Review

Radial TiO₂ Nanorod-Based Mesocrystals: Synthesis, Characterization, and Applications

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Abstract: Radial TiO₂ nanorod-based mesocrystals (TiO₂-NR MCs) or so-called “sea-urchin-like microspheres” possess not only attractive appearance but also excellent potential as photocatalyst and electrode materials. As a new type of TiO₂-NR MCs, we have recently developed a radial heteromesocrystal photocatalyst consisting of SnO₂(head) and rutile TiO₂ nanorods(tail) (TiO₂-NR//SnO₂ HEMCs, symbol “//” denotes heteroepitaxial junction) with the SnO₂ head oriented in the central direction in a series of the studies on the nanohybrid photocatalysts with atomically commensurate junctions. This review article reports the fundamentals of TiO₂-NR MCs and the applications to photocatalysts and electrodes. Firstly, the synthesis and characterization of TiO₂-NR//SnO₂ HEMCs is described. Secondly, the photocatalytic activity of recent TiO₂-NR MCs and the photocatalytic action mechanism are discussed. Thirdly, the applications of TiO₂-NR MCs and the analogs to the electrodes of solar cells and lithium-ion batteries are considered. Finally, we summarize the conclusions with the possible future subjects.

Keywords: TiO₂-based mesocrystals; homomesocrystals; heteromesocrystals; photocatalysts; oxygen reduction reaction; electrodes

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1. Introduction

Among various photocatalyst materials, TiO₂ is the most promising one in terms of suitability and safety in environmental purification and anti-bacterial applications due to strong photoinduced oxidation ability, extreme stability, non-toxicity, and inexpensiveness [1,2]. While the photocatalytic activity of TiO₂ particles is sensitive to the crystal phase, crystallinity, and dimension [3], the assembled structure of TiO₂ particles or the mesocrystal (MC) structure can have a great effect on the photocatalytic activity [4,5]. The geometries of the TiO₂-based MCs so far reported can be classified into two-dimensional (2D) and three-dimensional (3D) types (Scheme 1). Majima and co-workers prepared 2D-TiO₂ MCs consisting of TiO₂ plates with 3–5 μm size and 100–300 nm thickness linking through the edges (TiO₂-NPL MCs) using a simple impregnation method (2D-type in Scheme 1) [5]. Gold nanoparticle-loaded TiO₂ (Au/TiO₂) works as a visible-light responsive photocatalyst under excitation of the localized surface plasmon resonance [6]. The Au/TiO₂-NPL MC plasmonic photocatalyst was shown to exhibit significantly higher organic pollutant degradation activity than the usual Au/TiO₂ particles due to the effective charge separation via the anisotropic interparticle electron transfer. The development of 3D-TiO₂ MCs has been triggered by the study of dye-sensitized solar cells [7]. The cell performance was dramatically enhanced by using a TiO₂ nanocrystalline film electrode in which anatase TiO₂ nanoparticles (NPs) with 20–30 nm diameter are interconnected randomly to yield a mesoporous structure and a large surface area (3D-type I in Scheme 1). More recently, radial homomesocrystals consisting of rutile TiO₂ nanorods (TiO₂-NR HOMCs), so-called “sea-urchin-like microspheres” (3D-type II in Scheme 1), have attracted much interest due to features including a high light harvesting ability due to multiple light scattering between the reflective rutile TiO₂ NRs [8,9] and large surface area comparable with that of NPs.

These unique nano/micro-sized properties render the radial TiO_2 -NR HOMCs fascinating as a photocatalyst material. Unexpectedly, the photocatalytic activity for aerobic oxidation of organics still remains low, probably because of the poor ability of rutile TiO_2 for oxygen reduction reaction (ORR) [10,11]. Thus, if the abilities of effective charge separation and electrocatalytic activity for ORR can be endowed with radial TiO_2 -NR HOMCs, the photocatalytic activity would be enhanced, and their applications should be greatly extended. To achieve this, we have recently developed a radial heteromesocrystal photocatalyst consisting of SnO_2 (head) and rutile TiO_2 nanorods (tail) (TiO_2 -NR// SnO_2 HEMCs, “//” denotes heteroepitaxial junction) (3D-type III in Scheme 1) and studied the photocatalytic activity for aerobic oxidation of organics.

