Elastic Modulus and Thermal Conductivity of Thiol-ene/TiO_2 Nanocomposites

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A. Size and shape of TiO_2 nanoparticles

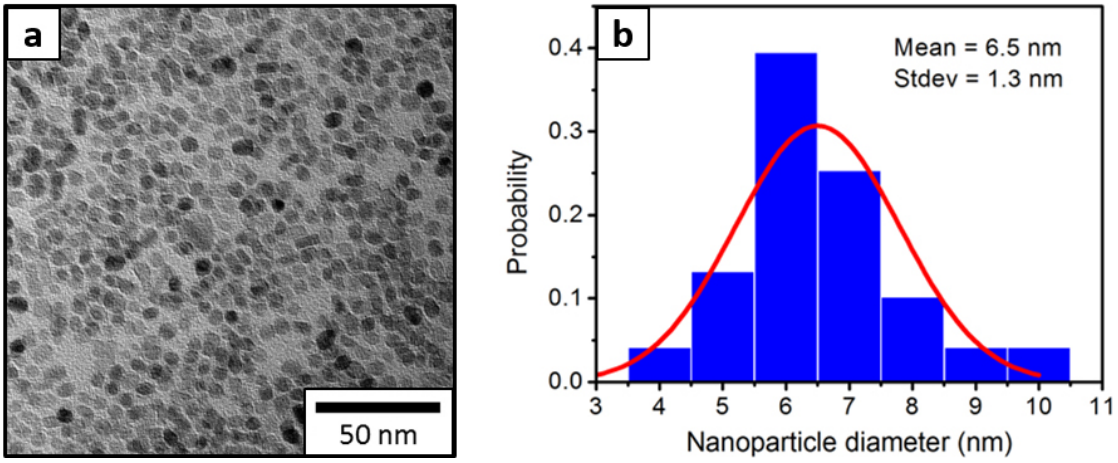

Figure S1. (a) A representative TEM image and (b) the corresponding diameter distribution of the as-synthesized TiO_2 nanoparticles.

B. Crystallinity of TiO_2 nanoparticles

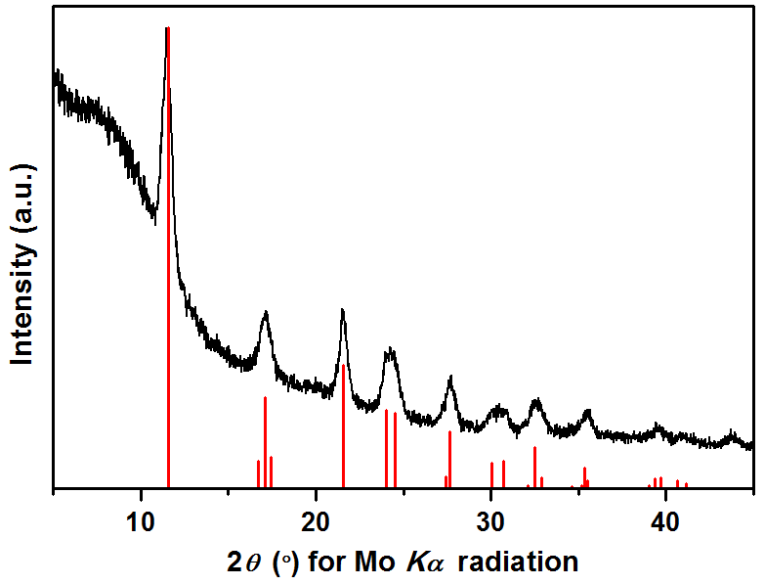

Figure S2. X-ray powder diffractogram of TiO_2 nanoparticles (black curve), matching the standard TiO_2 anatase diffraction lines (in red).

