COMMUNICATION

NiO-TiO₂ p-n heterostructured nanocables bridged by zero-bandgap rGO for highly efficient photocatalytic water splitting

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Abstract
The construction of p-n junctions with built-in electric field effect between two photocatalytic semiconductors is an efficient strategy to separate photogenerated carriers and enhances photocatalytic activity. However the effect is limited because the built-in electric field can be saturated because of the charge accumulation during the photocatalysis process. In this work, we demonstrate that inserting a layer of zero-bandgap graphene at the interface between p-type NiO and n-type TiO₂ can further enhance the separation of photogenerated carriers by building double-shelled NiO/rGO/TiO₂ heterostructured coaxial nanocables. This double-shell nanostructure is proved possessing a remarkably high photocatalytic activity through water splitting experiments and photoelectrochemical measurements. The main mechanism for enhancement of photocatalytic activity is that zero-bandgap rGO can increased the barrier height by lowering the Fermi level of the NiO nanofiber core and increasing the Fermi level of the TiO₂ nanowire shell, and enhance the strength of built-in electron field. Furthermore, the design of NiO/rGO/TiO₂ heterostructured coaxial nanocables can ensure that the UV light can be absorbed by the TiO₂ at the outer shell, whereas visible light can reach the NiO inner core,

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 thus leading to an efficient use of the white light spectrum. This heterostructured coaxial nanocable is a promising candidate for applications in environmental and energy fields because of its facile and easily scalable synthesis combined to its superior broad-spectrum photocatalytic activity.

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Introduction

Photocatalysis is bound to play a key role for the search toward novel renewable energy sources [1]. Since the discovery of the photocatalytic splitting of water by TiO$_2$ in 1972 [2], significant efforts have been made to design highly active oxide semiconductor photocatalysts which could be used for solar energy conversion and environmental protection [3]. Many strategies have been developed to enhance photocatalytic activity [4], for instance by increasing the photocatalytically active surface-area [5,6], by harvesting a wider portion of the solar light spectrum [7] and by improving the separation of photo-induced carriers [8]. Heterostructured photocatalysts containing p-n junctions and Schottky junctions have been constructed to improve the separation of photo-induced carriers [9,10]. The role of the secondary phase in the surface heterostructure is to drain or trap the photo-induced electrons leading to an improved separation of electron/hole pairs. At the same time, it can be used to extend the domain of activity of the photocatalyst toward the full solar spectrum. Among those, p-n junctions formed upon direct contact of p-type and n-type semiconductors have attracted wide interest because a gradient of potential which favors charge separation is established at the level of the junction [11]. Recently, a new concept for enhancing the separation of photo-induced carriers was proposed, whereby a built-in electric field within the photocatalyst particle is used to separate the electron-hole pair [12]. Built-in electron field may arise from p-n junctions [13], polymorph junctions [14], polar surface terminations [15] and ferroelectric phenomena [16]. The presence of the built-in electron field changes the band bending at the interface and provides a driving force for the separation of photogenerated electrons and holes, resulting in an increase of photochemical reactivity [17].

With a bandgap of 3.2 eV, TiO$_2$ exhibits high photocatalytic activity under UV light illumination, making it a popular candidate for photocatalysis [18,19]. For water splitting applications, heterostructures can overcome two inherent disadvantages of TiO$_2$, namely its low quantum efficiency and its negligible utilization of visible light [20,21]. Nickel oxide (NiO), as a p-type wide-bandgap semiconductor with an indirect band gap of about 3.55 eV, has received increasing attention owing to its various applications in catalysis [22], battery cathodes [23], fuel-cell electrodes [24], nanogenerator [25], electrochemical supercapacitors [26] and gas sensors [27]. One-dimensional NiO nanomaterials have comparable properties to NiO nanoparticles but with more rapid electron transport along the long direction, and with a lower amount of grain boundaries. Shao et al. first synthesized NiO nanofibers by the electrospinning method [28]. These nanofibers can be easily recycled because of their one-dimensional, wire-like morphology, making them useful for air and water purification applications. Assembling TiO$_2$ nanostructures on NiO nanofibers leads to the formation of one-dimensional TiO$_2$/NiO heterostructured nanostructures with p-n junctions, as demonstrated in our previous work on NiO/TiO$_2$ nanobelts p-n heterostructures [29]. When the material is irradiated with a light of sufficient energy, an internal electrical field is established, resulting in a decrease of the recombination rate and an improvement of the photocatalytic efficiency.