Scheme 1. Representative geometries of the TiO_2 -based MCs.

This review article describes the synthesis, characterization, and the photocatalytic activity of TiO_2 -NR// SnO_2 HEMCs and other recent TiO_2 -NR HOMCs. The photocatalytic action mechanism of TiO_2 -NR// SnO_2 HEMCs is also discussed by comparison with TiO_2 -NR HOMCs. Further, the applications of TiO_2 -NR HOMCs and the analogs to the electrodes for solar cells and lithium-ion batteries are considered. Finally, the conclusions are summarized with the possible future subjects.

2. Synthesis and Characterization

In 2006, Yang and Gao synthesized sea-urchin-like TiO_2 nanostructures ($\sim 1\ \mu\text{m}$) (3D-type II in Scheme 1) for the first time using a sol–solvothermal method from a water–benzene solution of TiCl_4 and $\text{Ti}(\text{OBu})_4$ without using any template or surfactant [12]. Several review papers on the synthesis and characterization of TiO_2 -NR HOMCs have already been reported [8,9,13]. Here, we explain the method for synthesizing TiO_2 -NR// SnO_2 HEMCs (3D-type III in Scheme 1). TiO_2 -NR// SnO_2 HEMCs were synthesized using a hydrothermal method in the presence of SnO_2 seeds with particle size of 22–43 nm [14]. HCl (6 M, 30 mL) and $\text{Ti}(\text{OBu})_4$ (0.4 mL) were mixed in a reaction vessel made of Teflon (50 mL), and the solution was slowly stirred for 0.5 h at ambient temperature. SnO_2 nanocrystals (0.01 g) were dispersed into the mixed solution by ultrasonic irradiation and stirred for 24 h. The reaction vessel was sealed in a stainless-steel cylinder, and then it was placed in an oil bath, the temperature of which was maintained at $150\ ^\circ\text{C}$ for various reaction times (t_{HT}). Solid products produced after the reaction were collected by centrifugation. The same synthetic procedures were conducted using HNO_3 and H_2SO_4 in the place of HCl .

The product morphology is strongly affected by the kinds of acids used in the hydrothermal reaction (Figure 1a–c). In the case of HCl , 3D-radial microspheres with a diameter of $\sim 3\ \mu\text{m}$ are produced at $t_{\text{HT}} = 8\ \text{h}$. The specific surface area of the particles was determined by the Brunauer–Emmett–Teller (BET) method to be $41.1 \pm 0.2\ \text{m}^2\ \text{g}^{-1}$, which is 1.75×10^2 times larger than the value for the spherical particle with a diameter of $3\ \mu\text{m}$.

On the one hand, the use of HNO_3 or H_2SO_4 produces irregularly shaped aggregates. In the XRD pattern of the sample prepared with HCl , there are sharp peaks at $2\theta = 27.38^\circ$, 36.04° , 41.18° , and 54.28° indexed as the diffraction from the (110), (101), (111), and (211) crystal planes of rutile TiO_2 (ICDD 00-021-1276), respectively, in addition to the peaks at $2\theta = 26.5^\circ$, 33.78° , and 51.74° assignable to the diffraction from the (110), (101), and (211) planes of SnO_2 , respectively (ICDD 01-075-2893) (Figure 1d).

Figure 1. SEM images for the TiO_2 - SnO_2 hybrids prepared by the hydrothermal method under acidic conditions using HCl (a), HNO_3 (b), and H_2SO_4 (c): hydrothermal reaction time (t_{HT}) = 8 h. (d) X-ray diffraction patterns of the samples before and after the hydrothermal method under acidic conditions using HCl . The figures are taken from Reference [15] (reproduced with permission from Akita, A.; Kobayashi, H.; Tada, H., *Chem. Phys. Lett.*; published by Elsevier, 2020).

