

Highly Flexible Coaxial Nanohybrids Made from Porous TiO₂ Nanotubes

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The present work reports facile, large-area production of coaxial nanohybrids by simple electrodeposition of a number of materials into top-porous TiO₂ nanotubes. The nanohybrids are found for the first time to be *highly flexible* after peeling off from mother substrates.

TiO₂, especially the well-aligned TiO₂ nanomaterials, has attracted a great deal of attention for photoelectric devices, photocatalysis, electrochemical sensors, and photoelectrolysis.^{1–13} As n-type semiconductors, they have been used in dye-sensitized solar cell (DSSCs)^{1–4} and in organic/inorganic solar cell devices.^{14–17} In DSSCs, the use of liquid electrolyte leads to serious leakage issues. One solution to solve the problem is to use polymeric sensitizers as the hole transport material to make fully solid state solar cells. TiO₂ serves as the electron transport alternative to 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) in the polymeric solar cell to give organic–inorganic hybrid solar cells. The p-type conducting polymers can be polypyrrole (PPy) or poly(3-hexylthiophene) (P3HT).^{18–20} In this type of solar cell, TiO₂ NTs are introduced to form an interdigitated, ordered p–n heterojunction with p-type materials, and this structure is expected to be able to facilitate exciton dissociation and charge transfer.^{21,22} However, it is difficult to fill nanotubes with conducting polymer by normal solution casting processes.^{14,23} The possible dewetting of conducting polymers from the TiO₂ surface will deteriorate charge separation at the interface.

On the other hand, normally prepared TiO₂ NTs are usually bundled at the top layer and have large outer tube spacing, making electrodeposition very difficult to initiate and to occur inside the tubes as de-

ABSTRACT Anatase TiO₂, an n-type semiconductor, has gained considerable research interest over several decades due to its photocatalytic activity. Most recently, its properties for photoelectrical conversion in solar cells has been explored. Anodized TiO₂ nanotube (NT) arrays have been developed and possess improved photocatalytic, sensing, photoelectrolytic, and photovoltaic properties. The present work describes using TiO₂ as the building block to form ordered heterojunctions *via* simple electrodeposition with materials of potential interest, including conducting polymers (polypyrrole, poly(3-hexylthiophene)), inorganic semiconducting materials (CdS), and metals (Ni and Au, etc.). A key finding is that the synthesized TiO₂ NT–nanowires(nanotubes) nanohybrids are highly flexible after being peeled off from mother substrates, which is in contrast to more fragile pure TiO₂ NTs. These highly flexible coaxial nanohybrids are expected to have potent applications.

KEYWORDS: flexible · conducting polymer · coaxial nanohybrids · TiO₂ nanotube

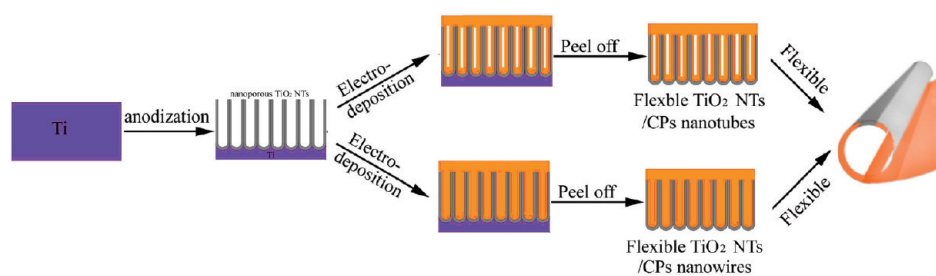
sired. The control over a one-dimensional, ordered structure remains rather difficult at present.^{24–29} Recently, we and other groups have reported novel TiO₂ nanotube structures with nanoporous morphology on top (top-porous NTs, TPNTs, Supporting Information Figure S1),^{30–32} making it possible to achieve electrodeposition only inside the tubes and to allow *in situ* formation of coaxial nanohybrids. Moreover, self-supported TiO₂ with high flexibility has never been reported since people normally think TiO₂ is too fragile to be bent. Although, Gratzel *et al.* reported TiO₂ NT-based flexible DSSCs on a Ti substrate;^{33,34} bending was only limited to a small scale. One way to enhance the toughness of materials is to incorporate a soft phase (for example, polymers, metals, etc.) to form interpenetrating structures. In this communication, we report that these issues could be solved and desirable structures achieved. Nanohybrids with interdigitated p–n ordered heterojunction, which are well-aligned and possess high flexibility, can be readily prepared by electrodeposition into TiO₂–TPNTs and then peeled off.

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Scheme 1. Schematic representation of the preparation of coaxial p–n junction of TiO₂ nanotubes and conducting polymer (CP) composite materials.

RESULTS AND DISCUSSION

As shown in Scheme 1, fabrication started with making TiO₂–TPNTs by a two-step anodization process, followed by electrodeposition of conducting polymers, metals, or inorganic semiconductors as nanowires or nanotubes, to form coaxial nanohybrids. These p–n junctions can be peeled off titanium substrates in a saturated HgCl₂ solution to get flexible TiO₂ NT–conducting polymer composite materials. In production of TiO₂ NT arrays, nanoporous structures are formed on the top surface of NTs with a newly developed anodization approach and are different from the usual NT structure prepared by conventional methods.