Graphene and reduced graphene oxide (rGO), both single layers of sp$^2$-bonded carbon atoms tightly packed into two-dimensional honeycomb structures [30], have outstanding electronic and optoelectronic properties [31,32]. Their high electrical conductivity, good chemical stability and large specific surface available to substrate adsorption make them excellent candidates for the construction of hybrid photocatalysts [33,34]. Thus, rGO nanosheets have been used to wrap n-type TiO$_2$ nanobelts [35], leading to an enhancement of the photo-induced carrier separation, albeit limited. One expects that when a layer of zero-bandgap graphene connects n-type and p-type semiconductors, the disadvantages of the p-n hybrid photocatalyst could be overcome by the bridging effect of the zero-bandgap graphene.

Here, we report the design, synthesis, characterization, and photocatalytic properties of a novel NiO/rGO/TiO$_2$ p-n heterostructured coaxial nanocable. This material was prepared by installing zero-bandgap rGO at the surface of electrospun NiO nanofibers and then by assembling a layer of TiO$_2$ nanostructure on top of it. This nanocable can not only increase UV light harvesting by the TiO$_2$ nanowire layer, but also enhance the separation of photogenerated electron/hole pairs. This work may inspire the future development of various heterostructures dedicated to photocatalysis and photoelectrocatalysis.

Results and discussions

X-ray diffraction (XRD) analysis was employed to characterize the crystal phase of NiO nanofibers, NiO/rGO nanofibers, TiO$_2$ flower-like nanostructures, and NiO/rGO/TiO$_2$ hierarchical heterostructured coaxial nanocables. As shown in Figure 1a, all the diffraction peaks of the NiO nanofibers (curve a) matched those of the cubic phase of NiO (PDF-71-1179) [36] whereas those of TiO$_2$ (curve c) matched those of anatase (PDF-21-1272) [37]. For NiO/rGO nanofibers (curve b), only peaks corresponding to NiO could be observed which is expected due to the low amount and low crystallinity of rGO relative to NiO [38]. For NiO/TiO$_2$ heterostructures (Figure S1)
and NiO/rGO/TiO2 hierarchical heterostructures (curve d), all the diffraction peaks can be well indexed to either NiO or TiO2, which is consistent with the expected structure of the coaxial nanocable. Raman spectroscopy was used to assess the presence rGO on NiO/rGO and NiO/rGO/TiO2. The presence of characteristic D and G peaks found [39] respectively at 1580 and 1338 cm$^{-1}$ (Figure 1b) confirms that rGO nanosheets were successfully assembled on NiO/rGO and NiO/rGO/TiO2 heterostructured coaxial nanocables.

The chemical composition and valence state of the elements were examined by X-ray photoelectron spectroscopy (XPS). The full range of XPS spectra of NiO/rGO/TiO2 hierarchical heterostructures (Figure S2) reveals that the sample is solely constituted of Ni, Ti, O and C in the absence of any contaminants. As shown in Figure S1c, the XPS band of the C 1s core level was deconvoluted into five components, the sp$^2$ carbon (284.6 eV), C–O–C (285.6 eV), C–OH or α-C in –C–COOH (286.7 eV), C–O (288.0 eV) and COOH (289.1 eV) respectively. The predominance of the sp$^2$ carbon contribution indicates that most oxygenated groups on GO sheets were efficiently removed by the hydrothermal reduction process, in good agreement with previous reports on rGO fabrication [40-43].

Figure 1d shows the UV–vis diffuse reflectance spectra of pure NiO nanofibers, NiO/rGO nanofibers, NiO/TiO2 and NiO/rGO/TiO2 nanocables. Absorption peaks in the 300–800 nm region are clearly observed for the NiO nanofibers [44]. After coating with the rGO layer, the visible light absorption is enhanced, corresponding also to a variation of color of the samples (NiO is green, and NiO/rGO is dark green). Samples containing TiO2 such as NiO/TiO2 and NiO/rGO/TiO2 showed enhanced absorption in the UV range. The enhancement of UV absorption is attributed to the TiO2 nanowires, which are expected to enhance the UV-photocatalytic performance in the hybrid systems.

