Core-Shell Heterostructures of Rutile and Anatase TiO₂ Nanofibers for Photocatalytic Solar Energy Conversion

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ABSTRACT

Two types of core-shell heterostructure TiO_2 nanofibers (noted as core@shell TiO_2 NFs) were synthesized by sequential hydrothermal, calcination, and impregnation processes. Rutile TiO_2 nanofibers (R TiO_2 NFs) core with anatase TiO_2 nanoparticles (A TiO_2 NPs) shell is denoted as R@A TiO_2 NFs, and the reverse structure with anatase TiO_2 NFs core (A TiO_2 NFs) and rutile TiO_2 nanoparticles shell (R TiO_2 NPs) is denoted as A@R TiO_2 NFs. In our study, the photodegradation of organic dyes and Kelvin probe force microscopy (KPFM) analysis were applied to shed light on the mechanism of the excited electron-hole pair separation. The results of photodegradation showed that the A@R TiO_2 NFs has the highest activity under UV-B and UV-A irradiation, being nearly 3-fold higher as compared to AEROXIDE[®] TiO_2 P25. The results in conjunction with KPFM measurements indicated that in the heterostructure, electron-hole pairs are efficiently separated and the excited electrons stay in the anatase phase, and holes are injected to the rutile phase. When the A@R TiO_2 NFs heterostructures are decorated with Pt nanoparticles (Pt-A@R TiO_2 NFs), the nanocomposite is particularly active in photocatalytic hydrogen evolution from ethanol-water mixtures with a production rate of $\sim 8,500 \mu\text{mol/h}\cdot\text{g}$. Our study not only explains the role of anatase-rutile junctions in photocarrier separation, but also projects the development of other efficient photocatalytic heterostructures for green energy production and conversion.

INTRODUCTION

Various forms of titanium dioxide (TiO_2) have been applied in several fields including electronics¹⁻⁴, energy⁵⁻⁸, as well as environmental engineering^{6, 9-13} all which capitalize on the semiconducting behavior of this inexpensive, abundant and chemically stable material. Both common crystal structures of TiO_2 , rutile and anatase, have large band gap (3.0 and 3.2 eV, respectively) limiting the principal optical absorption to the short wavelength UV photons only. To be able to harvest the visible spectrum, and thus make TiO_2 suitable for solar applications, a number of strategies have been worked out in the last decade.¹⁴⁻¹⁵

The first strategy is tuning the band structure of TiO_2 . According to first principles modeling of the density of states, the conduction and valence bands of TiO_2 are occupied by Ti $2p$ and O $2p$ orbitals, respectively.¹⁶⁻²⁰ With slight doping of non-metals such as nitrogen or sulphur (both in the anionic and interstitial positions)²¹⁻²⁶ to the lattice, new electronic states appear above the valence band edge. Whereas doping metal ions (in the cationic sites) results in additional states below the conduction band edge, thus lowering the band gap.²⁷⁻³¹ An induced amorphous superficial layer by hydrogenating the surface of TiO_2 is the second approach to improve optical absorption. Hydrogenation induces oxygen vacancies, thus introducing mid-gap states.³²⁻³⁷ The third method to improve effective photoresponse of the material is obtained by separating the photogenerated excitons. Decorating the surface with metals of large work function (typically Pt or Pd) forms Schottky junctions, whereas decorating semiconductors of p-type characteristics (CuO, Cu_2O or NiO) form p-n nanodiodes. In such structures, electrons that are excited to the conduction band of TiO_2 inject to the other material and face a barrier to return, thus improving the long-term spatial separation of electrons and holes.³⁸⁻⁴² A fourth way to influence the overall photoabsorption may be achieved by bringing TiO_2 in contact with plasmonic metal nanoparticles,

such as Au or Ag. In this case, hot electrons in the metal will inject to the semiconductor.⁴³⁻⁴⁵ It is worth mentioning here, that nanoparticles not only decorate TiO₂, but also yolk-shell heterostructure of TiO₂ with Pt, Au, and S. This has been demonstrated to facilitate enhanced photogeneration and separation processes.^{43, 46-48}

