Heterostructured TiO$_2$ Nanorod@Nanobowl Arrays for Efficient Photoelectrochemical Water Splitting

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Heterostructured TiO$_2$ nanorod@nanobowl (NR@NB) arrays consisting of rutile TiO$_2$ nanorods grown on the inner surface of arrayed anatase TiO$_2$ nanobowls are designed and fabricated as a new type of photoanodes for photoelectrochemical (PEC) water splitting. The unique heterostructures with a hierarchical architecture are readily fabricated by interfacial nanosphere lithography followed by hydrothermal growth. Owing to the two-dimensionally arrayed structure of anatase nanobowls and the nearly radial alignment of rutile nanorods, the TiO$_2$ NR@NB arrays provide multiple scattering centers and hence exhibit an enhanced light harvesting ability. Meanwhile, the large surface area of the NR@NB arrays enhances the contact with the electrolyte while the nanorods offer direct pathways for fast electron transfer. Moreover, the rutile/anatase phase junction in the NR@NB heterostructure improves charge separation because of the facilitated electron transfer. Accordingly, the PEC measurements of the TiO$_2$ NR@NB arrays on the fluoride-doped tin oxide (FTO) substrate show significantly enhanced photocatalytic properties for water splitting. Under AM1.5G solar light irradiation, the unmodified TiO$_2$ NR@NB array photoelectrode yields a photocurrent density of 1.24 mA cm$^{-2}$ at 1.23 V with respect to the reversible hydrogen electrode, which is almost two times higher than that of the TiO$_2$ nanorods grown directly on the FTO substrate.

1. Introduction

Photoelectrochemical (PEC) splitting of water represents a promising strategy for the low cost and environmentally friendly production of clean hydrogen fuel by solar energy.[1–4] A key challenge in this area is to fabricate nanostructured photoelectrodes with desirable properties such as wide range absorption, high carrier mobility, long carrier lifetime, high stability, and environmental benignity.[5,6] In this regard, morphology engineering offers promises to overcome the shortcomings of the available semiconductor materials through enhancing light absorption, increasing electrolyte accessible area, and shortening diffusion distance of minority carriers,[7,8] as well as selectively exposed crystal facets.[9,10] On the other hand, chemical modifications such as elemental doping,[11] surface modification with catalysts[12] and plasmonic metal structures,[13,14] quantum dot sensitization,[15,16] and incorporation of functional heterojunctions[17] provide a promising strategy to enhance the PEC performance by modifying the intrinsic electronic properties of the electrode materials. In particular, the construction of heterojunction structures has been demonstrated to be an effective approach to improve charge separation by band-structure engineering, sensitization, and passivating layer.[18,19]

TiO$_2$ is one of the most widely investigated semiconductor anode materials for photoelectrochemical water splitting owing to its low cost, high stability, and nontoxicity.[20,21] A lot of work has been focused on the design and fabrication of various structures of TiO$_2$ photoanodes to enhance...
their photocatalytic performance,[22–24] such as nanotubes,[25] nanorods,[26] nanosheets,[27] and inverse opals.[28] Particularly, 1D single crystal TiO2 nanostructures have attracted considerable attention in photocatalysis because they can provide direct pathways for charge transport and decouple the directions of charge carrier collection,[21,29] however, their light scattering ability and surface area are still less than satisfactory.[30,31] The integration of 1D nanostructures into large-scale 2D and 3D higher-order architectures with rational design is a feasible and highly efficient strategy to obtain enhanced performance for photocatalytic solar energy conversion by combining or even magnifying the advantages of each component.[32–34] For example, branched or hyperbranched nanorod arrays consisting of 1D TiO2 nanostructures grown on TiO2 nanorod arrays have demonstrated significantly improved PEC performance for water splitting.[35–37] Notably, a high-performance PEC photoanode of 3D TiO2/SiO2 hierarchically branched nanowires with SnO2 nanowires as backbones and TiO2 nanorods as branches was fabricated by a combination of chemical vapor deposition and hydrothermal growth process.[38] On the other hand, 3D and 2D ordered macroporous TiO2 templated from colloidal crystals have been employed as substrates for the deposition of ZnO seeds by atomic layer deposition (ALD) and subsequent hydrothermal growth of ZnO nanowires. The produced hierarchically ordered, inverse opals coupled with nanowires,[39] nanobushes,[40] and urchin-like hollow structures[41] can be used as efficient PEC anodes because of enhanced light scattering, faster electron transfer, easier electrolyte penetration, and higher surface area for quantum dots loading. Recently, a novel 3D hierarchical TiO2 urchin assembled with a hollow TiO2 sphere core and a radial TiO2 nanorod shell was prepared via a colloidal template route combined with ALD and hydrothermal growth.[42] However, the ALD process involved in the fabrication of oxide hollow shell was costly and time-consuming, especially for depositing thin films on 3D complex structures.[43] It remains a challenge to develop facile solution routes for integrating 1D TiO2 nanostructures into hierarchically ordered, heterostructured photoanodes with an architectural design for optimized PEC performance for water splitting.