Transmission electron microscopy (TEM) analyses of the particles generated at the early stage of reaction provide information about the crystal growth mechanism and the state of the junction between SnO_2 and TiO_2 . The TEM image of a particle generated at $t_{\text{HT}} = 1$ h shows a single TiO_2 NR grown from a SnO_2 seed crystal with the mean lengths of short axis (~ 13 nm) and long axis (~ 90 nm) (Figure 2a). An atomically commensurate junction is also formed between the SnO_2 seed and TiO_2 NR, whose lattice spacings near the interface are close to the values of the (110) crystal planes. A plausible interface model is proposed based on the analysis of the high-resolution (HR)-TEM images (Figure 2b,c), where the TiO_2 -NR and SnO_2 are connected with an orientation of $(001)_{\text{TiO}_2} // (001)_{\text{SnO}_2}$, and the TiO_2 NR grows toward the [001] direction. Consequently, anisotropic one-dimensional (1D) TiO_2 -NR// SnO_2 particles are formed during the initial process of reaction. Density functional theory (DFT) simulations indicated that Cl^- ions act as a habit modifier in this reaction, i.e., their preferential adsorption on the oxygen-defect sites on the rutile $\text{TiO}_2(110)$ plane induces the anisotropic growth of TiO_2 in the [001] direction yielding the NR with the {110} side walls [15].

Figure 2. (a) TEM image for a particle prepared by the hydrothermal reaction at $t_{HT} = 1$ h, and the inset is the HR-TEM image for the interface of the same sample. Top view (b) and side view (c) for the interface model constructed from the HR-TEM image. The figure is taken from Reference [14] (reproduced with permission from Akita, A.; Tada, H., *Langmuir*; published by American Chemical Society, 2019).

To clarify the orientation of the 1D-TiO₂-NR//SnO₂ particles in the 3D-microsphere, scanning transmission electron microscopy (STEM)–energy dispersive spectroscopic (EDS), Figure 3a) elemental mapping was performed on a particle generated at $t_{HT} = 8$ h. Many 1D-TiO₂-NR//SnO₂ particles are self-assembled to form a radial 3D-microsphere (Figure 3a). Ti and O are uniformly distributed over the microsphere (Figure 3b,c). On the contrary, Sn is unevenly present near the center (Figure 3d). Clearly, each 1D-TiO₂-NR/SnO₂ particle is oriented with the SnO₂ head in the central direction of the microsphere.

Figure 3. (a) STEM–EDS elemental mapping for a particle prepared by the hydrothermal reaction at $t_{HT} = 8$ h ((b), Ti; (c), O; (d), Sn). The figure is taken from Reference [14] (reproduced with permission from Akita, A.; Tada, H., *Langmuir*; published by American Chemical Society, 2019).

The formation mechanism of TiO₂-NR//SnO₂ HEMCs can be explained as follows (Scheme 2). Initially, Ti(OBu)₄ undergoes hydrolysis–polycondensation in HCl solution

with SnO_2 seed nanocrystals, where HCl suppresses the hydrolysis–polycondensation to inhibit the homogeneous particle formation [16]. At $t_{\text{HT}} \leq 0.5$ h, the SnO_2 surface is covered by an amorphous TiO_2 layer (SnO_2 @amorphous- TiO_2). At $0.5 \text{ h} < t_{\text{HT}} < 1$ h, rutile TiO_2 nuclei occur on the SnO_2 surface to grow in the [001] direction with the most stable {110} facets exposed at the side planes. In this process, the adsorption of Cl^- ions on the TiO_2 {110} planes restricts their growth to induce the anisotropic growth along the [001] direction yielding 1D- TiO_2 -NR// SnO_2 particles [15]. The self-assembling to the radial 3D-microsphere can arise from the balance between the repulsion and attraction forces between the 1D- TiO_2 -NR// SnO_2 particles. Since the points of zero charge of rutile TiO_2 and SnO_2 are ~ 5 and ~ 3.5 , respectively [17], the SnO_2 head in the 1D- TiO_2 -NR// SnO_2 particle has smaller positive surface charge than the TiO_2 tail under the strong acidic conditions. Additionally, the van der Waals attractive force for SnO_2 particles would be larger than that for rutile TiO_2 particles since the former has a Hamaker constant of 5.5×10^{-20} J, larger than the latter of 4×10^{-20} J [18]. Consequently, the smaller repulsive and larger attractive forces between the SnO_2 heads of 1D- TiO_2 -NR// SnO_2 particles induce the formation of the radial 3D-microsphere with the heads oriented toward the central direction.