While anatase is known to have much higher photocatalytic activity than that of rutile, their mixed-phases have been known to have superior activity and have been utilized as commercial catalyst for decades. The band alignment between anatase and rutile mixed phases plays a decisive role in carrier separation after photogeneration. Electrochemical impedance analysis has confirmed that the flat band potential of anatase is about 0.2 eV lower than that of rutile. At the interface of the two phases, the photoexcited electrons tend to transfer from the anatase to the rutile, which has been corroborated by many researchers. However, Scanlon et al. proposed a reversed model of mixed-phase TiO₂ in which the conduction band of rutile lies above that of anatase. In their work, density functional theory simulations and X-ray photoemission measurements indicated a staggered band alignment of ~0.4 eV between anatase and rutile in which anatase had the higher electron affinity.⁴⁹

Moreover, the exposure facet and morphology of TiO₂ play crucial roles as well to its photocatalytic activity. For instant, exposure face of (111) of rutile TiO₂ have high oxidation activity whereas (110) have great reduction activity.⁵⁰⁻⁵¹ On the other hand, TiO₂ with low dimension like nanowire and nanofiber, which can be finely controlled by the pH value and reaction condition of the hydrothermal process, exhibit facilitated carrier transportation owing to the high crystallinity⁵²⁻⁵⁴. Therefore, engineering the junction between two phases and their morphology is crucial to properly address photocatalytic behavior in anatase-rutile systems. In this study, we experimentally demonstrate the validity of the above strategy for efficient exciton

separation. With a simple two-step calcination process, we synthesized core-shell anatase-rutile and rutile-anatase nanowires as well as their Pt-decorated derivatives. Photodegradation studies of methyl orange (MO), photocatalytic ethanol reforming to produce H₂, and photo-Kelvin probe assessment of surface charge accumulation reveal that core-shell nanostructures of TiO₂ indeed help electron-hole pair separation with anatase being the electron acceptor and rutile being the hole. The results obtained for the optimized photocatalyst heterostructures show superior performance in reference to commercial anatase-rutile bi-phase composite nanoparticles.

EXPERIMENTAL SECTION

Synthesis of TiO₂ core-shell nanofibers. TiO₂ core-shell nanofibers (NFs) were synthesized by a two-step calcination process. For the core material, TiO₂ NFs were obtained by hydrothermal synthesis of sodium-titanate NFs with subsequent ion-exchange and thermal treatment. In the process, 2.50 g of anatase phase TiO₂ powder (Sigma-Aldrich, 98%) was suspended in 62.5 mL of 10.0 M NaOH aqueous solution by ultrasonic agitation. Then, we transferred the suspension into a PTFE-lined autoclave and treated it at 150 °C for 24 h to facilitate the hydrothermal conversion of TiO₂ NPs to sodium tri-titanate (Na₂Ti₃O₇) NWs. Next, the obtained Na₂Ti₃O₇ (2.10 g) was emerged in 10 L hydrochloric acid with 0.1 M concentration overnight (HCl, Sigma-Aldrich, 37%) to partially exchange the sodium ions for protons. Finally, the sodium hydrogen tri-titanate (Na_xH_{2-x}Ti₃O₇) was filtered and dried in air at 80 °C, following by calcination at various temperatures (600, 700, 800, 900, 1000, 1100 and 1200 °C) for 12 h at 5 °C/min heating rate to obtain TiO₂ NFs with various anatase/rutile content. For the core-shell heterostructures of rutile and anatase TiO₂ NFs, the protocol is demonstrated in **Figure 1** in detail. 100 mg of either anatase

or rutile phase TiO_2 NFs were dispersed in 0.01 M, 0.05 M, and 0.10 M titanium tetrachloride (TiCl_4 , Sigma-Aldrich, 99.9%) and stirred for 24 h. Suction filtration was applied to collect TiCl_4 coated TiO_2 NFs and then the samples were subjected to calcination at either 450 or 650 °C to obtain anatase or rutile phase shell, respectively. The as-made TiO_2 NFs with anatase core and rutile shell are denoted as A@R TiO_2 NFs, whereas the reverse structure with rutile core and anatase shell is labeled as R@A TiO_2 NFs. Symbols X, Y, and Z in the nomenclature indicate the concentration (i.e. 0.01 M, 0.05 M, and 0.10 M) of the TiCl_4 solution applied in the impregnation step of the core NFs.