These top-porous networks can prevent NT bundling and allow a high tube packing density that can inhibit polymerization between gaps of TiO₂ NTs. TiO₂–TPNT with different diameters, length, and wall thickness can be produced by controlling the anodization conditions.³¹

The highly ordered TiO₂–TPNTs with tunable diameters and length were prepared in ethylene glycol solution containing HF (standard 48% aqueous HF) with delicate reaction conditions. Shown in Figure 1a–c are the field emission scanning electron microscopic (FESEM) images of TiO₂–TPNTs from top view and cross-sectional view. The samples were prepared in EG solution containing 3 vol % HF (standard 48% aqueous HF) at 60 and 40 V for 3 h at room temperature. It is seen that the TiO₂ NTs show porous morphology on top (Figure 1a,c) but nanotubular structure underneath (Figure 1b). The TiO₂–TPNTs are well-aligned with uniform diameter and wall thickness and without bundling, sealing, or etching pits. The average inner diameter of nano-

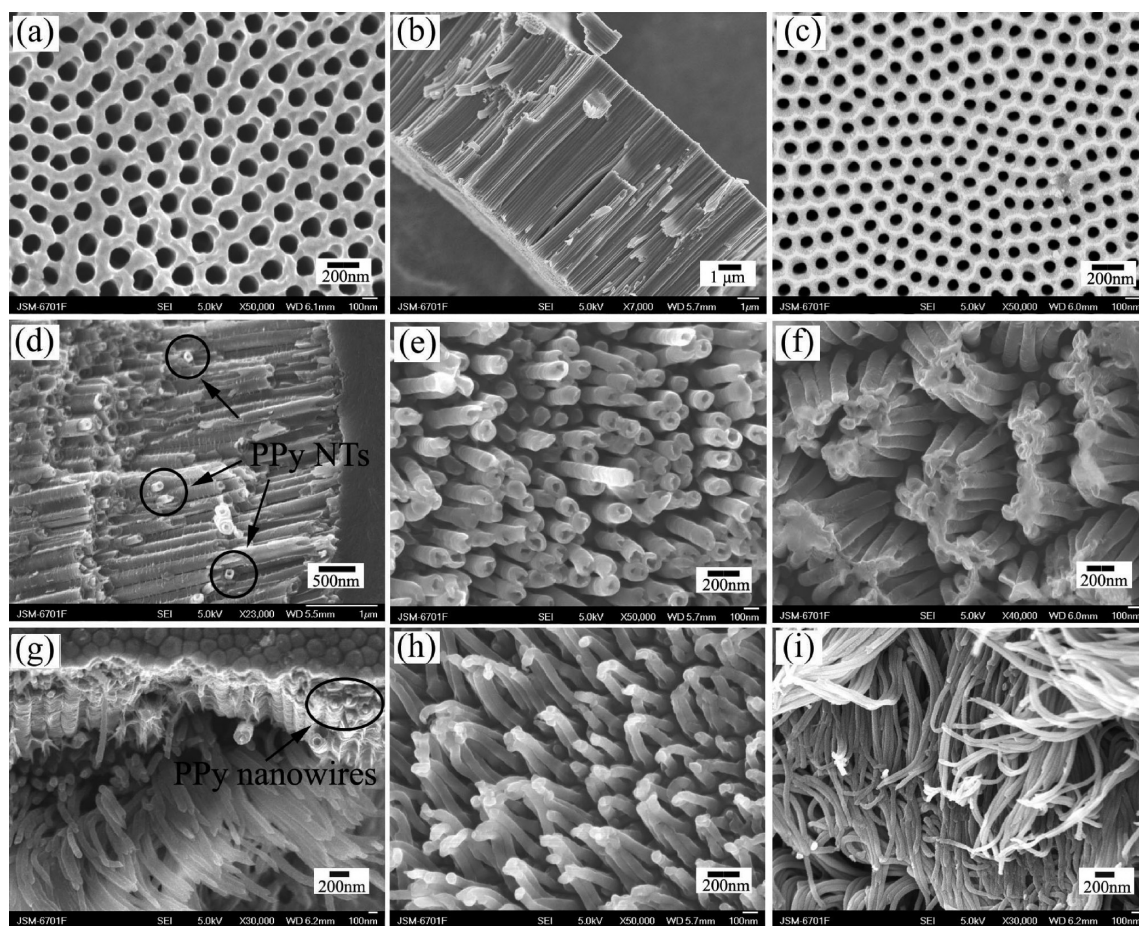


Figure 1. FESEM images of top-porous TiO₂ NT arrays and PPy NTs and nanowires. (a,c) Top surface views of perfectly aligned TiO₂ NTs, (b) cross-sectional view of the TiO₂ NTs, (d,g) cross-sectional and bottom surface views of coaxial PPy–TiO₂ NTs and nanowires, (e,h) images of PPy NTs and nanowires peeled off the substrates by mechanical force, (f,i) images of PPy NT and nanowire self-supporting films after dissolving the TiO₂ NTs in HF aqueous solution.