Scheme 2. A schematic representation of the formation and self-assembling of TiO_2 -NR// SnO_2 . The figure is taken from Reference [14] (reproduced with permission from Akita, A.; Tada, H., *Langmuir*; published by American Chemical Society, 2019).

3. Photocatalytic Applications

3.1. TiO_2 -Nanorod Homomesocrystals

The most outstanding feature of the TiO_2 -NR MCs is the high light harvesting ability due to the multiple light scattering between TiO_2 NRs, which should be more effective for rutile TiO_2 (refractive index, $n_{E//c} = 2.616$, $n_{E\perp c} = 2.903$) than anatase TiO_2 ($n_{E//c} = 2.554$, $n_{E\perp c} = 2.493$) [19]. The photocatalytic studies of radial rutile TiO_2 -NR HOMCs (3D-type II in Scheme 1) and the analogs are less than expected from the excellent potential. In this section, some of the studies performed over the last decade are introduced.

Zhao and co-workers prepared rutile TiO_2 -NR HOMCs (1–3 μm) with the specific surface area of $\sim 40 \text{ m}^2 \text{ g}^{-1}$ using a solvothermal method [20]. P-25 (specific surface area = $\sim 50 \text{ m}^2 \text{ g}^{-1}$, rutile/anatase = 30:70, Evonik) is known to exhibit a high level of photocatalytic activity for various reactions, being used as a benchmark photocatalyst. The photocatalytic activity of the TiO_2 -NR HOMCs (1–3 μm) and P-25 for degradation of methylene blue (MB) was studied under UV–visible irradiation. The TiO_2 -NR HOMCs (1–3 μm) show higher photocatalytic activity than P-25, which was ascribable to the efficient light absorption of the former. Further, the photocatalytic activity decreases with an increase in the diameter of the TiO_2 -NR HOMCs from ~ 1 to $\sim 3 \mu\text{m}$, although the reason is unclear.

The same group prepared Au NP (2–10 nm) and Ag NP (~20 nm)-loaded rutile TiO₂-NR HOMCs (1–2 µm) with a specific surface area of ~40 m² g^{−1} using a chemical reduction method [20]. The photocatalytic activity for MB degradation was examined under UV–visible irradiation. Unmodified TiO₂-NR HOMCs show photocatalytic activity comparable with that of P-25. Further, loading Ag and Au NPs significantly increases the photocatalytic activity. This is probably because of the enhancement of charge separation due to the interfacial electron transfer from TiO₂ to the metal NPs. The authors proposed that visible-light irradiation induces the hot-electron transfer from the metal NPs to TiO₂ to yield one-electron ORR on rutile TiO₂ causing the MB degradation, although no evidence is provided.

Xu, Li, and co-workers prepared rutile TiO₂-NR HOMCs (2–3 µm) with a very large specific surface area of 224 m² g^{−1} using a solvothermal method [21]. The diameter and length of TiO₂ NRs are 5–8 nm and ~0.2 µm, respectively. Under sunlight irradiation of the sample, Cr⁶⁺ ions are reduced to Cr³⁺ ions with the yield of ~100% at the concentration below 53.7 ppm. The removal capacity under irradiation of sunlight for 3 h was reported to reach ~1 g g^{−1}. In this case, it is worth noting that the reduction with a very positive standard electrode potential ($E^0(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = +1.36 \text{ V}$) is thermodynamically permitted [22].