Figure 1 The protocol of core-shell heterostructures (a) A@R TiO_2 NFs and (b) R@A TiO_2 NFs.

For platinum decorated A@R TiO_2 NFs (Pt-A@R TiO_2), 2.0 mg platinum chloride (PtCl_2 , Acors Organics, Pt $\geq$ 71.8%) and 200.0 mg as-prepared TiO_2 hybrid NFs were first suspended in 50 mL ethanol ($\text{C}_2\text{H}_5\text{OH}$, Sigma-Aldrich, 99.8%). The well-dispersed mixture was dried at 70 °C with vigorously stirring overnight to evaporate the solvent. Finally, the collected powder was calcined at 300 °C for 4 h under H_2/N_2 atmosphere.

Characterization of materials. The morphology of the materials was investigated by field

emission scanning electron microscope (FE-SEM, SU8010, Hitachi). The crystal and microstructure were characterized by X-ray diffraction (XRD, D2 phaser with Xflash 430, Bruker) and transmission electron microscopy (TEM, spherical-aberration corrected ULTRA-HRTEM, JEM-ARM200FTH, JEOL), respectively. For Raman scattering spectra of the various TiO₂ NFs, they were positioned on a high-resolution piezoelectric stage of the scanning microscopy (WiTec, Alpha 300S) and were excited by a 532 nm He-Ne laser (25 mW). The laser beam was focused with a 10× objective lens (Nikon plane objective, NA $\approx$ 0.9), and the diameter of the focused laser beam was about 10 μ m. Surface potential mapping was carried out by photo-Kelvin probe force microscopy (photo-KPFM, Digital Instruments, Nanoscopes III) using UV-B light ($\lambda_{\text{max}} \sim 312$ nm, 8 W) exposure. For the measurements, the nanomaterials were dispersed in ethanol and spin-coated on Au-coated (thickness of 100 nm) Si wafers. Si cantilever probes (Nanosensors, average force constant of 2.8 N/m) coated with Cr adhesion and Pt-Ir5 conductive layers were used in the measurements. With this method, the height variation and contact potential by electrostatic force between the conductive tip and the surface of the samples are measured simultaneously. A line is scanned using atomic force microscope (AFM) in tapping mode to acquire the topographic information of the material. Then, the same line is rescanned with the tip lifted to a height of 20 nm. During the second scan, a DC bias is applied at the tip to nullify the electrostatic oscillations, position by position, and the contact potential difference is observed and measured. The surface potential distributions were mapped both in the dark and under the illumination of a UV-B lamp. The surface potential difference is then denoted as the photo surface potential shift.

Photocatalytic activity measurement. For the photodegradation experiment, 20.0 mg of each photocatalyst was dispersed in 150.0 mL of $\sim$ 10.0 mg/L methyl orange (MO) aqueous solution. Two UV light sources (UV-B, Sankyo Denki, G15T8E, $\lambda_{\text{max}} \sim 312$ nm, 8.0 W; UV-A, Sankyo

Denki, F4T5BL, $\lambda_{\max}$ ~365 nm, 8.0 W) were placed above the container at a distance of ~10 cm from the surface of the solution. Before the photodegradation experiment, the suspensions were kept in the dark for 0.5 h to reach the initial adsorption equilibrium. At various time intervals (from 1 to 150 min) during the reaction, a small aliquot of dispersion was sampled, centrifuged and the supernatant fraction was subjected to optical transmission analysis using a UV/Vis spectrophotometer (in the spectral range of 300-800 nm). The pH value of degradation solution with MO is about 6.0 and during the degradation, the pH value of the solution still remain at around 6.0. By comparing the intensity of the MO characteristic peak located at $\lambda = 464$ nm with that of the calibration curve measured previously, the corresponding unreacted MO concentration was assessed by extrapolation.