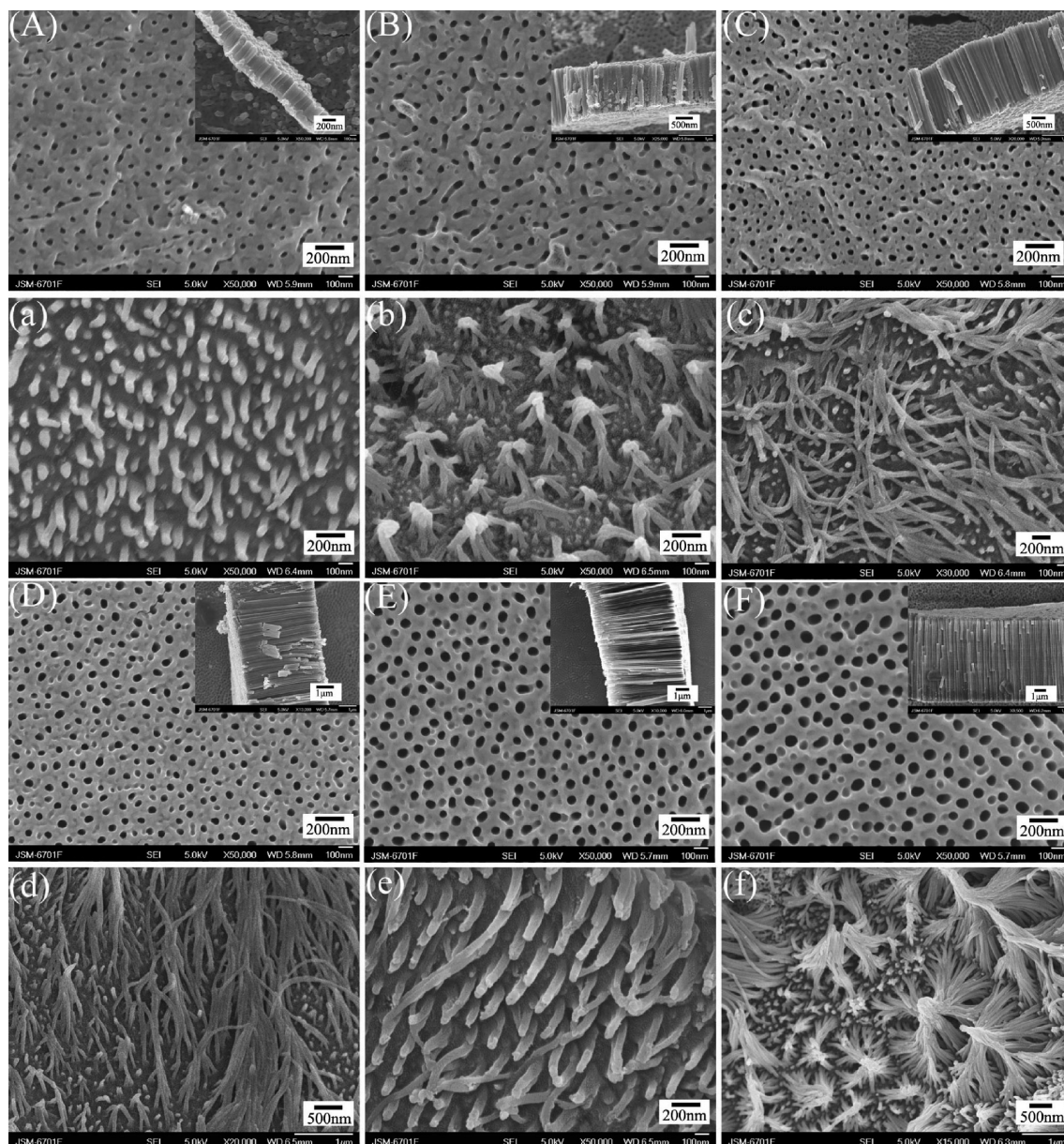


Figure 2. FESEM images of the controllable nanoporous TiO_2 NTs (A–F) and the PPy nanowires (a–f) after peeling off the TiO_2 NTs by mechanical force.

tubes from the FESEM is estimated to be 87 (8.5 μm long) and 135 nm. Electropolymerization of pyrrole resulted in either PPy nanotubes or nanowires depending on the polymerization time at set bias. Figure 1d–f shows that PPy nanotubes were formed in the TiO_2 –TPNTs of Figure 1a in a 0.1 M LiClO_4 acetonitrile solution containing 0.2 M pyrrole at 0.8 V for 5 min. Figure 1g–i shows that the PPy nanowires were deposited in TiO_2 –TPNTs shown in Figure 1c at 0.8 V for a longer polymerization period of 30 min. From the cross-sectional and bottom surface views of Figure 1d,g, we can see that the coaxial junctions of TiO_2 and PPy nanotubes and nanowires were well-formed. PPy filled the entire TiO_2 –TPNTs (from bottom to top of the TiO_2 –TPNTs), and the diameters matched very well with the diameter of TiO_2 –TPNTs. For other possible

applications, the PPy arrays can be gently peeled off by mechanical force with double adhesive tape (Figure 1e,h). Alternatively, the PPy nanowires and nanotubes can be obtained in full length after completely dissolving TiO_2 –TPNTs in a HF aqueous solution (Figure 1f,i). The diameter and length (from several hundred nanometers to several hundred micrometers) of the TiO_2 –TPNTs can be well-controlled by adjusting anodization conditions, such as voltage, reaction time, temperature, *etc.*³¹

The coaxial nanohybrids with different aspect ratios can be readily prepared in the same way (Figure 2). Figure 2A–F shows the top morphologies and the cross-sectional FESEM images of nanoporous TiO_2 NTs with different diameters (35–100 nm) and length (350 nm to 7.5 μm) obtained at 80 V by controlling anodization

