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Annealing-Free Anatase TiO_2 Nanocrystal Film as Electron Collection Layer in Organic Solar Cells

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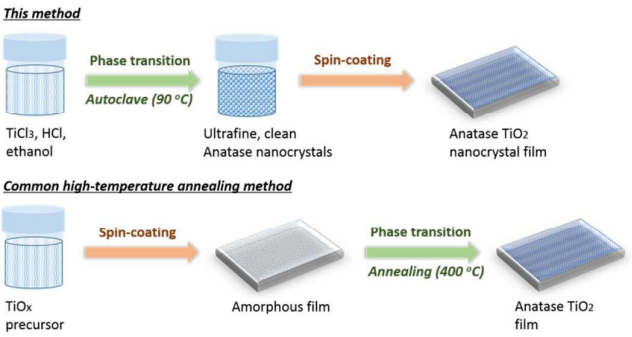
Anatase TiO_2 film, which is traditionally fabricated by high-temperature annealing of TiO_x precursors, has been widely used as electron collection layer in photovoltaics. In order to avoid the undesired high temperature treatment, in this work, we developed a convenient and moderate procedure to fabricate anatase TiO_2 nanocrystal film at room temperature. Ultrafine, clean and high-quality anatase TiO_2 nanocrystals have been pre-prepared in a simple solvothermal route and subsequently spin-coating the nanocrystal dispersion provides a well performed TiO_2 nanocrystal film without any further thermal treatment. The characteristics of TiO_2 nanocrystal film, in terms of crystallization phase, film morphology, optical and electronic properties, have been carefully studied, and at last, a typical [ITO/TiO_2/P3HT:PCBM/MoO_3/Ag] inverted photovoltaic device using TiO_2 nanocrystals as ECL has been fabricated and exhibits comparable power conversion efficiency (PCE) of 3.35% to that of the conventional device (3.39% PCE).

Introduction

Organic solar cells (OSCs) have attracted much attention in recent years because of their appealing advantages of low cost, light weight and mechanical flexibility comparing with conventional silicon solar cells.[1-5] In order to improve the performances and stabilities of OSCs, besides elegantly optimizing the material systems and nanoscale phase separations, effectively collecting the charge carriers should also be focused on.[6-8] Indeed, electron collection layers play a crucial role in influencing the device performance for their energy-aligning capabilities, and of the reported ECLs, anatase TiO_2 is much attractive for its high environmental stability, suitable energy levels and high electron mobility.[9-15]

The most common approach to fabricate anatase TiO_2 ECL is high-temperature annealing (above 400 °C) to thoroughly transform amorphous TiO_x precursors into anatase TiO_2 (scheme 1).[9, 16] Apparently, the annealing process complicates the device fabrication and limits the applications in thermal sensitive substrates. In order to overcome this defect, several approaches have been developed to construct TiO_2 ECLs in mild conditions, such as atomic layer deposition, electrochemical deposition, electrospray, high-pressure crystallization, chemical vapor deposition, chemical sintering and nanocomposites.[17-22] However, these methods require either strict experimental conditions or complex TiO_x sol-gel precursors, thus restrain the availability and simplicity of device processing. Therefore, it remains a great challenge for exploring a highly efficient and convenient approach to fabricate high-quality anatase TiO_2 film as ECL in thin film photovoltaics at low temperature.



Scheme 1. Illustration of the approach in this work and common high-temperature annealing method to fabricate anatase TiO_2 film as ECL for photovoltatics.

For common high-temperature annealing method, the essential phase transition to obtain anatase TiO_2 film was achieved above 400 °C and herein, we envisioned that the pre-prepared anatase TiO_2 followed by filming could avoid the undesired high temperature treatment (scheme 1). Recently it has been reported that the nanocrystal layer of ultrafine n-type semiconductor ZnO could serve as effective electron collection layer in perovskite solar cells[23]. Moreover, Snaith's group[24] and Boyen's group[25] separately reported similar approaches to fabricated nanocrystal TiO_2 films as ECLs. However, due to the large size of TiO_2 nanoparticals (diameter of around 4.5 nm and 6 nm, respectively), the addition of

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TiAcAc served as "electronic glue" and annealing at 135-150 °C to decompose TiAcAc to TiO_x and remove organic impurities were essential to fill the gaps between the large nanoparticals. In this work, we developed a convenient and moderate procedure to synthesize ultrafine (with diameter around 2-3 nm) and high-quality anatase TiO_2 nanocrystals without any additional surfactants or binders; then simply spin-coat the nanocrystal dispersion to give high-quality anatase TiO_2 nanocrystal film as ECL without any further treatments (Scheme 1). Finally, the utilization of this new approach was strongly indicated by efficient inverted OSCs.