Photocatalytic H_2 production by ethanol (C_2H_5OH , 95%) reforming was carried out from a 1 L mixture of equal volume C_2H_5OH and H_2O , in which 50.0 mg of each photocatalyst was suspended by ultrasonic agitation. The pH value of solution system was monitor and maintained at 6.0 during the entire reaction. UV-B light tubes (6 pieces, Sankyo Denki, G15T8E, $\lambda_{\max}$ ~312 nm, 8.0 W) were placed around the reactor in a hexagonal arrangement at a distance of ~5.0 cm. Aiming to avoid the sedimentation of photocatalytic materials and to purge the generated H_2 , a flow of N_2 gas (99.995%) was bubbled through the reactor at a rate of $400.0 \text{ mL} \cdot \text{min}^{-1}$ (mass flow meter, C100L, Sierra). A cold trap (cooled with liquid N_2) and the molecular sieve were connected to the outlet to condense the vapors of C_2H_5OH and H_2O . The concentration of generated H_2 in the stream was recorded using a pellistor-type gas detector (Status FGD3).

RESULTS AND DISCUSSION

To obtain the desired crystal phase and morphology of TiO₂ NFs, the calcination processes were carried out at various temperatures for 12 h. The morphology of TiO₂ NFs examined by FE-SEM (**Figure 2(a-g)**) shows almost the same features for the samples treated at temperatures below 1200 °C. However, the nanofibers became sintered above 1200 °C. X-ray powder diffraction (**Figure 2(h)**) indicates the formation of anatase phase between 600 °C and 800 °C. At 900 °C, a peak appears at 27.5° which corresponds to the (110) plane of rutile phase. As the calcination temperature is increased further, the intensity of anatase characteristic reflections in the pattern decrease, whereas the peaks for rutile phase emerge. Calcination at 1100 °C or above results in the formation of rutile without any signature of anatase. Raman spectroscopy gives further information about the crystallinity and chemical bonding of anatase and rutile phases (**Figure S1**). Red dashed lines represent the six characteristic peaks corresponding to anatase Raman modes E_g (144 cm⁻¹), E_g (200 cm⁻¹), B_{1g} (398 cm⁻¹), B_{1g}/A_{1g} (517 cm⁻¹), and E_g (640 cm⁻¹). The characteristic peak located at 517 cm⁻¹ is the superposition of two peaks corresponding to B_{1g} and A_{1g}. Therefore, it is hard to define the contributions of these modes. Whereas, the blue dashed lines located at 446 and 609 cm⁻¹ are the vibrational modes of the rutile phase. According to **Figure S1**, when the calcination temperature is below 900 °C, the absence of the Raman bands corresponding to rutile phase confirms the phase purity of the synthesized anatase TiO₂ NFs. As the calcination temperature increases, the anatase phase gradually transforms into rutile phase, which is in accordance with the Raman spectra. To determine the optimal core materials, photocatalytic degradation using TiO₂ NFs were carried out (**Figure 2(i)**). TiO₂ calcined at 700 °C, which is practically pure anatase, noted as TiO₂-700 °C NFs, shows the fastest decomposition rate in this series of TiO₂ NFs, and thus was chosen as anatase core material for the subsequent experiments. The microstructure of

TiO₂-700 °C NFs is shown in **Figure S2**. From **Figure S2 (a-b)**, it can be observed that the TiO₂-700 °C NFs have a length-to-diameter ratio greater than 50 which is a typical structure for the nanofiber. **Figure S2 (c,d)** presents the HRTEM investigations and indicates that the TiO₂-700 °C NFs specific orientations along the (101) crystalline planes and the lattice spacing d_{101} is 3.40 Å. Further observation by FFT transformation (inset image in **Figure S2 (d)**) confirmed that the structure of TiO₂-700 °C NFs is a single and highly crystalline structure.

Figure 2 FE-SEM images of core material TiO₂ NFs calcined at (a) 600, (b) 700, (c) 800, (d) 900, (e) 1000, (f) 1100, and (g) 1200 °C for 12 h; and (h) corresponding XRD patterns as well as (i) photodegradation rate plots under UV-B irradiation.

In order to optimize the further calcination process, we explored the time dependence of the crystal phase and microstructure of the rutile nanofibers. As displayed in **Figure 3**, the longer the heat treatment took, the better the crystallinity became. However, excessive annealing time compromises the microstructure as sintering of the nanofibers takes place after annealing for 36 h or longer. Accordingly, based on the FE-SEM and XRD data, we select the samples calcined at 700 °C (12 h) and 1100 °C (24 h) for further use as anatase and rutile core nanofibers, respectively.

Figure 3 FE-SEM images of TiO₂ NFs calcined at 1100 °C for (a) 12, (b) 24, (c) 36, (d) 48 h. (e) XRD patterns of TiO₂ calcined at 1100 °C with different calcination time.