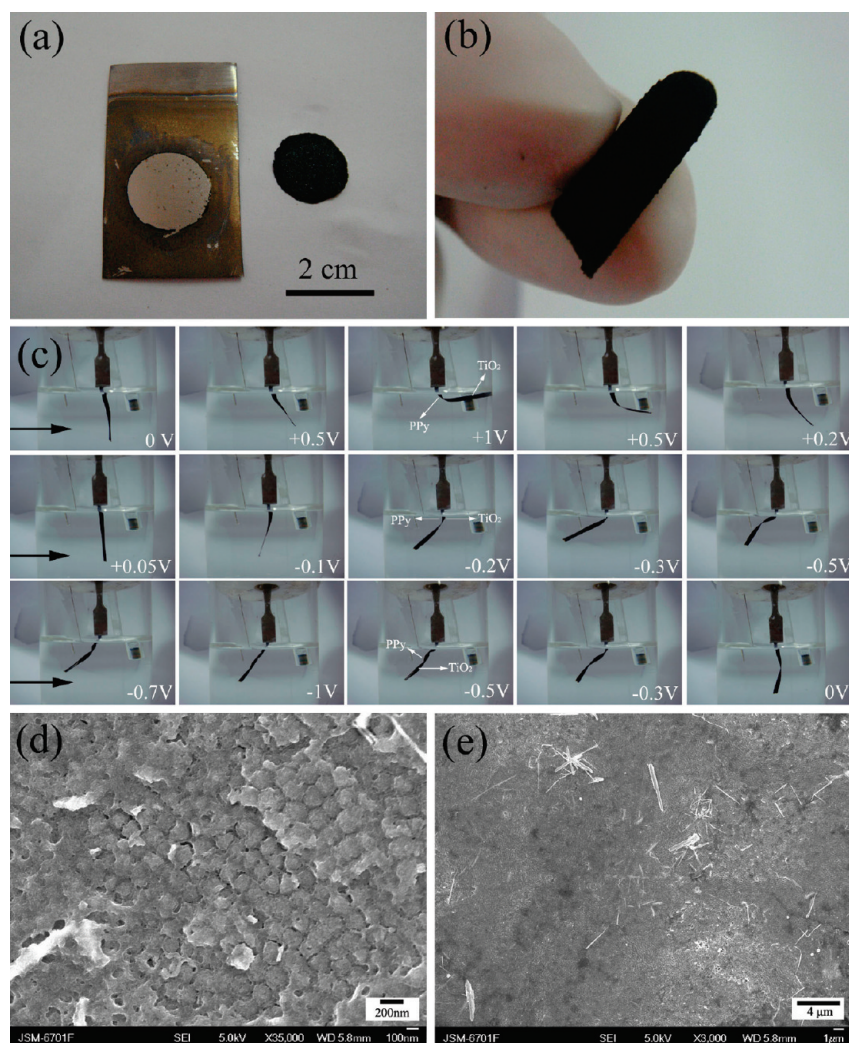


Figure 3. (a) Photograph of the peeled PPY-embedded TiO_2 NT film of large area and the mother Ti substrate, (b) the flexible, free-standing coaxial TiO_2 NT-PPy nanowire composite in (a). (c) Images recorded during the bending of coaxial TiO_2 NT-PPy by one cyclic voltammetric scanning cycle (-1 to $+1$ V; scan rate = $20 \text{ mV} \cdot \text{s}^{-1}$) in $1.0 \text{ mol L}^{-1} \text{ LiClO}_4$ aqueous solution. The actuator was held with the TiO_2 nanotube side to the right and the PPY film side to the left. (d,e) FESEM morphology of the back side of TiO_2 NT- TiO_2 -PPy film after 50 cycles.

time (10 min to 2 h). Sufficient electrodeposition time guaranteed that PPY filled the entire tubes. Figure 2a–f shows the back side of the prepared PPY nanowires lifted off from the TiO_2 -TPNTs. It is qualitatively seen that PPY arrays with different aspect ratios were obtained. Short PPY arrays were vertically aligned, while long nanowires bundled together, likely due to capillary force. These PPY arrays on flexible insulating substrates have potent applications in organic electronics. It is worth noting that mechanical peel-off usually results in the breakup of a large portion of nanowires, especially when nanowires are too long.

Not only could PPY nanowires/nanotubes be lifted off, but the TiO_2 -PPy coaxial nanohybrids could be readily delaminated from the Ti substrate after immersion in saturated HgCl_2 solution for several hours. Photographs of the peeled off TiO_2 NT-PPy film and the mother Ti substrate are shown in Figure 3a. It is seen

that the TiO_2 -TPNTs in the electrodeposition area can be lifted off together with PPY in high efficiency. It was found that the thicker the TiO_2 -TPNTs and PPY, the more easily the nanohybrids could be peeled off. Increasing both thicknesses caused significant reduction of adhesion strength due to the accumulation of internal stress. These results are practically useful for the choice of aspect ratios in preparing either supported or free-standing nanohybrids. Most importantly, the free-standing polymer-embedded TiO_2 NTs display surprisingly high flexibility compared to the TiO_2 NT film, as shown in Figure 3b. To further test the flexibility of the coaxial heterojunctions, the actuation properties of PPY were utilized.^{35,36} PPY/ TiO_2 -TPNTs were cut into strips of $20 \text{ mm} \times 2 \text{ mm} \times 0.03 \text{ mm}$ to observe the displacement upon applied bias (cyclic voltammetry, CV) in $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ LiClO}_4$ aqueous solution as the electrolyte in a standard three-electrode system. Figure 3c shows the images of bending events of the hybrid strip recorded during CV scanning from -1 to $+1$ V (vs Ag/AgCl) at a scan rate of 20 mV/s . The strip bent to the right when applying a positive potential and to the left when applying a negative potential. It is well-known that PPY can be oxidized and will expand due to the incorporation of hydrated anionic counterions (ClO_4^- in this case).^{37–39} Therefore, the strips bent toward the TiO_2 side. While in negative bias, PPY shrank as a consequence of dehydration and the strip bent toward the PPY side. When the negative potential was further increased to -0.5 V, the TiO_2 -

TPNTs/PPy strip curled to a helical structure (bending up to 720°). When the bias was switched back to the starting potential (0 V), the strip roughly came back to the original position, implying reversible switching. The electrochemical actuation can be used to evaluate both the flexibility and durability of nanohybrids. One main drawback of conducting polymer-based multilayer actuators is the low adhesion strength and thus the delamination of the active layer from the electrode.⁴⁰ The underlying interdigitated structure reported here can effectively prevent delamination from occurring. Meanwhile, regarding the stiffness of TiO_2 NTs, it is seen from Figure 3d,e that even after 50 cycles the back side of the TiO_2 NTs- TiO_2 -PPy film remained very compact and no cracks were found. The TiO_2 -polymer actuation performance remained reproducible even after the sample was stored for over 1 month, implying long-term stability of the nanohybrid. Figure S2 in the

Supporting Information shows the bending angle *versus* applied loads for strips of similar size of both composites and blank TiO₂ NT films of different thickness. It is seen that the deformation angles of blank TiO₂ of 20 and 100 μm thick were no more than 5°, while TiO₂–PPy composites deformed much larger angles even up to 90° (see also the video in the Supporting Information). It should be noted that the thinner the TiO₂ thickness, the better the flexibility will be. There is no doubt that embedding a conducting polymer in the TiO₂ NTs changes the TiO₂ material from fragile to flexible by forming an interpenetrating network.