Nanosphere lithography based on monolayer colloidal crystals (MCCs) is an effective method to construct 2D-patterned nanostructures with high controllability on a large scale.[44] Recently, nanosphere lithography at the gas–liquid interface, which employs MCCs floating at the solution surface as templates, has been demonstrated to be a facile, inexpensive, efficient, and versatile method for the controllable fabrication of large-area, transferable nanobowl arrays. A variety of nanobowl arrays made of metals and metal sulfides, such as Ag[45] and ZnS[46] nanobowl arrays and AgS–Ag heterostructured nanobowl arrays,[47] have been successfully fabricated by interfacial nanosphere lithography; nevertheless, the fabrication of metal oxide nanobowl arrays by this approach has not been realized yet. Herein, we report a facile two-step approach involving interfacial nanosphere lithography followed by hydrothermal growth for the construction of TiO2 nanorod@nanobowl (NR@NB) arrays consisting of rutile TiO2 nanorods grown on the inner surface of arrayed anatase TiO2 nanobowls. The unique heterostructured TiO2 NR@NB arrays exhibited significantly enhanced PEC performance for water splitting owing to their unique architecture that is beneficial to light harvest and charge separation and transfer.

2. Results and Discussion

2.1. Fabrication and Characterization of TiO2 NR@NB Arrays

An interfacial nanosphere lithography method combined with hydrothermal growth was used to fabricate the TiO2 NR@NB arrays, as illustrated in Figure 1. In the first step, MCC template was transferred onto the surface of a TiO2 sol, leading to the deposition of a thin layer of amorphous TiO2 precursor onto the bottom of each polystyrene (PS) sphere. Then, the as-formed TiO2–MCC composite film was picked up by the fluoride-doped tin oxide (FTO) substrate and underwent a calcination process for simultaneous template removal and TiO2 crystallization, resulting in the formation of anatase TiO2 NB arrays. In the second step, the as formed TiO2 nanobowl (NB) arrays on FTO were employed as a patterned substrate for the hydrothermal growth of rutile TiO2 nanorods, which resulted in heterostructured TiO2 NR@NB arrays.

Figure 2 shows the X-ray diffraction (XRD) patterns of the TiO2 NB arrays on FTO and the TiO2 NR@NB arrays obtained after 5 h of hydrothermal growth of TiO2 nanorods (NRs) on the NB arrays. For comparison, the XRD pattern of the TiO2 NR arrays grown directly on FTO is also presented. It can be seen that the NB arrays exhibit a well-resolved diffraction peak corresponding to the (101) reflection of anatase TiO2 in addition to the diffraction peaks ascribed to the FTO substrate, suggesting the formation of anatase TiO2 NB arrays. By contrast, the reflections assigned to rutile TiO2 can be observed for the NR arrays grown directly on the FTO substrate in addition to the diffraction peaks from FTO, suggesting that the hydrothermal growth yielded rutile TiO2 NR arrays. As expected, both anatase and rutile reflections appear in the XRD pattern of the NR@NB arrays, indicating the formation of TiO2 heterostructures consisting of anatase NBs and rutile NRs.

Figure 3 shows the representative scanning electron microscopy (SEM) images of the obtained TiO2 NB arrays and NR@NB arrays on the FTO substrate. The top view of the NB arrays (Figure 3a) suggests the formation of large-area, hexagonally packed nanobowl arrays with a periodicity ≈2 µm, retaining the periodic structure of the MCC template. As shown in the tilt view (Figure 3b), there are cavities in the lateral bowl walls at the connection regions of neighboring PS spheres. The high-magnification SEM image shown in Figure 3c suggests that the bowls about 2 µm in diameter and 0.5 µm in height have a relatively flat bottom, which are deformed from hemispherical shells owing to the calcination process. It may be noted that the bowl walls are less than 100 nm in thickness and the bowl bottom is thin enough to show the profile of the FTO underlayer. It may be noted that the TiO2 NB arrays formed on FTO are difficult to be peeled.
from the substrate without crushing, whereas the TiO\textsubscript{2} NB arrays formed on an Si substrate can be rather easily peeled from the substrate. Therefore, the TiO\textsubscript{2} NB arrays peeled from an Si substrate were used for the TEM characterization (Figure S1, Supporting Information). It can be seen that the intact NB arrays show periodic pores with a hexagonally packed structure and the selected-area electron diffraction (SAED) pattern shows well-resolved rings corresponding to the anatase TiO\textsubscript{2}, confirming the formation of pure anatase TiO\textsubscript{2} NB arrays. It is worth pointing out that the pore diameter and thus the periodicity of the NB arrays can be readily adjusted by using MCCs made of PS colloidal spheres with different diameters as templates under otherwise identical conditions (Figure S2, Supporting Information).