To synthesize various phases of TiO_2 as the shell material around the anatase and rutile cores, we impregnate the nanofibers with TiCl_4 solutions of various concentrations (0.01 M, 0.05 M, and 0.10 M), followed by calcination of the nanocomposites to transform the TiCl_4 coating to TiO_2 . Symbols X, Y, and Z in the nomenclature indicate the concentration (i.e. 0.01 M, 0.05 M, and 0.10 M) of the TiCl_4 solution applied in the impregnation step of the core NFs. Using different calcination temperatures, the crystal phase of the outer TiO_2 layer can be tuned. We find that at 450°C , the outer TiO_2 layer takes the anatase form, whereas at 650°C it transforms to rutile. These crystal formation temperatures are lower than the ones measured for the transition of titanate to anatase to rutile nanofiber. It is also lower than expected from the phase-diagram of TiO_2 . However, the small particle size and large surface energy may explain the observed phenomenon. X-ray diffraction of the core-shell structures confirms the coexistence of both phases (**Figure 4(a) and (b)**) regardless of the concentration of TiCl_4 solution applied for the impregnation process. All diffraction patterns display the corresponding crystalline TiO_2 shell phases, (101) plane of anatase at 25.4° on the rutile core, as well as (110) plane of rutile at 27.3° on the anatase core material.

Figure 4 XRD patterns of (a) R@A TiO_2 series and (b) A@R TiO_2 series synthesized using different concentrations of the TiCl_4 impregnation solution.

The photodegradation plots of methyl orange using both R@A TiO₂ NFs and A@R TiO₂ NFs series under UV-A and UV-B illumination and their corresponding reaction rate constants are shown in Figure 5(a, c) and in Figure 5(b, d), respectively. For the R@A TiO₂ series, the more concentrated the shell material used, the higher the photocatalytic activity recorded. However, due to the poor photocatalytic activity of the rutile core, the overall performance was worse than that of the reference AEROXIDE® TiO₂ P25 photocatalyst. On the other hand, for the inverse structure A@R TiO₂, we found a significantly higher rate constant. The optimal composition obtained with the 0.05M TiCl₄ impregnation (A@R TiO₂-Y) performed even better than the AEROXIDE® TiO₂ P25 reference. Different from bi-phase AEROXIDE® TiO₂ P25, which comprised with the mixed phase of around 80% anatase phase and 20% rutile phase, the core-shell heterostructure has obvious phase separated nanostructure⁵⁵⁻⁵⁷. A@R TiO₂ NFs also exhibits the higher crystallinity (in Figure S3) and therefore fewer grain boundaries than AEROXIDE® TiO₂ P25. Hence, the reason for the superior photocatalytic behavior is a consequence of efficient photo-charge generation in the relatively thick anatase core, and then their subsequent separation at the core-shell heterostructure interface. The collected carrier at the surface of core-shell heterostructure can transfer to the reactants much effectively.

Figure 5 The C/C_0 curves of the photocatalytic degradation of methyl orange under (a) UV-A and (c) UV-B irradiation. Panels (b) and (d) display the corresponding reaction rate constants.

High-resolution TEM images of the A@R TiO₂ NFs (**Figure 6**) show a core of ~80 nm in diameter, which is covered with a layer of uniform NPs. The lattice spacing of the shell NPs and core NFs are 2.50 Å and 3.51 Å, corresponding to (101) plane of rutile and (101) plane of anatase, respectively, shown in **Figure 6 (b)**. The electron diffraction pattern in the inset of **Figure 6 (a)** confirms the coexistence of the anatase and rutile phases.

Figure 6 (a) TEM images of A@R TiO₂-Y and (b) HR-TEM image of inner and outer TiO₂ structures.