Experimental section

Materials

$TiCl_3$ (15.0–20.0% basis in 30%HCl) and tetrabutyl titanate were purchased from Aladdin. Other chemicals used for synthesis were purchased from Beijing Chemical Works. P3HT and PCBM were purchased from Rieke Metals and Nano-C respectively and used as received. 1,2-dicholorobenzen was purchased from Sigma-Aldrich and used without further purification.

Synthesis of TiO_2 nanocrystals

The anatase TiO_2 nanocrystals were synthesized in a facile and moderate procedure: the mixture of $TiCl_3$ (15%–20%, 2 mL) and HCl (6 mol/L, 2 mL) in ethanol (30 mL) was heated at 90 °C for 6 h in an autoclave, followed by aging at room temperature for one week without further treatment. Before use, the TiO_2 nanoparticle dispersion was filtered through a 0.8 μm nylon syringe filter.

Preparation of nanocrystal TiO_2 film

The TiO_2 layer was obtained by spin-coating the dispersion of TiO_2 nanocrystals in ethanol at 2000 rpm for 1 min on ITO substrate and dried in air for 1 hour. The thickness of this TiO_2 layer in this spin-coating condition was estimated to be about 25–30 nm from the FE-SEM cross-section images (inset of Fig. 2a) and could be varied systematically by changing the spin-coating parameters or repeating the spin-coating process several times as needed.

Preparation of annealed TiO_2 film

4 mL tetrabutyl titanate was dissolved in 2 mL isopropanol in a conical flask for 5 min. 210 μL water and 17 μL concentrated HCl were mixed with 4 mL isopropanol for 5 min, then this solution was dropped into the conical flask over about 10 min, and the mixture was stirred for 12 h at room temperature. Before use, the resultant TiO_x precursor was diluted with isopropanol in the volume ratio of 1:3. The diluted solution was filtered through a 0.8 μm nylon syringe filter and then spin-coated (4000 rpm for 1 min) on ITO substrate and annealed at 400 °C for 30 min.

Device fabrication

The ITO glasses (~20 Ω/cm^2) were ultrasonically cleaned in detergent, deionized water, acetone and isopropyl alcohol. After routine solvent cleaning, the substrates were treated by O_2 plasma for 10 min. The TiO_2 layer (nanocrystal TiO_2 layer or annealed TiO_2 layer) was obtained by spin-coating without or with high temperature annealing as discussed before. Following that, an active layer was deposited on top of the TiO_2 layer by spin-coating a solution of the P3HT and PCBM blend with a weight ratio of 1:1 in 1,2-dicholorobenzen (40 mg/mL) at 700 rpm for 60 s in N_2 environment. The active layer was then dried in covered glass petri dishes for 1 hour without further thermal annealing. Finally, a MoO_3 layer (5.5 nm) and an Ag layer (100 nm) were deposited by vacuum thermal evaporation and a metal shadow mask was used to define the device area of 5 mm^2. The current density–voltage (*J*–*V*) characteristics of the devices were measured in air using a Keithley 2400 parameter analyzer under a simulated light (AM 1.5G) with intensity of 100 mW/cm^2.

Characterizations

X-Ray diffraction (XRD) study was performed on Bruker AXS D8 Focus apparatus using Cu Ka radiation (λ = 1.54056 Å). Ultraviolet photoelectron spectroscopy (UPS) spectra were recorded using a PREVAC XPS/UPS System under He irradiation ($h\nu$ = 21.2 eV). The transmittance of the TiO_2 films (on ITO/glass) was characterized using an UV-3600 Shimadzu UV–vis–NIR Spectrophotometer. Field emission scanning electron microscope (FE-SEM) images were measured on a JEOL JSM 4800F. Transmission electron microscope (TEM) images were taken using an FEI Tecnai G2 operated at 200 kV. The atomic force microscopy (AFM) measurements were performed on an S II Nanonavi probe station 300 HV (Seiko, Japan) in contact mode.