Poly(3-hexylthiophene) (P3HT) represents another important conducting polymer in solar cells as a good hole transport material having high hole mobility.^{41,42} Buildup of solar cell devices using P3HT and TiO₂ NTs as the hole and electron transport materials has been attempted by Grimes *et al.*,¹⁴ in which P3HT had to be infiltrated into TiO₂ nanotubes. However, the infiltration was limited with dewetting or incompatibility of the two phases as a possible reason of the low efficiency. As mentioned above, the deposition of P3HT directly into TiO₂ nanotubes would be a promising way to construct P3HT/TiO₂ devices in one step. On the other hand, it is very hard to achieve one-dimensional P3HT materials with successive phase and vertical alignment, such as nanowires and nanotubes.⁴³ TiO₂–TPNTs are promising as templates to guide P3HT nanowire growth and simultaneously form p–n ordered heterojunctions.

Figure 4a shows the FESEM image where the P3HT nanowires grew out of TiO₂–TPNTs in the 0.2 M tetrabutylammonium hexafluorophosphate (TBAHFP) acetonitrile solution at 2 mA · cm⁻² for 10 min. When the electrochemical polymerization time or the current density was further increased, the P3HT spread and cover the top surface of TiO₂–TPNTs. A cracked image clearly shows P3HT extended through the tube length (Figure 4b).

Alternatively, the P3HT nanowires/nanotubes could be peeled off by mechanical force or dissolution of TiO₂ phase in HF solution for other device configurations. Figure 4c shows the top surface of a P3HT nanowire film peeled off from TiO₂–TPNTs by mechanical force. It indicates that very uniform P3HT arrays were obtained when P3HT was peeled off from the template composed of NTs of shorter length. Figure 4d shows very high aspect ratio P3HT nanowires obtained after dissolving TiO₂–TPNTs in HF solution. The peeled off P3HT creates an opportunity to make polymer solar cells with ordered heterojunction with C₆₀ derivatives as the electron transport material.⁴⁴ For example, spin coating of PCBM from solutions with different concentrations

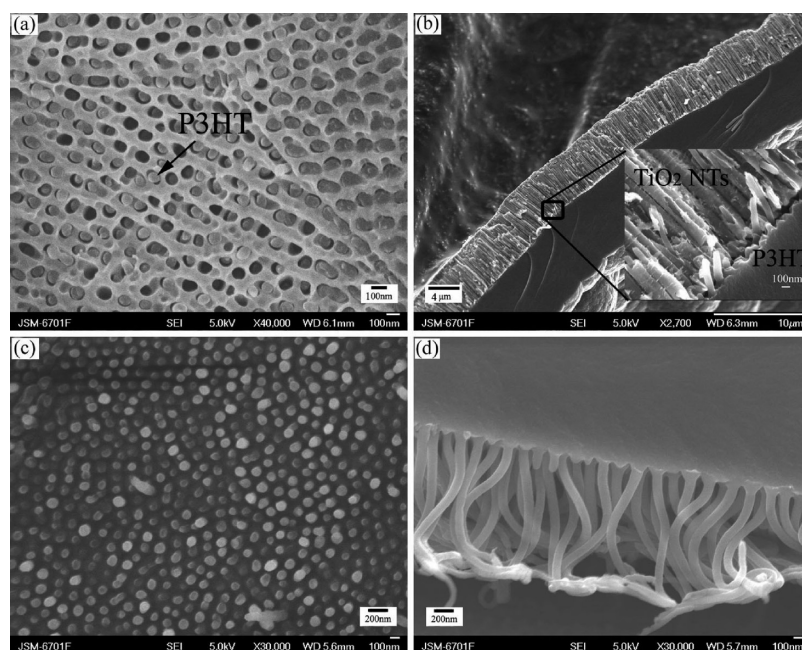


Figure 4. FESEM images of TiO₂–TPNTs and P3HT nanowires. Top surface (a) and cross-sectional (b) images of P3HT nanowire-embedded TiO₂–TPNTs. (c) P3HT nanowire film peeled off from TiO₂–TPNTs by mechanical force, (d) cross-sectional view of P3HT nanowires from TiO₂–TPNTs after dissolving the scaffold in HF aqueous solution.

onto the peeled off, flexible P3HT sheets could form interdigitated P3HT/PCBM structures. Figure 5a shows the schematic representation of the process. Figure 5b,c shows the FESEM images of P3HT NT films peeled off from TiO₂–TPNTs by mechanical force before and after a single spin coating with PCBM. It is seen that the gaps between P3HT nanotubes were partly filled with PCBM. After spin coating three times, most of the P3HT nanotubes had been covered with PCBM except a few very high pillars (Figure 5d). It is reasonable that P3HT can be completely covered with PCBM by additional spin-coating cycles or by increasing the concentration, while P3HT nanotubes were largely preserved as seen from the fractured edge of the composite film (Figure S3 in the Supporting Information). Figure 5e,f shows the atomic force microscopy (AFM) images of a P3HT NT film peeled from TiO₂–TPNTs before and after spin coating PCBM. The short P3HT nanotubes are about 200 nm before spin coating PCBM, and the gaps between the P3HT can be filled after spin coating PCBM with greatly reduced height difference (Figure 5f). This will be a promising method to form large-area P3HT/PCBM ordered heterojunction materials with great design flexibility.