Next, the studies of anatase TiO₂-NR HOMCs are described. Zhang and co-workers synthesized an anatase analog of 3D-rutile TiO₂-NR HOMCs for the first time [23]. It is known that anatase TiO₂ shows higher photocatalytic activity than rutile TiO₂ in most aerobic oxidation reactions [24]. Wang and co-workers reported the large-scale synthesis of urchin-like mesoporous TiO₂ hollow spheres (UMTHS) (~0.45 µm) surrounded by single-crystal anatase nanohorns with a diameter of 10–20 nm and a length of 40–60 nm [25]. The synthesized sample with a large specific surface area of 129 m² g^{−1} and excellent light harvesting efficiency exhibits photocatalytic activity for removal of gaseous nitric oxide (NO) superior to P-25.

Xu and co-workers prepared hierarchical golden wattle-like microspheres consisting of rutile TiO₂ NRs with a diameter of 40–60 nm and a length of 400–500 nm using a solvothermal method using a reaction solution of acetone (20 mL) containing titanium *n*-butoxide (4 mL) and HCl (*x* mL, 36–38 wt%) [26]. The HCl concentration in the reaction solution plays an important role in controlling the size and morphology of products. The photocatalytic activities of the samples and P-25 for the degradation of phenol were assessed under UV-light irradiation ($\lambda_{\text{ex}} = 365 \text{ nm}$). The photocatalytic activity strongly depends on *x*, and the sample prepared at *x* = 2 mL exhibits photocatalytic activity comparable to that of P-25. The authors attributed the high photocatalytic activity of the sample to the suppression of the recombination by smooth electron transportation through the 1D-TiO₂ NRs with high crystallinity, efficient light harvesting ability, and large surface area or large number of adsorption sites for phenol.

Li, Liu, Wang, and co-workers synthesized ultrathin nanobelt-assembled urchin-like anatase TiO₂ nanostructures (~0.25 µm) with a large specific surface area of 171 m² g^{−1} using a one-step hydrothermal route [27]. The length of the nanobelts is several µm, and the width and thickness are in the ranges of 50 to 100 and 23 to 30 nm, respectively. The sample was shown to exhibit photocatalytic activities significantly higher than commercial anatase TiO₂ NPs and P-25 for the degradation of methyl orange and phenol under irradiation of UV-light ($\lambda_{\text{ex}} = 365 \text{ nm}$).

Einaga and co-workers partially reduced sea-urchin-like TiO₂ microspheres (~0.25 µm) consisting of anatase TiO₂ NRs by heating at various temperatures (*T_c*) under vacuum [28]. The photocatalytic activity of the samples for benzene degradation depends on *T_c* with a maximum at *T_c* = 250 °C. The optimal sample shows significantly higher activity than P-25 for the decomposition of benzene to CO₂ with good stability.

3.2. TiO₂-Nanorod//SnO₂ Heteromesocrystals

Acetaldehyde is a useful intermediate for various chemical products, medicines, and pharmaceuticals [29]. Industrially, acetaldehyde is produced by the Wacker oxidation of ethylene with PdCl₂-CuCl₂ as the catalyst at high temperature and pressure [30]. From the perspective from the Sustainable Development Goals (SDGs), the solar-driven production of acetaldehyde from biomass-derived ethanol with high selectivity is highly desired [31]. Gas-phase photocatalytic oxidation of ethanol to acetaldehyde was studied under UV-light irradiation of TiO₂-NR//SnO₂ HEMCs (3D-type III in Scheme 1) and TiO₂-NR HOMCs (3D-type II in Scheme 1) ($\lambda > 300$ nm, $I = 2.0$ mW cm⁻²) (Figure 4a) [32]. In each system, irradiation yields acetaldehyde, while no acetaldehyde is generated in the dark. The apparent first-order rate constants (k_{AA}) were 1.9×10^{-2} h⁻¹ for TiO₂-NR HOMCs and 3.2×10^{-2} h⁻¹ for TiO₂-NR//SnO₂ HEMCs. The external quantum yield (ϕ_{ex}) or apparent quantum yield at $\lambda_{ex} = 365$ nm was also calculated to be 7.7% for TiO₂-NR HOMCs and 13.4% for TiO₂-NR//SnO₂ HEMCs, which is larger than the values reported for the TiO₂-photocatalyzed oxidation of ethanol to acetaldehyde (<~10%) [33–35].