Results and discussion

TiO_2 nanoparitcles were synthesized in a mild and facile procedure without any additional surfactants or binders. The morphologies of the resulted TiO_2 nanoparticles were characterized by TEM measurement. As shown in Fig. 1a, ultrafine and homogeneous TiO_2 nanoparticles were obtained by this method and the sizes distributed mainly in the range of 2–3 nm (inset of Fig. 1a), which were quite essential for fabricating high-quality TiO_2 film by spin-coating (*vide infra*). The crystalline phase of TiO_2 nanoparticles was determined carefully by HRTEM and XRD measurements. As shown in the inset of Fig. 1b, the apparent lattice fringes (d_{200} = 0.19 nm) on the particles revealed the anatase crystallization[26] and the assembled nanoparticles on the substrate exhibited continuous crystalline regions (Fig. S1 in ESI†), which proved a good crystallinity degree of the nanoparticle assembled film. Meanwhile, the XRD pattern (Fig. 1b) of the TiO_2 nanocrystal film confirmed that the film was composed of small size anatase nanocrystals due to the widened standard anatase diffraction peaks (JCPDS no. 21-1272). It should be noted that the anatase TiO_2 nanocrystals prepared by this method were dispersed well in ethanol to form transparent colloid solution without any additional surfactants or binders which were undesired for fabricating high-quality TiO_2 layer because they would bring organic impurities and needed thermal decomposition to remove. This character combining with the

advantage of ultrafine sizes of the TiO_2 nanoparticles enabled us to fabricate a transparent and compact TiO_2 layer by simply spin-coating the nanocrystal dispersion. It should be highlighted that the TiO_2 layer produced by this method was already pre-crystalized to anatase phase and able to directly apply as ECL in thin film photovoltaics without further crystallization treatments involving of annealing step. In order to study the advantages of room-temperature processed nanocrystal TiO_2 layer as ECL in depth, conventional TiO_2 layer which was deposited from TiO_x sol-gel and then annealed at 400 °C to obtain anatase phase was prepared on ITO substrate for comparison.

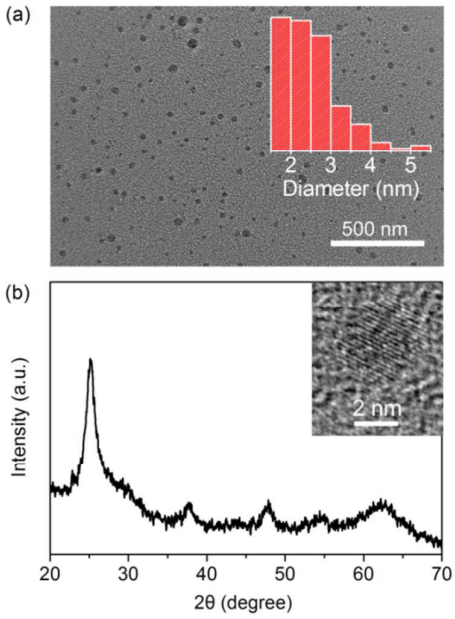

Fig. 1 (a) TEM image of the TiO_2 nanoparticles. Inset shows the size distribution histogram (155 particles measured), (b) XRD pattern of the anatase TiO_2 nanocrystals. Inset is HRTEM crystalline lattice fringes.

The morphology of the spin-coated anatase TiO_2 nanocrystal film was studied by FE-SEM and AFM measurements. In the FE-SEM images (Fig. 2a), tiny nanocrystals assembled tightly to form compact layer. Because of the ultrafine size of the nanocrystals, interspaces between neighbouring particles could be drastically avoided to consolidate the film and benefit the electrical contact to electron transport. Both the top view and cross-section FE-SEM images (Fig. 2a) showed that the nanocrystal TiO_2 film was compact with no visible cracks or porosity, providing the important foundation for this film to serve as ECL. There were partial raised clusters on the nanocrystalline film surface and the AFM measurement revealed that the root mean square (RMS) surface roughness of the film was 5.77 nm (Fig. 2b), which is obviously higher than that of the conventional high-temperature annealed TiO_2 film (0.98 nm, Fig. S2 in ESI†). The higher roughness derived from the nanoparticle assembled surface could enhance the TiO_2/active layer interfacial surface area, which might be benefit to the carrier collection at the interface of ECL and active layer with shorter electron–hole diffusion lengths comparing with the film thickness.[27-29]

