FDA-6FpDA-H was 24 % and the acid value was about 0 mg KOH g<sup>-1</sup> using titration. The weight-average molecular weight estimated by GPC was 3440 with a polydispersity index of 1.26. FTIR (cm<sup>-1</sup>): 1787 (CO), 1731 (CO), 1604 (C<sub>6</sub>H<sub>5</sub>), 1518 (C<sub>6</sub>H<sub>5</sub>), 1436 (C<sub>6</sub>H<sub>5</sub>), 1373 (CN).

### Synthesis of polyimide-titania precursors and their hybrid films

The reaction scheme for polyimide-titania precursors is shown in Scheme 2. The compositions for preparing the hybrid thin films are listed in Table 1, which are named as TPX. TPX represents the theoretical amount (X wt%) of titania in the hybrid film. Using TP50 as an example, firstly, 1.06 g (3.1 × 10<sup>-3</sup> mole) of Ti(OBu)<sub>4</sub> and 2.5 ml of butanol were added to 25 ml round bottom flask. Butanol was used to avoid alcohol interchange reaction with titanium *n*-butoxide. 0.25 g (1.8 × 10<sup>-4</sup> mole COOH) of 6FDA-6FpDA-COOH dissolved in 2.5 ml of



**Scheme 2** Synthesis of the polyimide-titania precursor and hybrid thin films, TP30-TP90: (i) esterification reaction, (ii) hydrolysis and condensation reaction under acid catalyzed conditions, (iii) spin-coating and thermal curing

**Table 1** Reaction composition and properties of the studied films, TP0-TP100

Sample	Reactant composition		Hybrid film						
	6FDA-6FpDA-COOH (wt%)	Ti(OBu) <sub>4</sub> (wt%)	TiO <sub>2</sub> content <sup>a</sup> (wt%)	TiO <sub>2</sub> content <sup>b</sup> (wt%)	<i>h</i> <sup>c</sup> /nm	<i>R</i> <sub>q</sub> <sup>d</sup> /nm	λ <sub>max</sub> /nm	λ <sub>edge</sub> /nm	<i>n</i> <sup>e</sup> , 633 nm
TP0	100	0	0	0	972	6.45	280	346	1.571
TP30	35.4	64.6	30	21.0	582	5.12	286	358	1.625
TP50	19.0	81.0	50	46.8	345	1.60	287	361	1.752
TP70	9.2	90.8	70	69.1	318	0.36	292	364	1.834
TP90	2.5	97.5	90	88.6	201	0.21	296	363	1.943
TP100	0	100	100	100	130	0.30	297	365	1.993

<sup>a</sup> Theoretical titania content in the hybrid films. <sup>b</sup> Experimental titania content estimated from TGA curves. <sup>c</sup> *h*: Film thickness <sup>d</sup> *R*<sub>q</sub>: the root mean square roughness determined from AFM. <sup>e</sup> *n*: Refractive index

DMAc were added drop-wise to the above solution with a syringe and the mixture was then stirred at room temperature for 30 min. In the following, 0.0625 g (37 wt%) of HCl aqueous solution, 0.073 g of H<sub>2</sub>O, and 1.25 ml of butanol were well-mixed and added very slowly to the above mixture and stirred at room temperature for 30 min to obtain the precursor solution of TP50. To prepare the TP50 hybrid thin film, the precursor solution was filtered through a 0.2 μm PTFE filter and spin-coated on to a silicon wafer at 2000 rpm for 20 s. Then, the films were soft-baked at 60 °C on a hot plate for 10 min, at 150 °C for 30 min, and then at 350 °C in a furnace for 90 min under nitrogen.

In order to study the effect of the carboxylic acid end groups on the morphology of the hybrid materials, a comparable film (TA50) without the acid end group was prepared using a similar procedure to that for TP50 except that 0.25 g of 6FDA-6FpDA-H was used to replace the 0.25 g of 6FDA-6FpDA-COOH.