The SEM image of the rutile TiO\textsubscript{2} NR arrays grown on the bare FTO substrate suggests that the hydrothermal growth at 150 °C for 5 h resulted in the nearly perpendicular growth of TiO\textsubscript{2} NRs ≈100–200 nm in width and 1–2 µm in length (Figure S3a, Supporting Information). The SAED pattern of a TiO\textsubscript{2} nanorod stripped from the substrate shows clear diffraction spots indexed to the rutile TiO\textsubscript{2} (Figure S3b, Supporting Information), which is consistent with the XRD result shown in Figure 1, indicating that the nanorod is a single-crystalline rutile TiO\textsubscript{2} nanorods elongated along the [001] direction. The related high-resolution TEM (HRTEM) image (Figure S3c, Supporting Information) shows clear lattice fringes with \(d\) spacings of 0.32 and 0.29 nm, which can be ascribed to the (110) and (001) planes of rutile, respectively, confirming the formation of [001]-oriented rutile TiO\textsubscript{2} nanorods.

If the FTO substrate covered by the anatase TiO\textsubscript{2} NB arrays was employed instead of the bare FTO substrate, unique TiO\textsubscript{2} NR@NB arrays can be produced after 5 h of hydrothermal growth of TiO\textsubscript{2} nanorods. The low-magnification top-view SEM shown in Figure 3d apparently shows closely packed nanobowls with a periodic spacing about 2 µm. Figure 3e shows a tilt-view SEM image with a higher magnification, which suggests that nanorod arrays grew all
over the bowls. The further enlarged SEM image shown in Figure 3f suggests that both the bottom and the walls of the bowls are covered by the arrayed NRs about 100–200 nm in width and 1–2 µm in length, resulting in the TiO₂ NR@NB arrays consisting of nanorods almost radially aligned on the inner surface of the nanobowls. It may be noted that the NR@NB arrays maintained close contact with the FTO substrate owing to the strong adherence of the initial TiO₂ NB arrays to the FTO substrate, whereas the NR@NB arrays formed on the Si substrate could easily peel off during the hydrothermal reaction due to the weak adherence of the initial NB arrays to the Si substrate. Therefore, the microstructure of the NR@NB arrays formed on FTO was further characterized by the transmission electron microscopy (TEM) observations of the crushed nanoarrays stripped from the FTO substrate (Figure 4). As shown in Figure 4a, the nanorods grew on the bottom and walls of the closely packed nanobowls. Figure 4b clearly shows the coexistence of the well-defined nanorods and the irregular fragments of the nanobowls. The SAED pattern of the NR gives clear diffraction spots corresponding to rutile TiO₂ (Figure 4c), whereas the SAED pattern corresponding to the larger area containing both the nanorods and the nanobowl fragments exhibits both the spots assigned to rutile TiO₂ and the intermittent rings indexed to the anatase TiO₂ (Figure 4d). This result demonstrates that the nanorods are [001]-oriented rutile single crystals and the nanobowls are composed of polycrystalline anatase. It is consistent with the HRTEM observations (Figure 4e,f), which show that the nanorod exhibits clear lattice fringes indexed to the (110) and (001) of the rutile TiO₂, while the nanobowl fragments show lattice fringes ascribed to the anatase phase. The above results demonstrate that the rutile nanorods grew directly on the anatase nanobowls to form a heterojunction between rutile and anatase, which could facilitate charge separation since the photogenerated electrons tend to flow from rutile to anatase. [48,69]

In order to investigate the growth process of the NR@NB arrays, we observed the products harvested at different intervals of reaction with SEM. As shown in Figure 5a, short TiO₂ nanorods ≈200 nm in length and ≈30 nm in diameter were obtained after 2 h of hydrothermal growth. The nanorods grew randomly both on the walls and the bottom of the nanobowls. With increasing reaction time, the nanorods became longer gradually, and the diameter increased to ≈50 nm at 3 h (Figure 5b) and ≈80 nm at 4 h (Figure 5c). When the reaction time was increased to 5 h, well-defined NR@NB arrays consisting of TiO₂ nanorods 1–2 µm in length and 100–200 nm in diameter grown on

Figure 4. a,b) TEM images of fragments of TiO₂ NR@NB arrays. SAED patterns corresponding to the areas enclosed by c) the smaller and d) larger circles in panel (b). HRTEM images of e) a TiO₂ nanorod and f) nanobowl fragments.