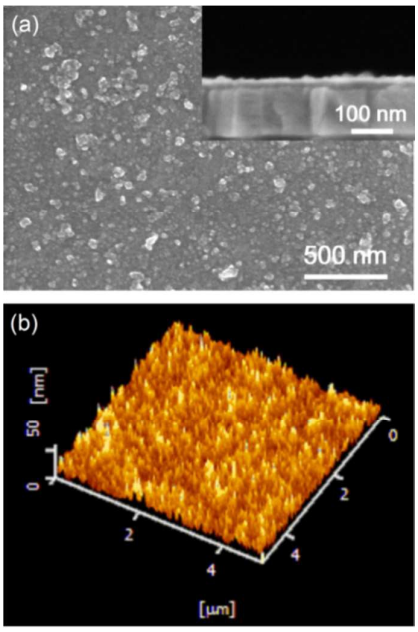

Fig. 2 (a) Top view and cross-section (inset) FE-SEM images of the TiO_2 nanocrystal film. (b) AFM image of the TiO_2 nanocrystal film.

The optical transmittance spectra of various TiO_2 films on ITO substrates, including nanocrystalline TiO_2/ITO prepared by this method, conventional high-temperature annealed TiO_2/ITO and bare ITO, were compared (Fig. 3), and the thickness of the TiO_2 films on ITO was consistent with that in the optimized OSCs. Compared with bare ITO, the TiO_2 nanocrystal film could decrease the transmittance of ultraviolet light (350–400 nm) and enhance the transmittance beyond 450 nm. The decrease of transmittance in the ultraviolet region was caused by the absorption of the nanocrystal TiO_2 film (Fig S3 in ESI†). This feature could protect the active layer from UV radiation and simultaneously enhance the transmittance of incident light in visible region. The protection effect of TiO_2 film to active layer by decreasing the transmittance of ultraviolet (350-400 nm) light was investigated through time-dependent absorption measurements under the irradiation of simulated AM 1.5 sunlight. The active layers on the ITO/PEDOT:PSS substrate and ITO/TiO_2 substrate were irradiated under AM 1.5 sunlight, and the absorption spectra were recorded at various time. As shown in Fig S4 of ESI†, the absorbances are decreased gradually along with extending irradiation time. After irradiation of 7 h, 98.86% and 98.00% of initial absorbances are remained for the active layers on the substrates with and without TiO_2 layer, respectively. It directly proves the protection effect of TiO_2 film to active layer by decreasing the transmittance of ultraviolet light. For the annealed TiO_2/ITO, the transmittance decreased on a large scale especially in range of 420–580 nm, probably due to the destruction of ITO film during the high-temperature treatment.[19] In most high-

temperature processed TiO_2 based solar cells, thermostable substrate such as FTO was explored instead of ITO, which would bring with low transmittance and conductivity for the electrode. Herein, the utilization of the room-temperature processed nanocrystal TiO_2 layer not only protected ITO from thermal destruction but also enabled the fabrication of solar cells on other thermal sensitive substrates such as polyethyleneterephthalate (PET).[2]

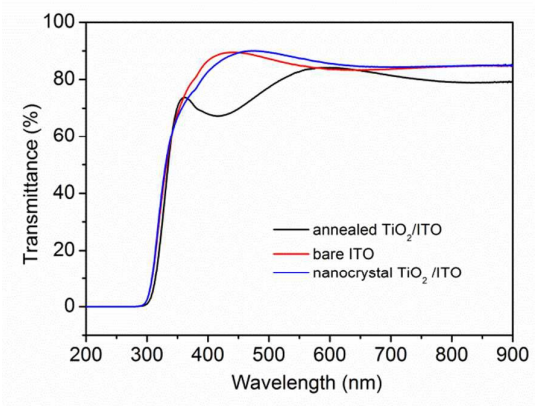

Fig. 3 Optical transmittance spectra of nanocrystal and annealed TiO_2 films on ITO substrates.