### Preparation of titania films (TP100)

The titania parent film (TP100) was prepared by the following procedure: 6.8 g (0.02 moles) of Ti(OBu)<sub>4</sub> and 15 ml of butanol were added to a 50 ml round bottom flask. 0.25 g (37 wt%) of HCl aqueous solution, 0.56 g of H<sub>2</sub>O, and 5 ml of butanol were mixed very well to get a homogeneous solution. Then, the solution was added very slowly into the above Ti(OBu)<sub>4</sub> solution and stirred at room temperature for 1 h. To prepare the TP100 hybrid thin film, the precursor solution was filtered with a 0.2 μm PTFE filter prior to use and spin-coated on to a silicon wafer at 2000 rpm for 20 s. Then, the substrates coated with the films were soft-baked at 60 °C on a hot plate for 10 min, cured at 150 °C for 30 min, and then at 350 °C in a furnace for 90 min under nitrogen.

### Characterization

FTIR spectra of the prepared films on the doubly polished silicon wafers were obtained with a Perkin Elmer PARAGON 1000. Gel permeation chromatography (GPC) analysis was performed on a Waters GPC system consisting of Waters 2414 RI detector, Shodex columns (KF-802, 803, 805), Waters 717 plus auto-sampler, and Waters 515 HPLC pump. The system was calibrated using polystyrene standards. THF was used as the eluent, at a flow rate of 1.0 ml min<sup>-1</sup>.

TGA and DSC thermal analyses were conducted on a Perkin Elmer pyris 1 TGA and a TA Q100 with a refrigerated cooling system, respectively. Both measurements were performed under continuous nitrogen flow, at a heating rate 10 °C min<sup>-1</sup>. An atomic force microscope (AFM, Nanoscope Inc., Model DI 5000) and field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) were used to examine the surface morphology of the coated films. The microstructure of the prepared films was examined using a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F). X-Ray diffraction was performed on a MicroMax 002 X-ray scattering instrument (XRD, Osmic, PSAXS-USH-WAXS-002) using Cu Kα radiation (1.5406 Å) with comparable intensity to a focused beam from a rotating anode generator at room temperature.

UV-Vis-NIR optical absorption spectra of the prepared films on quartz were obtained using a Perkin Elmer Lambda 20 at

room temperature. An ellipsometer (SOPRA, GES-5E) was used to measure the refractive index (*n*) and the extinction coefficient (*k*) of the prepared films in the wavelength range of 300–800 nm. The thickness (*h*) of the prepared film was also determined simultaneously. Reflectance measurements were performed using a multi channel photo detector (Photal, MCPD-3000) from 380 nm to 780 nm at a 10° angle of incidence. To eliminate back reflection from the glass, the other side of glass was covered with black tape.

### Results and discussion

Fig. 1 shows the FTIR spectra of 6FDA-6FpDA-COOH (TP0), TP50, and TP100 films on double polished silicon wafers. In the spectrum of 6FDA-6FpDA-COOH, the characteristic imide groups are observed as below: 1788 cm<sup>-1</sup> (C=O asym., str.), 1726 cm<sup>-1</sup> (C=O sym., str.), and 1370 cm<sup>-1</sup> (C-N str.), respectively. Besides, the characteristic peak of polyamic acid at 1690 cm<sup>-1</sup> disappears, which suggests successful solution-imidization. Also, the characteristic peak of the carboxylic acid end group is shown in the region of 3100–3600 cm<sup>-1</sup>. The acid value of TP0 determined by titration was 40 mg KOH g<sup>-1</sup>. The average molecular weight estimated by the acid value was around 3000, which was in fair agreement with that estimated by GPC, 3670. These results reveal that the organo-soluble polyimide, 6FDA-6FpDA-COOH, with carboxylic acid end groups is successfully synthesized. The low molecular weight of TP0 was designed to ensure good miscibility between the polyimide and titania for preparing homogeneous hybrid films. Higher molecular weight polyimides could be used to prepare the polyimide-titania hybrid materials, similar to our previous report of polyimide-silica hybrid films.<sup>4b</sup>

In the FTIR spectrum of the polyimide-titania thin film, TP50, the large reduction of the absorption peak at 3200–3600 cm<sup>-1</sup> suggests an esterification reaction between carboxylic acid