Figure 3. SEM images of a–c) TiO₂ NB arrays and d–f) TiO₂ NR@NB arrays obtained after 5 h of hydrothermal growth.
the inner surface of TiO$_2$ nanobowls were produced, as shown in Figure 3 d–f. However, further prolongation of the reaction time to 6 h resulted in an overfull growth of the nanorods, leading to the complete filling of the nanobowls and the vanishing of the bowl-like structure (Figure 5 d). These results indicate that both the length and the diameter of the TiO$_2$ nanorods can be adjusted by changing the reaction time, and the TiO$_2$ NR@NB arrays with different loading densities of TiO$_2$ inside nanobowls can be obtained accordingly.

2.2. PEC and Optical Properties of TiO$_2$ NR@NB Arrays

The photoelectrochemical properties of the TiO$_2$ NR@NB arrays on FTO obtained after 5 h of hydrothermal growth were measured in aqueous solution containing 1 m NaOH with the TiO$_2$ NB arrays and NR arrays employed as the contrast samples. The linear sweep voltammograms of the different photoanodes measured under AM 1.5G solar light irradiation are presented in Figure 6a with only neglectable current density measured under dark conditions (Figure S4, Supporting Information). As shown in Figure 6a, the saturated photocurrent density of the TiO$_2$ NB arrays is less than 0.1 mA cm$^{-2}$. Such a low photocurrent density could be attributed to the small loading mass of TiO$_2$ on FTO due to the extremely thin walls of the nanobowls. On the other hand, the TiO$_2$ NR arrays show a saturated photocurrent density of 0.68 mA cm$^{-2}$ at 1.23 V versus the reversible hydrogen electrode (RHE), which is comparable to the values reported for the arrays of 1.8 µm long TiO$_2$ nanorods[50] and TiCl$_4$ treated TiO$_2$ nanorods.[26] If the TiO$_2$ NR@NB arrays were used as the photoanode, significant improvement in the PEC performance for water splitting was observed. The saturated photocurrent density of the TiO$_2$ NR@NB arrays reached 1.24 mA cm$^{-2}$ at 1.23 V versus RHE, which represents an almost twofold increase in the current density compared with the TiO$_2$ NR arrays. This remarkable twofold enhancement in PEC performance could be ascribed to the advantageous features offered by the unique NR@NB heterostructures, such as multiple light scattering, increased surface area for contact with the electrolyte, and construction of the anatase–rutile

![Figure 5](image1.png)  
**Figure 5.** SEM images of TiO$_2$ NR@NB arrays with different hydrothermal reaction times: a) 2 h, b) 3 h, c) 4 h, and d) 6 h.

![Figure 6](image2.png)  
**Figure 6.** a) Linear sweep voltammograms of TiO$_2$ NB, NR, and NR@NB array electrodes recorded in a 1 m NaOH solution under simulated one sun illumination (AM 1.5G, 100 mW cm$^{-2}$). b) Chronoamperometric $I$–$t$ curves for TiO$_2$ NB, NR, and NR@NB array electrodes collected at 1.23 V versus RHE under AM 1.5G illumination. c) Photoconversion efficiency of TiO$_2$ NR and NR@NB array electrodes as a function of applied potential. d) IPCE plots of TiO$_2$ NR and NR@NB array electrodes collected at 1.23 V versus RHE.
heterojunction. It is noteworthy that the photocurrent density of the heterostructured TiO₂ NR@NB arrays is considerably higher than that of the 3D hierarchical TiO₂ urchins prepared via a colloid template route combined with ALD and hydrothermal growth (=0.95 mA cm⁻² at 1.23 V vs RHE),[42] which could be rationalized by considering that the 3D TiO₂ urchins consisted of a poorly crystallized, spherical TiO₂ thin layer produced by ALD with TiO₂ nanorods grown on its outer surface, leading to retarded charge transfer from the nanorods to the FTO substrate. Moreover, the TiO₂ NR@NB arrays exhibit a PEC performance considerably higher than that of the branched TiO₂ nanorod arrays with surface anatase/rutile junctions (=1.0 mA cm⁻² at 1.23 V vs RHE),[36] and slightly higher than that of the hyperbranched TiO₂ nanowire arrays prepared by a complicated three-step procedure (1.21 mA cm⁻² at 1.23 V vs RHE).[43] It is expected that further improvement in the PEC performance of the current unmodified TiO₂ NR@NB arrays could be realized by optimized surface passivation[56,59] and elemental doping.[51,52]