Figure 4. (a) Comparison of the photocatalytic activities of TiO₂-NR//SnO₂ HEMCs ($t_{HT} = 8$ h) and TiO₂-NR HOMCs ($t_{HT} = 8$ h) for gas-phase oxidation of ethanol under UV-light irradiation ($\lambda = 365$ nm, $I = 2.0$ mW cm⁻²). (b) PL spectra were measured for TiO₂-NR//SnO₂ HEMCs, TiO₂-NR HOMCs, and TiO₂ NPs for comparison at 77 K with an excitation wavelength of 340 nm. The figure is taken from Reference [32] (reproduced with permission from Akita, A.; Sugita, S.; Naya, S.; Tada, H., *Catal. Commun.*; published by Elsevier, 2021).

Photoluminescence (PL) spectra of TiO₂-NR//SnO₂ HEMC, TiO₂-NR HOMC, and rutile TiO₂ NPs for comparison were measured (Figure 4b) to evaluate the relative charge separation efficiency in the photocatalytic process [36]. Rutile TiO₂ NPs have three signals around 410 (B₁), 520 (B₂), and 800 nm (B₃) assigned to the interband emission and the emissions by the recombination at shallow [37] and deep vacancy sites [38], respectively. In the spectra of TiO₂-NR//SnO₂ HEMCs and TiO₂-NR HOMCs, the B₂ band almost disappears. It is also worth noting that the emission intensity of TiO₂-NR//SnO₂ HEMCs is weaker than that of TiO₂-NR HOMCs. Thus, the charge separation is suggested to occur more effectively in the TiO₂-NR//SnO₂ HEMC system than the TiO₂ NP and TiO₂-NR HOMC systems through the interfacial electron transfer from TiO₂ to SnO₂ [39].

3.3. Photocatalytic Action Mechanism

The key to boosting the photocatalytic activity of the radial rutile TiO₂-NR MCs for aerobic oxidation of organics is imparting them to the electrocatalytic activity for multiple ORR in addition to the charge separation enhancement [10,11,40]. Photocatalytic two-electron ORR has received much attention as a “green” route for producing H₂O₂ [41], and so far, highly active electrocatalysts such as Au NPs [42–44] and Pd NPs [45] have been reported. The development of the electrocatalyst for four-electron ORR is a major

challenge in proton exchange membrane fuel cells, and Pt-based catalysts have mainly been studied [46]. Abe, Ohtani, and co-workers previously showed that loading of Pt NPs on WO_3 drastically increases the photocatalytic activity for aerobic oxidative decomposition of organics [47]. Recently, some metal oxides such as SnO_2 [48] and CoFe_2O_4 [49] have been shown to exhibit electrocatalytic activity for multiple-electron ORR, and consequently, the coupling with TiO_2 can increase the photocatalytic activity for aerobic oxidation of organics.

The striking photocatalytic activity of $\text{TiO}_2\text{-NR}/\text{SnO}_2$ HEMCs (3D-type III in Scheme 1) for the partial oxidation of ethanol can stem from the following features (Scheme 3). Firstly, the radial $\text{TiO}_2\text{-NRs}$ of several microns in length enable efficient light absorption due to the multiple light scattering between the highly reflective rutile TiO_2 NRs exciting the electrons in the valence band (VB) to the conduction band (CB). Secondly, the CB-electrons in the TiO_2 NRs are transported in the [001] direction due to the highest conductivity direction [50] and effectively transferred to the CB of SnO_2 through the high-quality interface [39]. Thirdly, the heteroepitaxial junction-induced CB-band bending in SnO_2 enhances the charge separation [39]. The CB-edge potentials of rutile TiO_2 [51] and FTO (or SnO_2) [52] are located around +0.11 and +0.48 V (vs. SHE at pH 0), respectively. Fourthly, the electrons collected in SnO_2 can induce two-electron ORR ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = +0.695$ V) due to the electrocatalytic activity [48], whereas one-electron ORR ($E^0(\text{O}_2/\text{O}_2^-) = -0.33$ V) [22] is thermodynamically difficult on TiO_2 NRs. Thus, $\text{TiO}_2\text{-NR}/\text{SnO}_2$ HEMCs exhibit much higher photocatalytic activity than $\text{TiO}_2\text{-NR}$ HOMCs [32]. Fifthly, the reaction field of the oxidation by the VB holes in rutile TiO_2 is limited to the near-surface [53], and also, the adsorptivity of rutile TiO_2 for acetaldehyde is weak [54]. Consequently, the over-oxidation of acetaldehyde can be effectively inhibited.