The electronic properties, in terms of energy levels and electron mobility, of the TiO_2 nanocrystal film were also studied. Based on the UPS and UV–Vis absorption spectra (Fig. S5 and S6 in ESI†), the valence band (VB) and band gap of the TiO_2 nanocrystal film were determined to be 7.0 eV and 3.3 eV respectively, and as a consequence, the conduction band (CB) was calculated to be 3.7 eV. The energy levels of this TiO_2 nanocrystal film were in good agreement with those of other reported TiO_2 ECLs,[18, 19] which demonstrated its energy-aligning capability as effective ECL. The electron mobility of the TiO_2 nanocrystal film was estimated by the space charge limited current (SCLC) method (Fig. S7 in ESI†) and the value of 2.7×10^{-3} cm^2 V^{-1} s^{-1} could surpass that of the previously reported anatase TiO_2 nanorods (2.33×10^{-4} cm^2 V^{-1} s^{-1}) measured by the same method.[30] These electronic properties endow the TiO_2 nanocrystal film with effective electron collecting and transporting ability.

In order to illustrate the utilization of the TiO_2 nanocrystal film with favourable morphology, optical and electronic properties, a prove-of-concept inverted OSC has been fabricated which explored the TiO_2 nanocrystal film as ECL (device **1**). On the pre-clean ITO substrate, the TiO_2 nanocrystal film was fabricated by spin-coating the dispersion of TiO_2 nanocrystals in ethanol. Without any further treatment on the TiO_2 nanocrystal film, a P3HT:PCBM active layer, a MoO_3 layer and an Ag electrode were deposited successively (for details, please see experiment section). Fig. 4a showed a FE-SEM cross-section of the device and illustrated the schematic device structure. Device **1** exhibited a satisfying photovoltaic performance with an open circuit voltage (V_{oc}) of 0.59 V, a short-circuit current density (J_{sc}) of 9.27 mA cm^{-2}, a fill

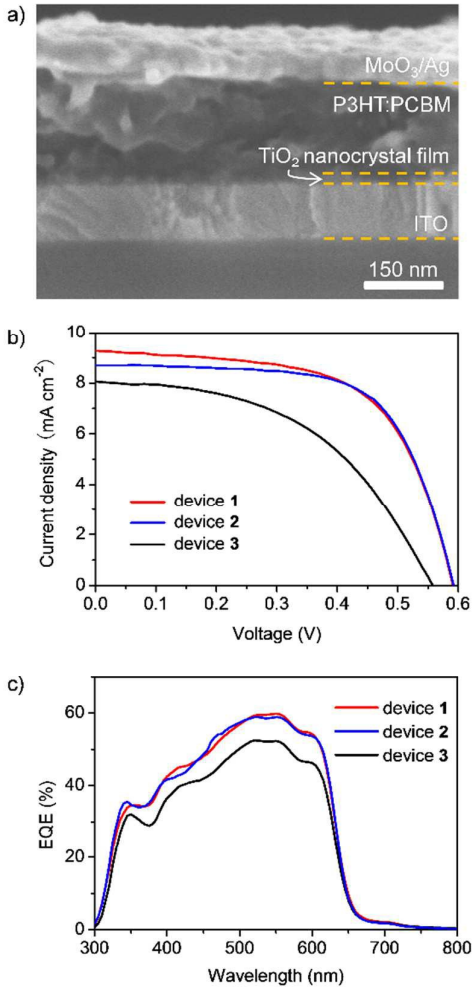

Fig. 4 (a) FE-SEM cross-section image of device **1**. (b) Current density *versus* voltage (*J*–*V*) curves of device **1**–**3** (with the structures of device **1**: ITO/TiO_2 nanocrystal layer (25–30 nm)/P3HT:PCBM (210 nm)/MoO_3 (5.5 nm)/Ag (70 nm), device **2**: ITO/PEDOT:PSS (40 nm)/P3HT:PCBM (210 nm)/LiF (1 nm)/Al (100 nm), and device **3**: ITO/ annealed TiO_2 layer (35 nm)/P3HT:PCBM (210 nm)/MoO_3 (5.5 nm)/Ag (70 nm)). (c) EQE spectra of devices **1**–**3**.