The chemical and structural stability of the TiO₂ NR@NB arrays during PEC water splitting was revealed by the photocurrent density–time (I-t) curves. As shown in Figure 6b, all the three photoanodes showed stable photocurrent densities at an applied bias of 1.23 V versus RHE with repeated on-off cycles. The rectangular shaped photocurrent transients indicate a relatively weak electron back recombination.[53] Moreover, the photocurrent density of the TiO₂ NR@NB arrays was very stable under continuous illumination for over 100 min (Figure S5, Supporting Information). Actually, the morphology of the TiO₂ NR@NB arrays was kept unchanged after the continuous photocurrent density measurement (Figure S6, Supporting Information). These results demonstrated that the TiO₂ NB@NR arrays exhibited remarkable photoactivity and photostability.

The photoconversion efficiency (η) of the photoanodes was calculated according to the equation[51]

\[
\eta = I(1.23 - V) / J_{\text{light}}
\]

where \( V \) is the applied voltage versus RHE, \( I \) is the photocurrent density at the measured potential, and \( J_{\text{light}} \) is the irradiance intensity of 100 mW cm⁻² (AM 1.5G). The calculated η values of the TiO₂ NR and NR@NB arrays are plotted as a function of biasing potential, which are shown in Figure 6c. It can be seen that the NR arrays exhibited a maximum η value of 0.41% at 0.44 V versus RHE. Notably, a maximum conversion efficiency of 0.66% at 0.52 V versus RHE was achieved for the NR@NB arrays.

The incident photon to current conversion efficiency (IPCE) was measured for the TiO₂ NR and NR@NB arrays at 1.23 V versus RHE from amperometry measurements using a monochromator in conjunction with a power meter and photodiode according to the equation \( \text{IPCE} = (1240 \frac{\lambda}{\lambda_{\text{light}}}) \) \( \square \) [54]

where \( I \) is the measured photocurrent density (mA cm⁻²) at a specific wavelength, \( \lambda \) is the wavelength of incident light, and \( J_{\text{light}} \) is the measured irradiance (mW cm⁻²) at a specific wavelength. As shown in Figure 6d, compared with the NR arrays, the NR@NB arrays exhibited a significant increase in IPCE in the wavelength range 300–430 nm with the IPCE maximum increase from 42% to 77%. Such an enhancement could be related to the increased surface area and enhanced light scattering ability arising from the hierarchical architecture as well as the existence of the anatase–rutilie heterojunction, indicating that the heterostructured NR@NB arrays could effectively harvest the UV light and facilitate charge separation and transfer for PEC water splitting.

In order to elucidate the mechanisms for the enhanced PEC performance of the TiO₂ NR@NB arrays, we measured the diffuse reflectance spectra and the EIS Nyquist plots of the TiO₂ NR and NR@NB arrays, which are shown in Figure 7. The reflectance spectra shown in Figure 7a shows that when the wavelength of the incident light is above 350 nm, the NR@NB arrays exhibited considerably higher reflectance with a maximum reflectance about 51%, which may be ascribed to the enhanced light scattering for the NR@NB arrays. This result is reminiscent of the results obtained from 3D hierarchically ordered nanobushes consisting of ZnO nanowires randomly grown on the inner walls of TiO₂ inverse opals,[40] highlighting the benefits of the 3D structured photoanodes with specially engineered scattering centers compared to the 1D nanowire array. For comparison, the diffuse reflectance spectrum of the bare TiO₂ NB arrays was also measured (Figure S7, Supporting Information), which