While both anatase and rutile are wide band gap semiconductors with suitable band edge positions for many redox reactions, their eventual catalytic activity is very low due to the lack of proper catalytic sites on the surface. Accordingly, despite the favored thermodynamics, the overall reaction rates are typically low. To overcome this drawback, the surface of TiO₂ is often decorated with catalytic metals and metal oxides to facilitate better reactant adsorption and reaction. For H₂

evolution reactions, Pd and Pt are trivial choices owing to excellent adsorption and easy dissociation of H₂ on the surface. In addition, in photocatalytic reactions, both Pt and Pd in TiO₂ help the separation of photogenerated electrons and holes as electrons can inject from the conduction band of the semiconductor to the Fermi level of such high work function metals, is inhibited by the Schottky barrier. To exploit the benefits of such an interface, we decorated the surface of the best performing core-shell NFs (A@R TiO₂-Y) with Pt nanoparticles. The series of TiO₂ NFs photocatalytic hydrogen generation performance under UV-B is shown in **Figure 7**. The rutile core material TiO₂ NFs series showed an undetectable photocatalytic hydrogen production under UV-B irradiation. Even with the help of Pt NPs, neither the Pt-rutile TiO₂ NFs nor the Pt-R@A TiO₂-Y NFs have practically any activity in the reaction. This might be explained by the low activity of rutile in this reaction and the thin anatase shell that is inadequate to absorb photons and to generate electron-hole pair. In contrast, when Pt NPs are decorated to anatase only NFs or to its derivative with rutile shell, we observed significant H₂ evolution rates for all catalysts. The Pt-anatase TiO₂ NFs showed 6,000 µmol/h·g under UV-B irradiation, whereas the core-shell heterostructure nanostructure with Pt NPs (Pt-A@R TiO₂-Y NFs) had an even higher photocatalytic H₂ production rate of ~8,500 µmol/h·g. For evaluated the energy conversion efficiency of hydrogen evolution, the efficiency of the energy conversion from photo energy to chemical energy stored in hydrogen are calculated the following equation²³:

$$\text{photo energy conversion}(\%) = 100 \times \frac{\text{output energy of hydrogen evolved}}{\text{energy of incident light}}$$

The photo-energy conversion is ~4.1% for Pt-anatase TiO₂ NFs and ~5.8% for Pt-A@R TiO₂-Y NFs at UV-B illumination, respectively.

To further display the microstructure of the decorated core/shell TiO₂ NFs, the TEM images of Pt-A@R TiO₂-Y NFs are taken and shown in **Figure S4**. It shows small nanoparticles of Pt with a diameter of 2.4±0.7 nm uniformly dispersed on the rutile shell. EDS analysis (**Figure S4 (b, c)**) confirms the nanoparticles are Pt and have a concentration of 0.8 at.%, which is slightly lower than the nominal 1.0 at.% probably due to sublimation of the Pt-precursor during the decomposition step after impregnating the core-shell TiO₂ structure.

Figure 7 The hydrogen production rate by using various samples under UV-B irradiation.

The band alignment and injection of light-induced electron-hole pairs across the heterostructure of anatase and rutile, as well as between TiO₂ and Pt, determine the kind of and the amount of charge that can be accumulated on the surface. Since the surface charge density has a great influence on the overall photocatalytic performance of the catalyst (in terms of available electrons and holes for redox reactions), it is necessary to assess the surface charging process. Here,

we applied KPFM and measured the change of work function of the catalyst nanostructures with and without light illumination (**Figure 8**). The surface potentials of various TiO₂-based nanofibers in the dark and under UV light are summarized in Table 1. In the measurements, the catalyst nanofibers were deposited on Au coated chip to ensure a stable reference potential (5.1 eV, the work function of Au) which shall not change with or without light exposure. Panels in **Figure 8(□-1)** show the topography of various types of nanofibers, while **Figure 8(□-2)** and **Figure 8(□-3)** display the corresponding surface potential maps with and without UV-B illumination. Here, the notations are as follows: (a) rutile NFs, (b) anatase NFs, (c) R@A TiO₂-Y NFs, (d) A@R TiO₂-Y NFs, and (e) Pt-A@R TiO₂-Y NFs. The work function difference (ΔSP) of each TiO₂-based hybrid nanofiber with and without light illumination is due to electrons being injected to the surface of the material. For the dark condition, we find the work functions being very similar for (a), (b), (c), and (d), which implies that there is no significant charge migration and/or separation in the two-phase systems. Under illumination, the work function remains almost the same for both (a) and (c). This meant that the photoabsorption charge separation does not take place. In the case of (b), the illumination decreased the work function significantly. However, when a rutile shell is applied on the anatase core, in the case of (d), we found a very small change of the work function again. This implied that despite the good photogeneration in the anatase core, electrons either cannot migrate to the surface through the anatase-rutile junction or become compensated for by opposite charges diffusing to and trapping in the rutile shell. This latter mechanism, trapping of holes in rutile shell, was reasonably supported by the results obtained using Pt-decorated hybrid nanowires. Namely, when illuminating (e), we found the work function is significantly decreased by nearly 300 mV. Such a decrease meant that electrons were efficiently injected in the Pt nanoparticles. This was only possible if the photogenerated electrons be injected first from the