Scheme 3. Action mechanism of $\text{TiO}_2\text{-NR}/\text{SnO}_2$ HEMC photocatalyst. The figure is taken from Reference [32] (reproduced with permission from Akita, A.; Sugita, S.; Naya, S.; Tada, H., *Catal. Commun.*; published by Elsevier, 2021).

4. Electrochemical Applications

Besides the photocatalysts, the radial $\text{TiO}_2\text{-NR}$ HOMCs (3D-type II in Scheme 1) and the analogs can be suitably applied to the electrodes for the solar cells and lithium-ion batteries by taking the unique geometrical, optical, and electrochemical properties. In this section, some of the studies reported over the last decade are described.

4.1. Solar Cells

Jang and co-workers synthesized radial TiO_2 HOMCs with a size of 4–7 μm consisting of rutile TiO_2 NRs with a diameter of ~ 50 nm and length of few micrometers using a

simple solvothermal route [55]. A CdS/CdSe/ZnS quantum dot-sensitized solar cell was constructed using a base electrode including the rutile TiO₂ HOMCs and anatase TiO₂ NPs with a diameter of ~20 nm. The solar cell provided a conversion efficiency of 4.2% with a short-circuit photocurrent of 18.2 mA cm⁻² and an open-circuit voltage of 531 mV, while the conversion efficiency of the reference cell using the TiO₂ NP electrode without rutile TiO₂ HOMCs was 3.5%. The superior performance of the cell made of the hybrid photoanode of rutile TiO₂ NR HOMCs and anatase TiO₂ NPs was ascribable to the high light harvesting and charge collection properties of the rutile TiO₂ NR HOMCs.

Wang and co-workers fabricated a dye(Z907)-sensitized solar cell using UMTHS as an active layer of photoanode with Co(bpy)₃^{3+/2+} electrolyte [25]. The solar cell provided an impressive power conversion efficiency of 5.5% under one-sun irradiation (AM-1.5). The excellent cell performance was ascribable to the large surface area and high light-scattering property of UMTHS.

Zhou and co-workers synthesized flower-like and sea-urchin-like TiO₂ NR HOMCs using a solvothermal method [56]. The geometrical effect of the TiO₂ photoanode on the performance of a dye(N719)-sensitized solar cell was studied. The conversion efficiency increases in the order of sphere-like (0.82%) < flower-like (3.61%) < sea-urchin-like (8.04%). The authors suggested that the superior performance of the cell with the sea-urchin-like TiO₂ photoanode partly results from the 1D-channel of electron transport in the rutile TiO₂ NR enhancing the charge separation.

Peng and co-workers formed a film consisting of rutile TiO₂ NR HOMCs with a diameter of 5–6 µm on Ti foil (TiO₂ NR MC/Ti) using a hydrothermal method [57]. A quasi-solid-state dye(N719)-sensitized solar cell was fabricated, and a high conversion efficiency of 7.27% was achieved by using the film as an underlayer of a nanosized anatase TiO₂ film. A similar effect was obtained in a dye(N719)-sensitized solar cell using the TiO₂ NR MC/Ti covered with anatase nanotubes as a photoanode [58]. Interestingly, in these systems, the combination of 3D-type I and 3D-type II in Scheme 1 remarkably enhances the cell performance due to their large surface area and effective light scattering property.