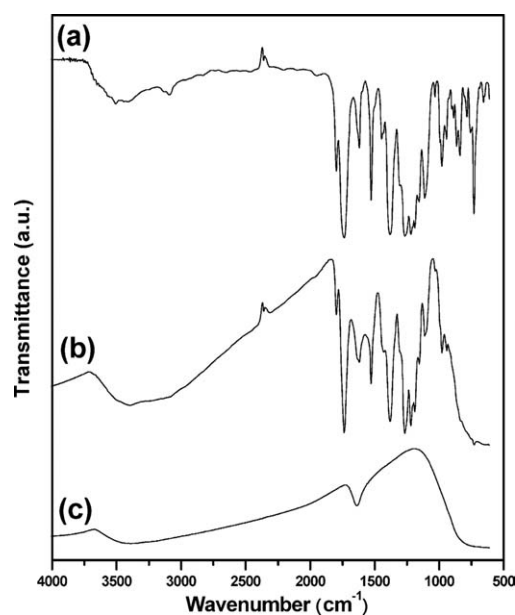
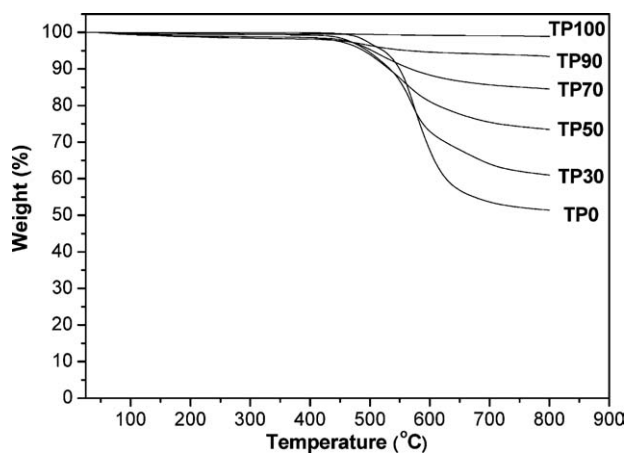


Fig. 1 FTIR spectra of the studied films on double polished silicon wafers: (a) 6FDA-6FpDA-COOH (TP0), (b) TP50, and (c) TP100.

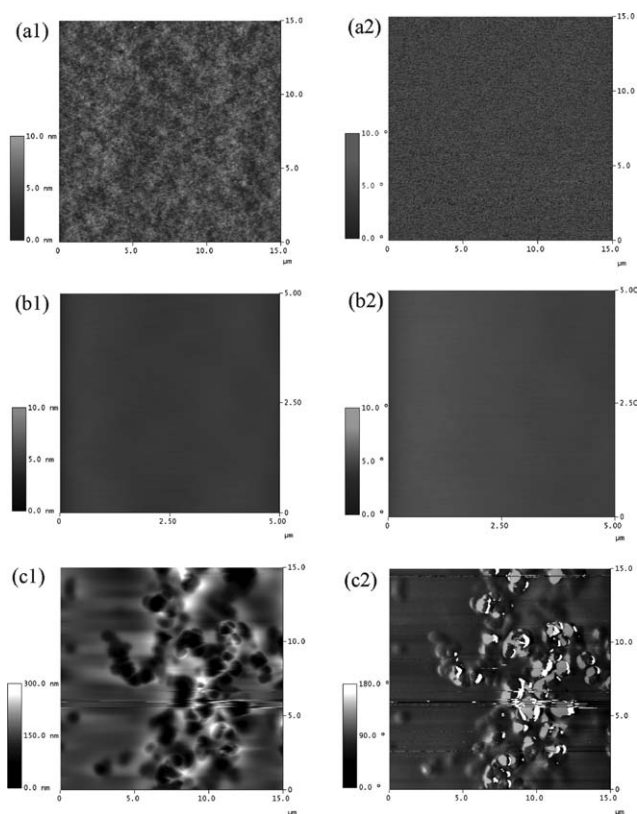


**Fig. 2** TGA curves of the studied materials, TP0–TP100, at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen flow.

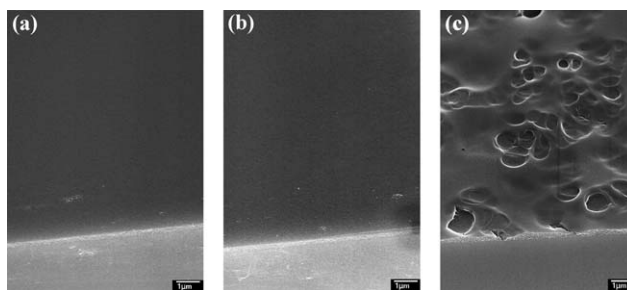
and titanium butoxide occurred. In addition, the inorganic Ti–O–Ti band is also observed at  $600\text{--}850\text{ cm}^{-1}$ . The coordination characteristic peak of the carboxylate groups with titanium could not be clearly observed in the  $1630\text{--}1340\text{ cm}^{-1}$  region due to overlap with the absorption of the phenylene and imide groups. The FTIR spectrum of TP100 is similar to that in the literature<sup>6d</sup> or our previous report.<sup>7b</sup>