anatase core to the rutile shell and then, from there to the metal on the surface. Accordingly, in the Pt-A@R heterostructure, the anatase core functioned as a source of photogenerated electron pairs, the rutile shell acted as a hole trap, whereas the Pt nanoparticles drained any surplus electrons present in the rutile underneath. In order to gain the insight of the carrier transfer in heterojunction TiO₂ NFs, UV-visible spectroscopy (in **Figure S5**) and ultraviolet photoelectron spectroscopy (in **Figure S6**) were conducted to gain further information about the band structure of TiO₂ materials including A TiO₂ NFs, R TiO₂ NFs, A TiO₂ NPs and R TiO₂ NPs. The calculated bandgap (BG), valence band maximum (VBM) and conduction band minimum (CBM) are demonstrated in **Table 2**.

The reactive oxygen species (ROS) test including benzoquinone and ammonium oxalate were carried out to monitor photogenerated carriers and their effects to degradation. The results are demonstrated in **Figure S7**. Here, benzoquinone acts as a scavenger of superoxide radical, whereas ammonia oxalate acts as a scavenger of the photogenerated hole. In other word, the target with benzoquinone as scavenger inhibit the degradation of MO from the contribution of the photogenerated electron. Ammonia oxalate as scavenger, on the other hand, can retard the degradation causing by the photogenerated hole. Comparing targets with scavengers to the control without scavenger can clearly tell which carrier contributes degradation of MO. **Figure S7 (a)** and **(b)** show C/C₀ degradation plots of rutile TiO₂ NFs and R@A TiO₂ NFs. Because of inferior photocatalytic activity of rutile TiO₂, the degradation of MO still remains over 60% after 150 min test in both systems with the absence of scavengers. The degradation with the presence of benzoquinone and ammonia oxalate in **Figure S7 (a)** shows merely the same behavior with around 90% MO remaining. Interestingly, in **Figure S7 (b)** the degradation with the presence of benzoquinone show inferior to with the presence of ammonia oxalate. It can be attributed to ease collection of electron than hole for scavenger in the R@A TiO₂ NFs.

Figure S7 (c), (d) and (e) show different degradation behavior of anatase with scavenger. In **Figure S7 (c)**, the results give the information that electron dominates the degradation process in anatase TiO_2 . The opposite degradation behavior of A@R TiO_2 with the presence of scavengers compared with anatase TiO_2 NFs indicated the excited holes are easily transferred to the surface rutile TiO_2 NPs in this heterojunction and captured by ammonia oxalate. Therefore, the degradation process obviously deteriorates with the presence of ammonia oxalate. Yet, the degradation process of MO was still obvious with the presence of benzoquinone in **Figure S7 (d)**. That implies photogenerated electrons still partially anticipate in the degradation. **Figure S7 (e)** was the degradation plots with Pt-A@R TiO_2 -Y. The slow degradation with the presence of benzoquinone told the photogenerated electron is easier transfer to the external layer with platinum nanoparticles.

Based on the analyses above, we may construct a simplified model of the band structure (**Figure 9**) being very similar to that proposed by the band structure for the core-shell heterostructures of anatase and rutile.⁴⁹ The aligned conduction bands of anatase and rutile allow for seamless electron injection between the two titania phases. However, the small offset of the valence band edges retards the injection of holes from rutile to anatase. On the other hand, platinum in contact with rutile forms a Schottky interface at which electrons can only be injected from the semiconductor to the metal.