In recent years, there is increased interest in all-inorganic heterojunction solar cells because of advantages such as very high stability and resistance to environment attacks.^{45,46} Recently, a number of core–shell heterojunction solar materials have been fabricated.^{47,48} TiO₂/CdS can form p–n junctions and harvest visible light due to the low band gap of CdS (2.42 eV). CdS quantum dots (QDs) absorbed on TiO₂ nanotubes have

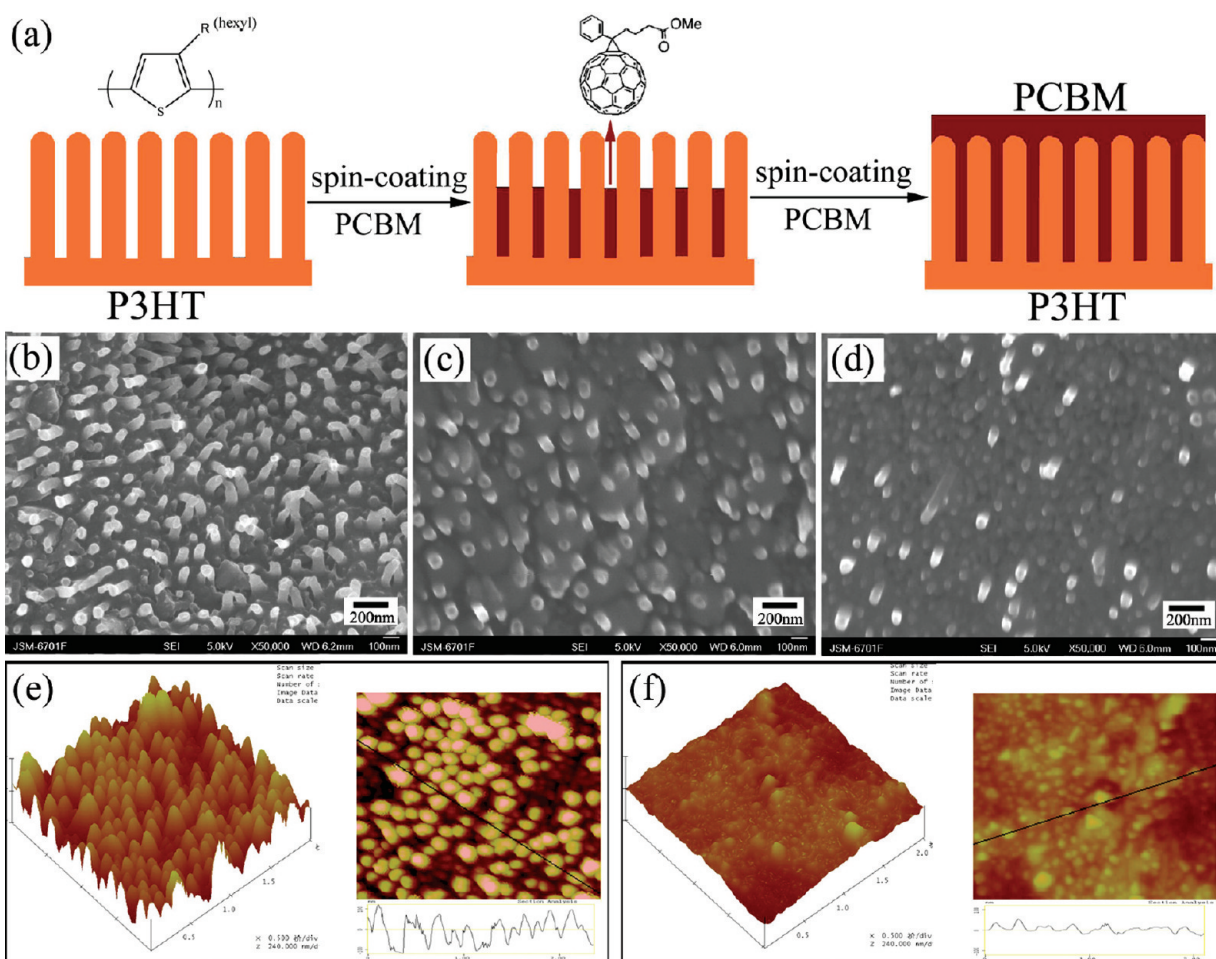


Figure 5. (a) Schematic representation of the preparation of the interlaced heterojunction of P3HT NTs and PCBM by spin-coating method. (b–d) FESEM images of the P3HT NT films peeled off from the TiO_2 by mechanical force before and after spin coating PCBM for one and three times. (e,f) AFM images of the P3HT NT film before and after spin coating PCBM.