factor (FF) of 0.61, and an overall power conversion efficiency (PCE) of 3.35% (best value of 30 devices with an average PCE of 3.11%) respectively under simulated AM 1.5 (100 mW cm^{-2}) sunlight (Fig. 4b). The performance of device **1** was comparable to that of the conventional OSC (device **2** with the structure of ITO/PEDOT:PSS (40 nm)/P3HT:PCBM (210 nm)/LiF (1 nm)/Al (100 nm)) with high-performance PCE of 3.39%. (Fig. 4b) This result strongly illustrated the effective electron collection and transport abilities of the nanocrystal TiO_2 layer and the feasibility to explore the TiO_2 nanocrystal film as ECL for OSCs. In addition, a reference inverted OSC (device **3**) with traditionally high-temperature annealed TiO_2 as ECL was fabricated on ITO substrate for comparison. The performance of device **3** gave a reduction on V_{oc}, J_{sc}, FF and thus an overall PCE which are 0.56 V, 8.07 mA cm^{-2}, 0.48 and 2.18% respectively (Fig. 4b), due to the optical and electronic

alteration of ITO/TiO_2 layers under high-temperature annealing.[19, 31] This comparison highlighted the advantage of fabricating TiO_2 nanocrystal film using this method in moderate condition to avoid the undesired high-temperature treatment on TiO_2 ECL.

To gain a deep insight into the effect of TiO_2 nanocrystal film, the external quantum efficiency spectrum (EQE) of device **1** was measured and compared with that of devices **2**-**3**. As shown in Fig 4c, the EQE spectrum of device **1** with TiO_2 nanocrystal film is comparable with that of conventional device **2**. The maximum of EQE value is 60% at 555 nm for device **1**. In contrast, the EQE spectrum of device **3** with high-temperature annealed TiO_2 film is much lower, and the maximum of EQE value decreases to 52% at 520 nm. The EQE measurements further indicate the effectiveness and advantage of the TiO_2 nanocrystal film fabricated by this annealing–free method.

Conclusion

An extremely convenient and moderate approach to fabricate anatase TiO_2 nanocrystal film as electron collection layer in photovoltaics has been developed. Ultrafine, clean and high-quality anatase TiO_2 nanocrystal dispersion has been pre-prepared in a simple route and spin-coating the nanocrystal dispersion at room temperature provides a well performed TiO_2 nanocrystal layer. It should be noted that, without any further treatments (such as high temperature annealing), the TiO_2 nanocrystal film exhibited favourable morphology, optical and electronic properties, and in consequence was successfully applied as ECL in inverted OSC. This approach has overcome the ugly defect of high-temperature annealing process in traditional fabrication of anatase TiO_2 ECLs. As thin TiO_2 ECLs are broadly used in other thin film solar cells such as inverted hybrid solar cells and planar perovskite solar cells besides OSCs, the annealing-free TiO_2 nanocrystal film has the potential to be employed in other photovoltaic systems and will meet further demands for low temperature processing plastic solar cells.

Acknowledgements

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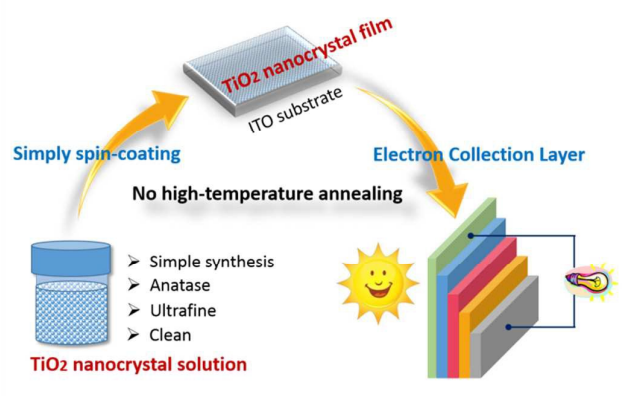
31 Ref: The high temperature annealing process leads to a serious degree of In species diffusion between the TiO_2 and ITO films, which lowers the conductivity of ITO and bring quenching centers into TiO_2 layer, thus has a negative effect on the efficiency.

TOC Figure



Annealing-free TiO_2 electron collection layer in organic solar cell based on ultrafine, clean and high-quality anatase TiO_2 nanocrystals.