4.2. Lithium-Ion Batteries

Archer, Lou, and co-workers synthesized TiO₂ nanosheet hierarchical spheres (TiO₂ NSHSs) with an average size of ~1 µm using a hydrothermal method [59]. TiO₂ NSHSs consisting of (001)-faceted anatase TiO₂ nanosheets with a thickness of ~3 nm and size of 100–300 nm has a mesoporous structure with a very large specific surface area of 170 m² g⁻¹. Consequently, TiO₂ NSHSs manifest an unusual high Coulombic efficiency for lithium extraction, excellent capacity retention over 175 mA h g⁻¹ even at 100 charge–discharge cycles, and superior rate of insertion-release in batteries.

Han and co-workers prepared radial rutile TiO₂ HOMCs using a hydrothermal method, and the geometry was maintained after annealing at 300 °C with a specific surface area of 115.3 m² g⁻¹ and a pore size of 2.26 nm [60]. The electrochemical properties were examined in a 1M LiPF₆ electrolyte solution of ethylene carbonate and dimethylcarbonate (1:1 v/v) for the application to lithium-ion batteries. The radial rutile TiO₂ HOMC electrode shows outstanding energy storage behavior, with a high capacity of 457 mA h g⁻¹ at the first discharge cycle, a reversible and high rate charge–discharge capability, high rate performance, and good cycling stability.

5. Conclusions and Future Subjects

This review article highlights the synthesis, characterization, and photocatalytic activity of TiO₂-NR//SnO₂ HEMCs. TiO₂-NR//SnO₂ HEMCs surpass TiO₂-NR HOMCs in photocatalytic activity. The striking photocatalytic activity of TiO₂-NR//SnO₂ HEMCs can stem from the following features: (1) Incident light is efficiently absorbed by the multiple light scattering between TiO₂ NRs, (2) smooth 1D-electron transport along the [001] direction due to the large electron mobility, (3) efficient interfacial electron transfer from TiO₂ to SnO₂ can occur through the high-quality interface, (4) effective charge separation can

be achieved by the heteroepitaxial junction-induced CB-potential gradient in SnO₂, and (5) the electrocatalytic activity of SnO₂ for multiple ORR can complete the catalytic cycle because the holes in the VB of TiO₂ have strong oxidizing ability. Consequently, the development from the HOMCs to HEMCs can extend the applications of the TiO₂ NR-based MC photocatalysts to various chemical transformations. In the meantime, TiO₂ NR-based MCs possess various features including large charge capacity, excellent electron-transport, electron-collecting properties, and robustness in addition to efficient light harvesting ability. As a result, TiO₂ NR-based MCs can also be a very promising electrode material for solar cells and lithium-ion batteries. Research to improve the cell performance by optimizing the geometry and physicochemical properties of TiO₂ NR-based MCs is ongoing.

There are two important subjects for the TiO₂ NR-based MCs. The first one relates to the sample production. In the hydrothermal synthesis of TiO₂-NR//SnO₂ HEMCs, the yield remains <50% even at $t_{HT} = 8$ h. The development of the technique enabling the synthesis of TiO₂-NR MCs in a shorter reaction time with a higher yield would accelerate research and raise feasibility. The second one is concerned with the application to photocatalysts. Since rutile TiO₂ NR-based MCs with an absorption edge of ~410 nm mainly absorb UV-light occupying only 3% of solar energy, endowing them with visible-light responsiveness and simultaneous enhancement of UV-light activity are crucial for applications to efficient solar-to-chemical transformations. So far, the study on the visible-light activation of the TiO₂-NR MCs is limited. Rodriguez and co-workers have recently reported the visible-light activation of TiO₂-NR MCs by Ru-doping for H₂ generation from methanol aqueous solution [61]. Finally, it has recently been revealed that heteroepitaxial junctions are impossible in the bulk system due to the significant lattice mismatch that can be formed in the nanohybrid systems [62]. We anticipate that the new approach of interface control at an atomic level can widely contribute to enhancement in the performance of nanohybrids as photocatalysts and other functional materials.

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