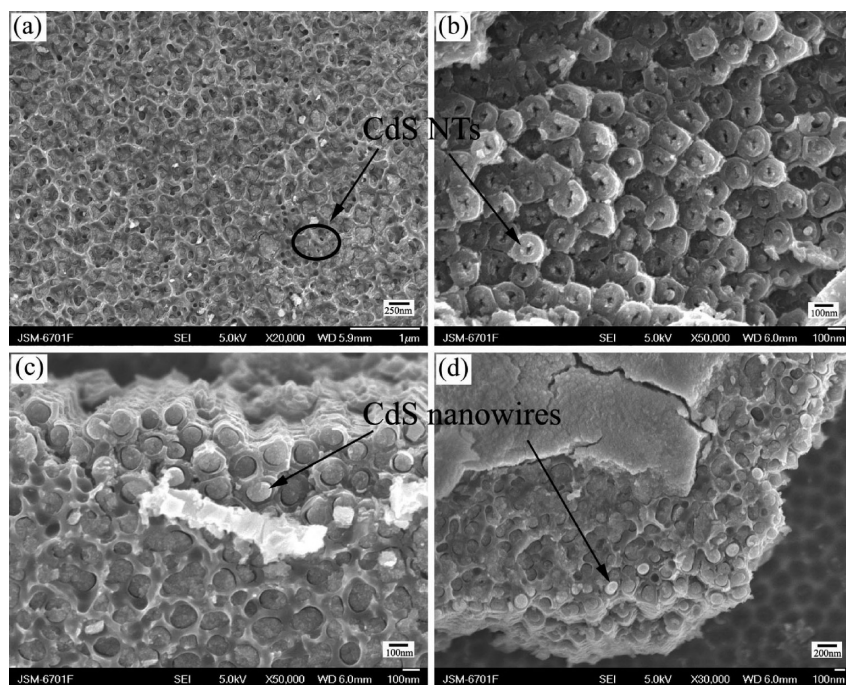


Figure 6. FESEM images of CdS/ TiO_2 composite materials. (a,b) CdS NTs/ TiO_2 TPNT junctions; (c,d) CdS nanowire/ TiO_2 TPNT junctions.

been used to broaden the light absorption for better photoelectric performance.^{49,50} However, an ordered TiO_2/CdS heterojunction has never been attempted. In our experiment, CdS was directly deposited into TiO_2 -TPNTs to form TiO_2/CdS coaxial junctions. Figure 5a,b shows the FESEM images of the prepared hybrids, in which CdS nanotubes were formed in TiO_2 -TPNTs of 110 nm in diameter. By increasing the deposition time, the CdS nanotubes turned to nanowires, as shown in Figure 6c,d.

Metal nanowires can be easily grown from nanotubes in a controlled manner to form metal/ TiO_2 -TPNTs coaxial hybrids. We deposited Ni nanowires inside TiO_2 -TPNTs to form Ni/ TiO_2 . Figure 7a shows the FESEM image of a Ni nanowire/ TiO_2 TPNT composite. Figure 7b shows the FESEM image of the

peeled-off Ni layer, and the inset is the photograph of the prepared Ni nanowire/TiO₂ TPNT material. It is seen that only a very small part of Ni was peeled off from nanotubes. Unlike the conducting polymers, the Ni nanowires have relatively strong adhesive force with TiO₂-TPNTs and are very hard to peel off by mechanical force. After dipping in saturated HgCl₂ solution for several hours, the Ni nanowire/TiO₂-TPNTs were obtained and could be actuated readily using a magnet, as shown in Figure 7c. By moving the magnet from right to left, the Ni nanowire/TiO₂ TPNT bent accordingly. After numerous cycles, the flexibility of this composite had not changed, and the TiO₂-TPNT structure remained intact (Figure 7d,e). Other metal-TiO₂ nanohybrids, such as Au nanowires inside TiO₂-TPNTs to form Au/TiO₂, can also be easily prepared (Figure S4 in the Supporting Information). These metal nanowire/TiO₂ semiconductive nanotube arrays have many potential technological applications, such as high-density recording devices, sensors, and actuators.

In conclusion, we have demonstrated a facile approach to achieve flexible TiO₂ nanotubes/conducting polymer (semiconductors, metals) nanowire and nanotube coaxial materials with large areas *via* electrochemical deposition in a top-porous TiO₂ NT template. It is the first time to successfully deposit conducting polymer nanowires and nanotubes into TiO₂ NTs to form well-positioned phases. The TiO₂ with special morphol-