C. SEM images of nanocomposite films

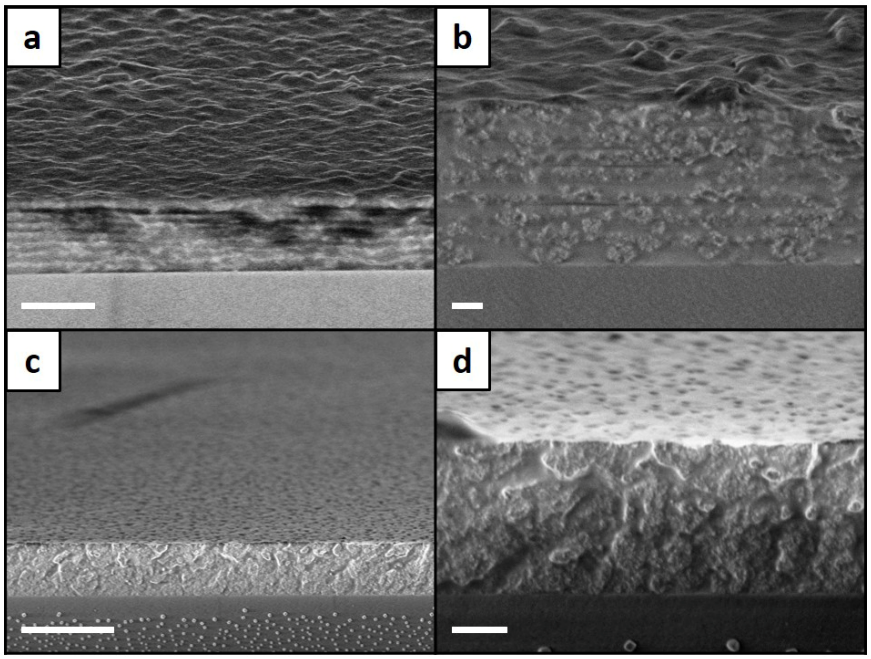

Figure S3. (a) An eight-layer TE/TiO_2 nanocomposite film containing 30 wt% TiO_2. (b) A close-up view of (a). (c) An eight-layer TE/TiO_2 nanocomposite film containing 90 wt% TiO_2. (d) A close-up view of (c). The films are supported on glass substrates and used in the BLS measurements. The scale bars are (a) 1 μm, (b) 200 nm, (c) 2 μm, and (d) 400 nm.