![Figure 7.](image-url)
shows a much lower reflectance in the visible region with a maximum reflectance less than 28%, indicating an enhanced light scattering of the NR@NB arrays compared with the bare NB arrays. When the wavelength is below 350 nm, both the TiO$_2$ NR and NR@NB array photoanodes showed significant decrease in the diffuse reflectance because of the light absorption of TiO$_2$. However, the NR@NB arrays showed lower diffuse reflectance in comparison to the NR photoanode at this wavelength range, which could be attributed to the higher absorption of the scattered light owing to the benefits of strong light scattering with minimum reflection losses. The enhanced light scattering ability can be attributed to the multiple scattering inside the nanobowls, which resulted in the higher intensity of light scattering and the longer pathways of light in the structure. On the other hand, the EIS Nyquist plots shown in Figure 7b suggest that the NR@NB arrays exhibited a smaller semicircle diameter in the measured frequency region. Since the diameter of the semicircle in the middle frequency region is related to the interfacial charge transfer resistance between the photoanode and the electrolyte, this observation indicates that the interfacial charge transfer resistance between the NR@NB arrays and the electrolyte was considerably smaller, which could be ascribed to the improved transport behavior of photogenerated holes owing to the increased contact surface area. Therefore, both the enhanced light scattering ability and the increased contact surface area would contribute to the enhancement in PEC performance for the TiO$_2$ NR@NB arrays.

Considering that the structure and morphology of the TiO$_2$ NR@NB arrays can be adjusted by changing the hydrothermal growth time, the PEC performance of the NR@NB arrays obtained at different reaction times was investigated (Figure S8, Supporting Information). At a reaction time of 2 h, a photocurrent density of 0.20 mA cm$^{-2}$ was measured at 1.23 V versus RHE, which is considerably larger than the original NB arrays (≈0.07 mA cm$^{-2}$). With increasing reaction time up to 5 h, the photocurrent density increased gradually and reached 1.24 mA cm$^{-2}$ at 1.23 V versus RHE. This result may be rationalized by considering that both the length and diameter of the TiO$_2$ nanorods were increased with increasing reaction time up to 5 h, while the bowl-like structure was preserved, thereby keeping a strong light scattering ability and a high TiO$_2$ loading mass. However, the prolongation of the reaction time to 6 h led to a decreased photocurrent density (0.92 mA cm$^{-2}$ at 1.23 V vs RHE). This result could be attributed to the vanishing of the bowl-like structure due to the overgrowth of the nanorods, which resulted in a decreased light scattering ability and hindered electrolyte penetration. This result is consistent with the relatively low photocurrent density (0.77 mA cm$^{-2}$ at 1.23 V vs RHE) measured for the TiO$_2$ NR@NB array electrode prepared by 5 h of hydrothermal growth on the nanobowls with a smaller diameter (namely, 1 µm), where the vanishing of the bowl-like structure also occurred because of the overgrowth of the nanorods on the smaller bowls (Figure S9, Supporting Information).

Consequently, the architecture of the TiO$_2$ NR@NB arrays can be optimized by balancing the light scattering ability, the TiO$_2$ loading mass, and the electrolyte accessible surface area for achieving the optimized PEC performance. Notably, the earlier reports on the synthesis of Bi$_2$WO$_6$ nanobowl arrays for PEC water splitting has shown that the 2D nanobowl arrays exhibited considerably enhanced PEC performance compared with the conventional film owing to enhanced light scattering and a larger surface area. This current results demonstrate that the growth of nanorod arrays on the inner surface of 2D arrayed nanobowls is able to further enhance the light scattering while increasing the loading mass and surface area of the photocatalyst on the electrode, thus significantly increasing the PEC performance.

Based on the experimental results, the PEC water splitting mechanism and charge transfer process in the TiO$_2$ NR@NB array electrode are schematically illustrated in Figure 8.