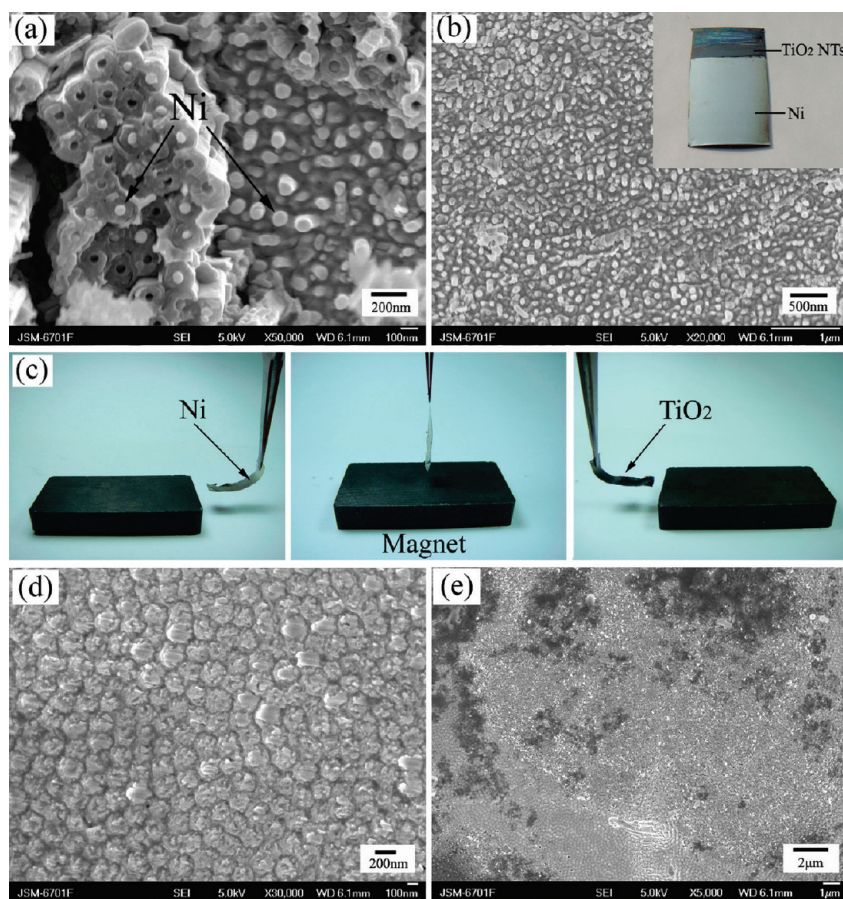


Figure 7. FESEM images of (a) Ni nanowires/TiO₂ NTs, (b) Ni film after scratched from the TiO₂ by mechanical force. The inset is the photograph of the new prepared Ni/TiO₂ material. (c) Flexibility test of the Ni nanowire/TiO₂ NT composite material. (d,e) Back side of the TiO₂ NTs images after numerous flexing cycles.

ogy plays a vital role in making this possible, in comparison to the conventional TiO₂ NTs. By depositing conducting polymers or inorganic semiconductor, or by spin coating PCBM on peeled-off nanowire arrays, ordered p-n heterojunctions were formed. The PPy/TiO₂ and Ni/TiO₂ coaxial nanohybrids were actuated *via* applied bias and magnetic field, respectively, verifying the high flexibility of these materials.

METHODS

Fabrication of Nanoporous TiO₂ NT Arrays: Highly oriented nanoporous TiO₂ nanotube arrays were prepared by the potentiostatic anodization in a two-electrode electrochemical cell. The commercial titanium foils were used as the anode after careful cleaning, and a graphite plate was used as the cathode. In order to effectively reduce the defect on the surface, the samples were preanodized in a 0.5 wt % NH₄F ethylene glycol solution at 60 V for 4 h, and then the TiO₂ NT film was removed by ultrasonication in 1 M HCl aqueous solution. Then they were anodized for the second time in the electrolyte containing ethylene glycol, 1–3% hydrofluoric acid, and 0.5 wt % NH₄F at 20–80 V for 10 min to 2 h to get the nanoporous TiO₂ NTs with different diameters and length. After anodization, the samples were washed with deionized water and then dried in the air. Then they were annealed at 500 °C for 2 h to get the anatase TiO₂ NTs arrays.

Fabrication of Coaxial TiO₂/Conducting Polymer p-n Junction

Nanomaterials: The coaxial TiO₂ nanotubes and polypyrrole nanowire and nanotube composite materials were electrochemically polymerized on a CHI660B electrochemical workstation (CHI Co., Shanghai, China) in a conventional three-electrode system in 0.1 M LiClO₄ acetonitrile solution containing 0.2 M pyrrole at 0.8 V for 5–30 min. A standard three-electrode setup was used, with nanoporous TiO₂ NT as working electrode, Pt as counter electrode, and Ag⁺ (0.01 M AgNO₃, CH₃CN)/Ag as the reference electrode (Bioanalytical Systems). The TiO₂ NTs and P3HT composite material were prepared in the 0.2 M tetrabutylammonium hexafluorophosphate (TBAHFP) acetonitrile solution containing 0.5 M 3-hexylthiophene monomer at 2–10 mA · cm⁻² for 10 min to 2 h.

Fabrication of the TiO₂ NTs/CdS p-n Junction and TiO₂ NTs/Metal Nanowire Composite Materials: CdS nanowires were deposited at a constant direct current density of 5 mA · cm⁻² at 110 °C for 2–10 min in a two-electrode electrochemical cell using a platinum plate as the anode and the porous TiO₂ NTs as the cathode. The

electrolyte solution consisted of 0.055 mol L⁻¹ CdSO₄ and 0.19 mol L⁻¹ element S in a DMSO solution. Au nanowires were electrodeposited in a two-electrode electrochemical cell with a Pt plate as the anode in a 10 mM H₂AuCl₆ solution at 20 mA/cm⁻² for 1–5 min, and the Ni nanowires were electrodeposited in an electrolyte solution containing 1 mol L⁻¹ NiSO₄ and 0.5 mol L⁻¹ H₃BO₃ at 50 mA/cm⁻² for 10 min.

Peel Off: After electrochemical deposition, some of the samples were immersed into the saturated HgCl₂ solution to peel off the p–n junction from the Ti substrate, and the TiO₂ NTs can be dissolved in the HF aqueous solution to get the conducting polymer self-supporting film. Also, the polymer self-supporting film can be peeled off by mechanical force, leaving part polymer nanowire or nanotube in the TiO₂ NTs.

Characterization: The morphology of the TiO₂ nanotube array was investigated by use of a field emission scanning electron microscope (JSM-6701F, JEOL Inc., Japan). To construct the poly-3-hexylthiophene (P3HT)/1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM) heterojunction, 10 mg of PCBM was dissolved in 1 mL of chlorobenzene and spin-coated to the P3HT nanowire film lifted off from the nanoporous TiO₂ NTs by mechanical force. After spin coating (10 s at 500 rpm, 60 s at 3000 rpm), the films were annealed at 130 °C for 30 min under N₂. The atomic force microscope was measured on a Nano-scope III (Digital Instrument) at ambient environment. The bending movements of the TiO₂ NT–PPy films (20 mm × 2 mm × 0.03 mm) were tested by cyclic voltammetric measurement from –1 to 1 V using a 1.0 mol L⁻¹ LiClO₄ aqueous solution as the electrolyte in a standard three-electrode system.

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Supporting Information Available: Additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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