Table 1. Surface potential of various TiO₂-based nanofibers in the dark or under UV light

No.	Materials	WF in the dark (V)	WF under UV light (V)	Δ WF (mV)
(a)	Rutile (R)	4.33	4.32	-10
(b)	Anatase (A)	4.50	4.40	-100
(c)	R@A TiO ₂ -Y	4.35	4.33	-20
(d)	A@R TiO ₂ -Y	4.50	4.47	-30
(e)	Pt-A@R TiO ₂ -Y	6.40	6.13	-270

Table 2. Calculated bandgap, valance band maximum and conduction band minimum of each type of TiO₂

Material	Bandgap (eV)	VB maximum (V)	CB minimum (V)
Anatase TiO ₂ NFs	3.22	-7.82	-4.65
Rutile TiO ₂ NFs	3.01	-7.67	-4.66
Anatase TiO ₂ NPs	3.14	-7.86	-4.72
Rutile TiO ₂ NPs	2.92	-7.58	-4.66

Figure 8 Surface topographic images (□-1), surface potential mappings in the dark (□-2) or under UV-B illumination (□-3) of five kinds of TiO₂-based materials: (a) rutile, (b) anatase, (c) R@A TiO₂-Y NFs, (d) A@R TiO₂-Y NFs, and (e) Pt-A@R TiO₂-Y NFs.

Figure 9 Schematic band structure and possible transfer routes of electrons and holes for Pt-A@R TiO₂.

CONCLUSIONS

In this study, rutile@anatase and anatase@rutile core-shell nanofibers and the Pt-decorated derivative of the latter were synthesized and studied in photocatalytic reactions, such as degradation of methyl orange and H₂ evolution from the ethanol-water mixture. Even without Pt on its surface, anatase@rutile NFs showed nearly 3-fold photocatalytic activity in the degradation of methyl orange as compared to the commercial AEROXIDE® TiO₂ P25. In photocatalytic hydrogen production, the corresponding Pt-decorated catalyst showed excellent activity with hydrogen generation rate of ~8,500 μmol/h·g. KPFM measurements suggested that the holes were efficiently transported to the rutile shell, where electron exchange between two phases, as well as injection of those into the Pt nanoparticles took place. Consequently, the Pt nanoparticles provided not only a catalytic surface, but also an electron-rich environment, where protons may be reduced

to hydrogen expediting the photocatalytic ethanol reforming reaction.

ASSOCIATED CONTENT

Additional supporting figures such as the Raman spectra for core material TiO₂ NFs calcined at different temperatures, TEM images for TiO₂-700 °C NFs and Pt- A@R TiO₂-Y, Kubelka-Munk plots and ultraviolet photoelectron spectrum for TiO₂ (rutile or anatase phases) of both the NFs and NPs are available free of charge on the ACS Publications website at DOI: 10.1021/acsami.XXXXXXX.

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Notes

The authors declare no competing financial interest.

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Table of Contents Graphic

Supporting Information

Core-Shell Heterostructures of Rutile and Anatase TiO₂ Nanofibers for Photocatalytic Solar Energy Conversion

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Figure S1. Raman spectra of core material TiO₂ NFs calcined at different temperatures.

Figure S2. (a) Low magnification and (b) high magnification TEM images of TiO_2 -700°C NFs. (c), (d) are high-resolution TEM image of TiO_2 -700°C NFs, anatase (101) face, and inset of (d) is the corresponding FFT pattern of anatase (101) face.

Figure S3. X-ray diffraction pattern of P25 TiO_2 , A TiO_2 NFs and A@R TiO_2 series.

Figure S4. (a) Bright and (b) dark-field TEM images as well as (c) EDS line mapping of Pt- A@R TiO₂-Y. The inset panels (c-1), (c-2) and (c-3) display the separate X-ray photon counts for Pt, Ti, and O, respectively.

Figure S5. Kubelka-Munk plots of (a) Anatase and Rutile TiO₂ NFs and (b) Anatase and Rutile TiO₂ NPs.

Figure S6. Ultraviolet photoelectron spectrum of (a) Anatase TiO₂ NFs, (b) Rutile TiO₂ NFs, (c) Anatase TiO₂ NPs and (d) Rutile TiO₂ NPs.

Figure S7. Reactive oxygen species test of (a) Rutile TiO₂ NFs, (b) R@A TiO₂ NFs, (c) Anatase TiO₂ NFs, (d) A@R TiO₂ NFs and (e) Pt-A@R TiO₂ NFs under UV-B irradiation.