Fig. 2 shows the TGA curves of the studied materials at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen flow. It is clearly seen that the all studied materials exhibit good thermal stability with thermal decomposition temperatures greater than  $480\text{ }^{\circ}\text{C}$ . The char yields of TP0 and TP100 at  $800\text{ }^{\circ}\text{C}$  are 51 and 99%, which contain 0 and 100% titania. Based on the char yields of these two materials, the titania contents in the hybrid materials are estimated as 21.0–88.6 wt% by assuming a linear relationship. They are in fair agreement with the theoretical content of 30–90 wt%, as shown in Table 1. This indicates that the titania has been successfully incorporated into the polyimide. The DSC curve of pure polyimide, TP0, shows a glass transition temperature ( $T_g$ ) of  $248\text{ }^{\circ}\text{C}$ . However, no  $T_g$  is observed for any of the polyimide–titania hybrid materials (TP30–TP90), as shown in the ESI†. It is probably that the titania limits the mobility of the polyimide segment and thus no  $T_g$  is observed.

Fig. 3(a) and 3(b) show the height and phase AFM images of TP50 and TP70 thin films. The root mean square surface roughness ( $R_q$ ) of the hybrid films analyzed by AFM is listed in Table 1. As shown in the table, the  $R_q$  values of the films TP30, TP50, TP70, TP90, and TP100, are 5.12, 1.61, 0.36, 0.21, and 0.31 nm, respectively. The low  $R_q$  and smooth images suggest that homogeneous hybrid films are prepared. On the contrary, a relatively rough surface ( $R_q = 38.6\text{ nm}$ ) is observed on the AFM image of TA50, as shown in Fig. 3(c). Note that the hybrid material TA50 was prepared from 6FDA–6FpDA–H (without carboxylic acid end groups) with  $\text{Ti}(\text{OBu})_4$  for comparison with that of 6FDA–6FpDA–COOH. The aggregated domain of  $\sim 1\text{ }\mu\text{m}$  shown in Fig. 3(c) is probably due to the titania, without the bonding with the polyimide moiety. Fig. 4(a–c) shows the cross-sectional SEM images of TP50, TP70, and TA50 obtained by tilting the specimen by  $45^{\circ}$ . The images of TP50 and TP70 show a uniform surface without apparent



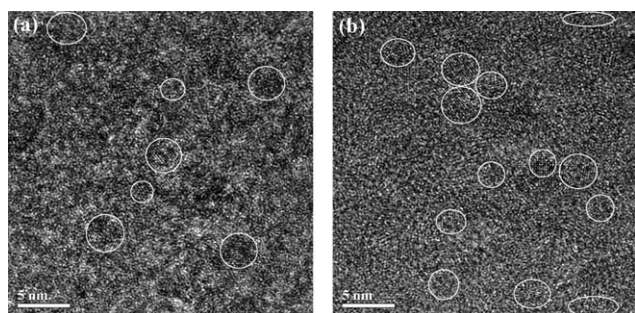
**Fig. 3** AFM images of the hybrid films coated on silicon wafers: (a) TP50, (b) TP70, and (c) TA50. (a1, b1, c1) and (a2, b2, c2) are height and phase images, respectively.



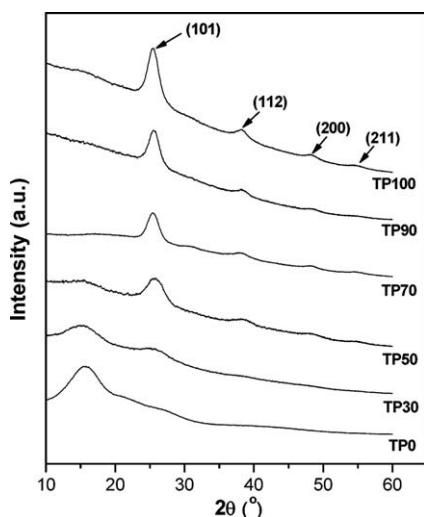
**Fig. 4** SEM images of the hybrid films coated on silicon wafers: (a) TP50, (b) TP70, and (c) TA50.

microstructure or significant titania aggregates. However, the image of TA50 in Fig. 4(c) shows the severe phase separation with a large aggregated domain similar to that from the AFM image of Fig. 3(c). Both the AFM and SEM images suggest the importance of carboxylic acid end groups of polyimide for bonding with titania and the resultant morphologies of the hybrid materials.