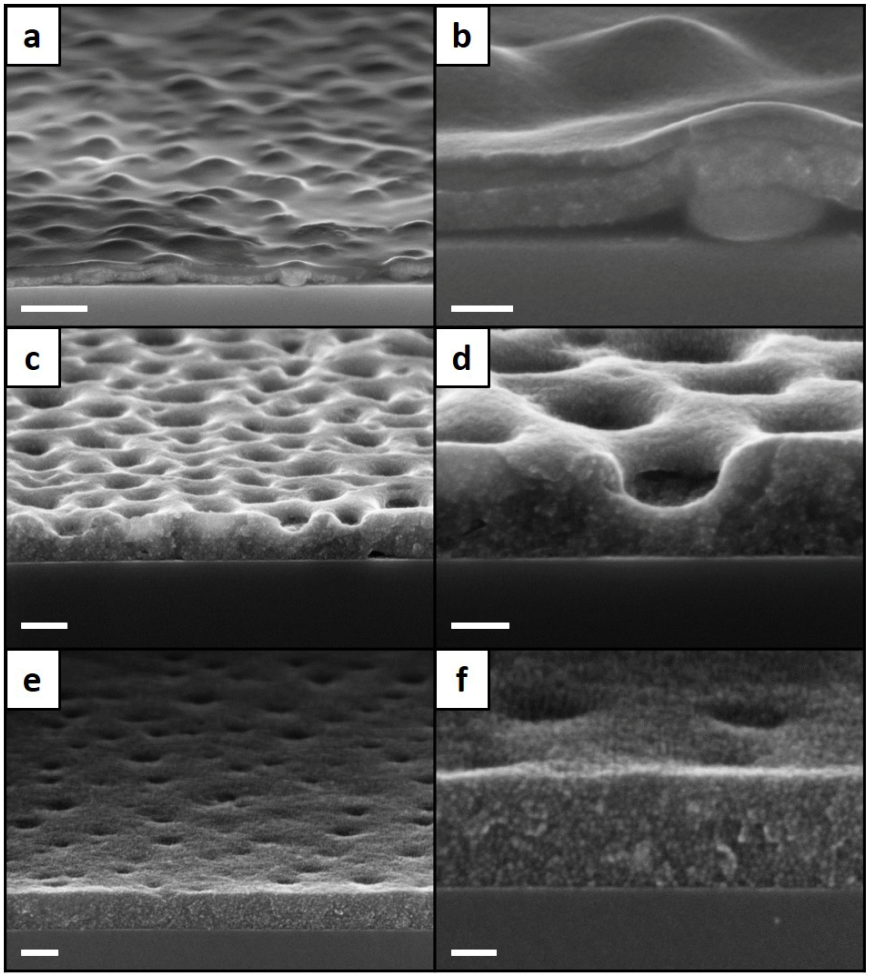

Figure S4. (a) A two-layer TE/TiO_2 nanocomposite film containing 40 wt% TiO_2. (b) A close-up view of (a). (c) A two-layer TE/TiO_2 nanocomposite film containing 80 wt% TiO_2. (d) A close-up view of (c). (e) A two-layer TiO_2 nanoparticle film containing 100 wt% TiO_2. (f) A close-up view of (e). The films are supported on Si substrates and used in the 3ω measurements. The scale bars are (a) 500 nm, (b) 100 nm, (c) 200 nm, (d) 100 nm, (e) 100 nm, and (f) 40 nm.

D. Synthetic procedure

Materials

Unless otherwise stated, all chemicals were obtained from commercial suppliers and used without further purification. Oleic acid (technical grade, 90%) was obtained from Sigma-Aldrich. Titanium(IV) *n*-butoxide (99%) and oleylamine (approx. C18-content 80-90%) were purchased from Acros Organics.

Synthesis of 4-allylcatechol and TiO_2 nanoparticles

4-Allylcatechol was synthesized as previously reported in the literature,[1] but with strongly modified work-up procedure, which included acidic hydrolyzation of the crude product and subsequent distillation of the product under high vacuum. Titania (TiO_2) nanoparticles were synthesized using a solvothermal method, according to a previously reported procedure[2] with slight modifications. Titanium (IV) butoxide (2.89 g, 2.89 mL, 8.5 mmol, 1 eq.) was added to a mixture of oleic acid (14.41 g, 16.24 mL, 51 mmol, 6 eq.), oleylamine (9.09 g, 11.19 mL, 34 mmol, 4 eq.) and ethanol (7.83 g, 9.93 mL, 170 mmol, 20 eq.). After stirring for 15 min, the mixture was transferred into a 50 mL Teflon container, which itself was placed into a bigger 250 mL Teflon inlay, already containing 34 mL of the hydrolysis solution of ethanol and water (96:4 v/v). The inlay was sealed in a stainless steel autoclave, which was then heated at 180 °C for 18 h. After cooling down to room temperature, the content of the inner inlay was decanted into a 50 mL centrifuge tube and the white solid was isolated by centrifugation (9000 rpm, 10 min) and dissolved in *n*-hexane (10 mL). The white residue of the inner inlay was dissolved in *n*-hexane (10-15 mL), transferred into a 50 mL centrifuge tube and precipitated by addition of ethanol (30-35 mL). The white precipitate was isolated by centrifugation (9000 rpm, 10 min) and redissolved in *n*-hexane (5 mL). Both nanoparticle solutions were combined and further purified by repeated

cycles of precipitation and dissolution (3 x 30/5 mL EtOH/*n*-hexane). Purified nanoparticles were stored in solution, protected from sunlight, to extend their shelf-life (stable solutions for at least up to a year).

Refunctionalization of TiO_2 nanoparticles

The as-synthesized titania nanoparticles (370 mg) in *n*-hexane (15 mL, *c* = 25 mg/mL) were refunctionalized by adding a solution of 4-allylcatechol (1.0 g, 6.7 mmol) in methanol (10 mL). The biphasic reaction mixture was sonicated at 40 °C for 15 min. After cooling to room temperature, the catechol-functionalized nanoparticles accumulated in the red-colored upper hexane phase. The lower (methanolic) phase was discarded and the nanoparticles in the hexane phase were precipitated by addition of an excess amount of methanol. The brown precipitate was isolated by centrifugation (9000 rpm, 10 min) and redissolved in toluene (3 mL). The nanoparticles were further purified by repeated precipitation and dissolution (3 x 40/3 mL MeOH/toluene).

References

(1) Kraft, P.; Eichenberger, W. Conception, Characterization and Correlation of New Marine Odorants. *Eur. J. Org. Chem.* **2003**, *2003*, 3735–3743.

(2) Dinh, C.-T.; Nguyen, T.-D.; Kleitz, F.; Do, T.-O. Shape-Controlled Synthesis of Highly Crystalline Titania Nanocrystals. *ACS Nano* **2009**, *3*, 3737–3743.