Figure 8. Schematic diagram of the band alignment and charge transfer in an anatase–rutile heterojunction, and the light scattering and electron transport in TiO$_2$ NR@NB array electrode for water splitting.
Under light illumination, the NR@NB arrays could considerably enhance light harvesting by multiple scattering of light among the radially oriented nanorods inside the nanobowls. The TiO$_2$ nanorods and nanobowls absorbed the photons and generated electron–hole pairs. At the TiO$_2$/electrolyte interface, band bending occurred due to the initial difference in electrochemical potentials, which drove the holes in TiO$_2$ to move to the TiO$_2$/electrolyte interface, thus oxidizing water to O$_2$. Meanwhile, the photogenerated electrons in TiO$_2$ nanorods were transferred along the 1D pathways to the TiO$_2$ nanobowls, and then were collected by the FTO substrate and transported to the Pt cathode for reducing water to H$_2$. It may be noted that the band alignment between rutile TiO$_2$ nanorods grown almost radially on the inner surface of TiO$_2$ nanobowls, and then were collected by the FTO substrate and transported to the Pt cathode for reducing water to H$_2$. It may be noted that the band alignment between rutile TiO$_2$ nanorods grown almost radially on the inner surface of the TiO$_2$ NB arrays, and then were collected by the FTO substrate and transported to the Pt cathode for reducing water to H$_2$. It may be noted that the band alignment between rutile TiO$_2$ nanorods grown almost radially on the inner surface of rutile TiO$_2$ and anatase TiO$_2$ is beneficial to the electron transfer from rutile to anatase due to the slightly lower conduction band energy of anatase.$^{[48,49]}$ In other words, the existence of the anatase–rutile heterojunction in the TiO$_2$ NR@NB arrays would considerably promote the charge separation and transfer process, leading to an enhancement in the PEC performance. Therefore, the unique TiO$_2$ NR@NB arrays hold promise for efficient PEC water splitting because of three key advantageous features: First, the hierarchical NR@NB structure had strong light scattering ability, thereby considerably enhancing light harvesting. Second, the TiO$_2$ nanorods almost radially aligned on the inner surface of TiO$_2$ nanobowls provided increased photocatalyst/electrolyte contact area offering fast hole transportation paths while the nanorods had intrinsic 1D pathways for fast electron transfer. Third, the rutile/anatase phase junction in the NR@NB heterostructure could improve charge separation owing to the facilitated flow of photogenerated electrons from rutile to anatase.

3. Conclusion

A novel photoanode architecture made of TiO$_2$ NR@NB arrays was designed and successfully fabricated for efficient photoelectrochemical water splitting by combining the art of interfacial nanosphere lithography with hydrothermal growth. The heterostructured TiO$_2$ NR@NB arrays consisted of rutile TiO$_2$ nanorods grown almost radially on the inner surface of arrayed anatase TiO$_2$ nanobowls. Under solar simulator with AM 1.5 G light of 100 mW cm$^{-2}$ intensity, the photocurrent density of the NR@NB array photoanode reached 1.24 mA cm$^{-2}$ at 1.23 V versus RHE, which represents almost twofold enhancement in the PEC performance for water splitting compared with the conventional TiO$_2$ NR arrays. Such a significant improvement in the PEC performance may be rationalized by considering that the unique TiO$_2$ NR@NB arrays possessed multiple scattering centers, increased electrolyte accessible surface area, and beneficial anatase–rutile heterojunction, which endowed the hierarchical heterostructure with enhanced light scattering ability, faster transfer of photogenerated holes, and facilitated charge separation. It may be reasonably expected that the PEC performance of the unmodified TiO$_2$ NR@NB arrays could be further improved if additional chemical modifications are combined with the morphology engineering. Overall, this work may open new avenues toward building complex semiconductor nanostructures with desirable architectures for efficient harvesting and utilization of solar energy.

4. Experimental Section

Materials: Monodisperse carboxylated polystyrene (PS) spheres ~2 µm in diameter were purchased from Tianjin Base-line Chrom Tech Research Centre. Titanium(V) sulfate (Ti(SO$_4$)$_2$ $>$96%), titanium tetrachloride (TiCl$_4$ $>$98%), and tetrabutyl titanate (TBT, $>$98%) were purchased from Sinopharm Chemical Reagent Co. Hydrochloric acid (36–38 wt%) was purchased from Xilong Chemical Co. Fluoride-doped tin oxide glass was obtained from Nippon Sheet Glass Co.

Characterization: The samples were characterized by scanning electron microscopy (SEM, Hitachi FE-54800, 5–10 kV), transmission electron microscopy (TEM, FEI Tecnai T20, 200 kV), high-resolution TEM (HRTEM, FEI Tecnai F30, 300 kV), and X-ray diffraction (XRD, Rigaku Dmax-2000, Cu Kα radiation). Diffuse reflectance spectra were recorded using a Perkin-Elmer Lambda 950 UV/vis/NIR spectrometer.

Preparation of MCC Templates: Monolayer colloidal crystals can be readily assembled at the water–air interface, and then transferred onto the surface of arbitrary substances.$^{[44]}$ Accordingly, MCC films were fabricated on a silicon or glass substrate using a method developed at our lab.$^{[57]}$ Typically, 20–25 µL water/ethanol (volume ratio: 3:1) dispersion containing monodisperse carboxylated PS colloidal spheres was dropped onto the top surface of a 1 cm $\times$ 1 cm piece of glass surrounded by water located at the mid bottom of a Petri dish. The dispersion spread freely on the water surface, resulting in a colorful MCC film. A few microliters of SDS solution (2 wt%) was then dropped onto the water surface to pack the MCC film on the water surface closely. Then, the MCC film was picked up by a silicon or glass plate and dehydrated naturally in air. Afterward, the obtained MCC film can be transferred to the surface of reactant solutions as a floating MCC template for interfacial nanosphere lithography.