The cross-sectional HRTEM images of the TP50 and TP70 films are shown in Fig. 5. As shown in the figure, titania nanocrystallites with an average size of 3–4 nm are shown in both hybrid materials. Fig. 6 shows the XRD patterns of the powder prepared from the TP0–TP100 films. In the XRD pattern of TP0, a very broad peak is observed in the range  $2\theta = 10\text{--}20^{\circ}$ , which originates from the amorphous characteristic of polyimide.



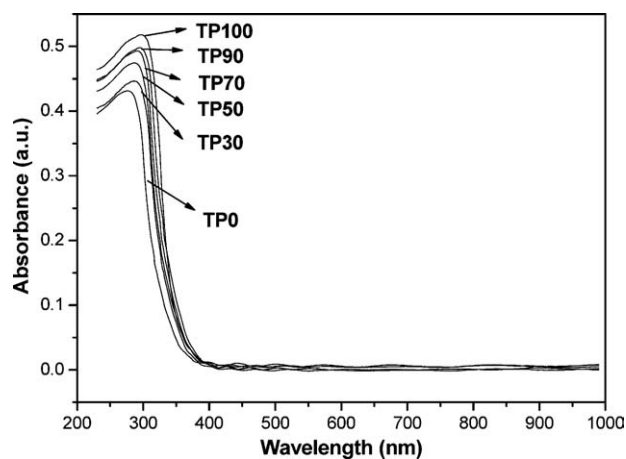
**Fig. 5** HRTEM images of the hybrid films: (a) TP50 and (b) TP70. The circles in the figure indicate the nanocrystalline-titania in the hybrid films.



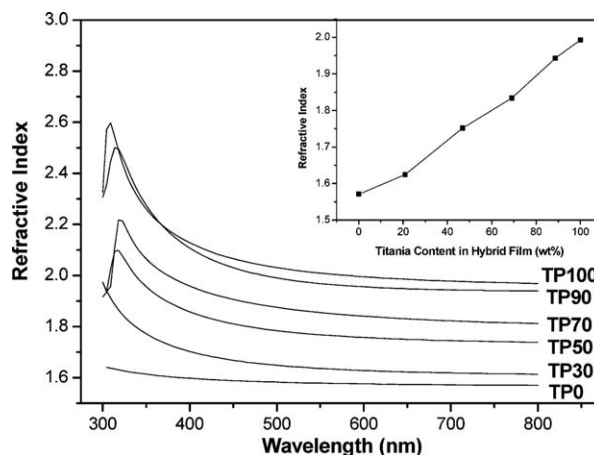
**Fig. 6** XRD patterns of the studied materials, TP0–TP100.

With increasing titania content, the intensity of a titania crystalline peak gradually increases in the range  $2\theta = 23\text{--}27^\circ$ , but that of the amorphous polyimide peak decreases. It suggests that the titania clusters are well dispersed in polyimides through the esterification and hydrolysis–condensation reactions. The broad width of the peaks is probably due to X-ray scattering resulting from the small titania nanocrystalline grains. Much more enhanced titania crystallization is obviously shown in TP100, four peaks,  $25.5^\circ$ ,  $38.4^\circ$ ,  $48.3^\circ$ , and  $54.8^\circ$ , corresponding to the (101), (112), (200), and (211) crystalline planes of the anatase titania phase, which are similar to those reported in the literature.<sup>6</sup>

Fig. 7 shows UV-Vis-NIR absorption spectra of the studied thin films, TP0–TP100. All the samples show high optical transparency in the visible region of 400–700 nm. The absorption band around 280–297 nm in the UV region is contributed from the chromophores of polyimide. By increasing the titania content, the intensity of the absorption band is enhanced and the corresponding band edge (346–365 nm) is red-shifted. Such band shift is usually observed for titania sizes less than 10 nm.<sup>14</sup> It indicates that highly homogeneous polyimide–nanocrystalline-titania hybrid materials are obtained. Fig. 8 shows the refractive index dispersion of the studied films at wavelengths of 300–800 nm while the insert figure shows the variation in