Fabrication of TiO$_2$ NR@NB Arrays: TiO$_2$ NR@NB heterostructured nanobowl arrays were fabricated by a two-step approach involving interfacial nanosphere lithography followed by hydrothermal growth:

Step 1. The fabrication of TiO$_2$ NB arrays was achieved by interfacial nanosphere lithography. Typically, the as-formed MCC films were transferred onto the surface of a TiO$_2$ sol formed from aqueous Ti(SO$_4$)$_2$ solution (5.4 wt%) by inserting the MCC-covered substrate into the solution with an inclining angle. Then, the reaction vessel was kept in an incubator thermostatted at 50 °C for 3 h. The deposition of amorphous TiO$_2$ onto the bottom of the PS spheres occurred by the thermal hydrolysis of Ti(SO$_4$)$_2$ through Ti(SO$_4$)$_2$ $+$ 2H$_2$O $\rightarrow$ TiO$_2$ $+$ 2H$_2$SO$_4$. The resultant TiO$_2$–MCC composite films were picked up from the solution surface by FTO substrates. The films were dried at room temperature and calcined at 500 °C for 2 h to remove template, resulting in the formation of crystalline TiO$_2$ nanobowl arrays on FTO substrates.

Step 2. TiO$_2$ NR arrays were grown directly on the inner surface of the TiO$_2$ NBs by the reported hydrothermal method$^{[59]}$ with some modifications. In a typical synthesis, 0.25 mL of tetrabutyl titanate was slowly added into a mixture solution of 6 mL of...
concentrated hydrochloric acid solution (36.0–38.0 wt%) and 6 mL of water, followed by magnetically stirring for 30 min. A piece of FTO glass covered by TiO$_2$ NB arrays was put in a Teflon-lined stainless autoclave and fixed at an angle against the inner wall with the conductive side facing down. Then, the reaction solution was transferred into a reactor for a hydrothermal treatment at 150 °C for 5 h. Afterward, the FTO substrate was taken out, rinsed with deionized water, and dried in ambient air, leading to the formation of TiO$_2$ NR@NB nanobowl arrays. For comparison purposes, hydrothermal growth of TiO$_2$ NR arrays directly on the FTO substrate was carried out following the literature[60] using a silicon reference solar cell. The current-voltage characterization of the TiO$_2$ nanoarrays was carried out following the literature, [60] which would help eliminate the surface trap states of TiO$_2$. [26] Typically, the as-prepared TiO$_2$ NB, NR, and NR@NB arrays on FTO were dipped in a 100 × 10$^{-3}$ M TiCl$_4$ solution thermostated at 70 °C for 1 h. After rinsed with water and dried at room temperature, the samples were calcined at 500 °C for 1 h.

**Photoelectrochemical Measurements:** The photoelectrochemical properties were measured in a standard three-electrode cell. The reference and counter electrodes were Ag/AgCl electrode and Pt wire, respectively. A 1.0 M NaOH aqueous solution was used as the electrolyte. The photoelectrode film area was fixed at 0.25 cm$^2$ for all the PEC measurements. The measured potential versus Ag/AgCl reference electrode was converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \, pH + E^{0}_{Ag/AgCl}$, where $E_{RHE}$ is the reversible potential versus RHE, $E^{0}_{Ag/AgCl}$ = 0.1976 V at 25 °C, and $E_{Ag/AgCl}$ is the experimentally measured potential against the Ag/AgCl reference electrode. The solar light simulator (Beijing Perfectlight Technology Co., LS-SXE300CUV 300 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm$^{-2}$) using a silicon reference solar cell. The current-density–voltage (J–V) characteristic curves and impedance measurements were recorded using an electrochemical workstation (CH Instrument, CHI 660C). The IPCE was calculated from amperometry measurements with three electrodes configuration at 1.23 V with respect to the reversible hydrogen electrode (RHE). A 150 W Xe lamp in conjunction with a monochromator (ZOLIX Instruments Co., omni-λ150) was used to generate a monochromatic beam. The electrochemical impedance spectra (EIS) were recorded under AM 1.5G illumination (100mW cm$^{-2}$) at a AC potential frequency range from 10$^3$ to 0.1 Hz with an amplitude of 10 mV.


**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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