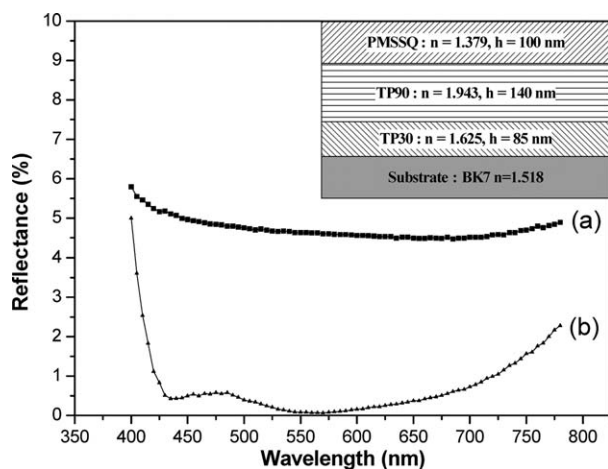
**Fig. 7** UV-Vis-NIR absorption spectra of the hybrid films on quartz, TP0–TP100.



**Fig. 8** Variation of the refractive index of the hybrid films, TP0–TP100, with wavelength. The insert figure shows the variation of refractive index with titania content.

refractive index with titania content. As shown in the figure, the refractive index at 633 nm increases linearly with titania content, 1.571 (TP0), 1.625 (TP30), 1.752 (TP50), 1.834 (TP70), and 1.943 (TP90), respectively. The refractive index of pure titania (TP100) is 1.993 at 633 nm, similar to our previous report.<sup>7b</sup> The extinction coefficient of the prepared films shown in the ESI† also suggests excellent optical transparency in the visible region. The refractive index of the hybrid film, TP90, is larger than for any other reported polymer–titania hybrid films<sup>6–11</sup> as far as we know. It indicates the successful approach of using a soluble polyimide with carboxylic end groups for preparing titania hybrid materials. The T90 hybrid optical film could have a crack-free film thicker than T100 since the polyimide moiety could release the thermal stress of titania during thermal curing. Note that the thick T100 films may have a cracking defect and limit its optical applications.

The prepared hybrid films may have potential applications in optical devices, such as anti-reflective coatings. Fig. 9 shows the structure of a three-layer anti-reflective coating on the BK7 substrate and the reflectance spectra. The BK7 optical glass



**Fig. 9** Variation of the reflectance with wavelength: (a) BK7 optical glass and (b) the three-layer anti-reflection coating. The insert figure shows the structure of the three-layer anti-reflection coating.

has a refractive index ( $n = 1.518$ ) higher than air ( $n = 1.0$ ) and leads to an average reflectance of about 5% in the visible range. The reflectance could be reduced significantly via a three-layer anti-reflection coating consisting of polymethyl silsesquioxane (PMSSQ), TP90, and TP30 as the first, second, and third layers, respectively. In order to reduce reflection through adjusting the phase of light, the optical thickness (physical thickness  $\times$  refractive index) is designed to be  $0.25 \lambda_0$ ,  $0.5 \lambda_0$ , and  $0.25 \lambda_0$  ( $\lambda_0 = 550$  nm) for the three-layer structure. Thus, the film thickness and refractive indices of PMSSQ, TP90, and TP30 are 100 nm and 1.379; 140 nm and 1.943; 85 nm and 1.625, respectively. An average reflectance of less than 0.5% in the visible range (425 nm to 675 nm) is obtained, which is significantly smaller than that of BK7 with 5%. It suggests the potential application of the prepared polyimide–titania hybrid films in optical devices.

## Conclusion

High refractive index polyimide–titania hybrid optical thin films were successfully synthesized from a soluble polyimide with carboxylic acid end groups with titanium butoxide by controlling the organic/inorganic mole ratio, water/acid content, and mixed solvent system. The titania content in the hybrid materials could be as high as 90 wt% and thus a relatively high refractive index of 1.943 was achieved. To the best of our knowledge, the refractive index is highest among the polymer–titania hybrid optical materials. The hybrid films also possessed excellent thermal properties, tunable high refractive index and optical transparency in the visible region. Three-layer anti-reflective coating based on the hybrid films possessed reflectance of less than 0.5% in the visible range. It suggested potential optical applications of the prepared polyimide–titania hybrid films.

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