Figure 2a and b shows the scanning electron microscopy (SEM) images of the pure NiO nanofibers, which were fabricated by electrospinning followed by calcination at 500 °C. The fibers have diameters ranging from 100 to 200 nm, and length from several hundreds of micrometers to several millimeters, with a relative smooth surface. Figure 2c shows the SEM image of graphene oxide (GO) as a wrinkled two-dimensional nanosheet of several micrometers in size. The thickness of the GO nanosheets as measured by atomic force microscopy (Figure S4) is 1.0 nm, hinting that most GO nanosheets are single layers [45]. After hydrothermal treatment of the GO solution, the rGO sheets cover the surface of NiO nanofiber in a veil-like fashion as shown in Figure 2d. The thickness of this veil is about 20 nm. Figure 2e shows that the as-synthesized TiO2 powder is constituted of TiO2 nanowires self-assembled into flower-like spherical nanostructures. The nanowires are uniform with length about 200-300 nm, width about 10-20 nm and with sharp ends (Figure 2f). The shape and

**Figure 1** (a) XRD patterns of NiO nanofibers (curve a), NiO/rGO nanofibers (curve b), flower-like TiO2 nanostructures (curve c) and NiO/rGO/TiO2 hierarchical heterostructures (curve d). (b) Raman spectra of NiO nanofibers, NiO/rGO nanofibers, and NiO/rGO/TiO2 hierarchical heterostructures excited by 532 nm laser. (c) XPS of C 1s for the NiO/rGO/TiO2 hierarchical heterostructures. (d) UV–vis diffuse reflectance spectra of NiO nanofibers, NiO/rGO nanofibers and NiO/rGO/TiO2 hierarchical heterostructures.
The morphology and structure of the samples were further characterized by high-resolution transmission electron microscopy (HRTEM). Figure 3a shows that the width of the NiO nanofiber is around 100 nm, which is consistent with the SEM observation. The nanofibers are polycrystalline, with a grain size of about 20-30 nm (Figure 3b). No distinct change was observed in the morphology of the NiO/rGO nanocable compared with the pure NiO nanofiber (Figure 3c). The thickness of the rGO nanosheets is about 20 nm, as shown in Figure 3d. The TiO$_2$ nanowires of 100 nm in length and 20 nm in diameter are attached to the NiO nanofibers, as shown in Figure 2g. Interestingly, the small size and homogeneous distribution of the TiO$_2$ nanowires will increase the effective surface area available for the photocatalytic reaction. Furthermore, the interconnected structure is expected to favor the diffusion of species in solution and of charge carriers within the structure.
Figure 3  TEM images of (a, b) NiO nanofiber (c, d) NiO/rGO nanofiber (e, f) NiO/rGO/TiO₂ hierarchical heterostructures (g, h) HRTEM images of NiO/rGO/TiO₂ hierarchical heterostructures.
nanoﬁber, forming a core-shell structure (Figure 3e). The HRTEM images of the framed areas in Figure 3f–h clearly reveal lattice fringes spacing of 2.39 Å and 3.50 Å, corresponding to the (200) plane of NiO and (101) plane of anatase TiO2, respectively.

Thus the HRTEM images conﬁrm the presence of three phases, the NiO nanoﬁbers in the inner layer, rGO sheets at the interface and TiO2 nanowires shells at the outer layer. The above results (SEM and HRTEM) demonstrate that double-shelled NiO/rGO/TiO2 heterostructured coaxial nanocables have been successfully fabricated. As shown in the Supporting information, the Mott–Schottky (M–S) plots (Figure S5) demonstrate that NiO is a p-type semiconductor whereas TiO2 is n-type [46].

To further characterize the rGO interlayer between the NiO nanoﬁber and the TiO2 nanowire, Raman mapping and optical microscopy were performed on NiO/rGO and NiO/rGO/TiO2 nanofibers (Figure 4). The Raman mapping was generated based on the changes in area under the D band at 1347 cm

1

and G band at 1598 cm

1

across the mapped region [47]. The Raman images of a single NiO/rGO and NiO/rGO/TiO2 nanocable (Figure 4a and c) perfectly correspond to the optical images (Figure 4b and d), which conﬁrms the existence of a continuous rGO layer covering the entire surface of the NiO nanoﬁber.

All the above characterization results conﬁrm that the NiO/rGO/TiO2 nano-heterostructured coaxial nanocable is a double shell structure. As shown in Figure 5, the core is a...
NIO fiber, the next layer is a layer of rGO nanosheets, and the outermost shell layer is constituted of TiO₂ nanowires. An advantage of this core/shell architecture is that carrier separation takes place in the radial direction and not the longer axial direction, with a carrier collection distance smaller or comparable to the minority carrier diffusion length. Hence, photogenerated carriers can diffuse in the NiO/rGO/TiO₂ hierarchical heterostructure without undergoing substantial bulk recombination [48]. Another advantage is that TiO₂ can absorb UV light, and visible light can pass through the shell and reach NiO nanofibers. This nanostructure can use the sunlight more efficiently. An additional consequence of this geometry is that the interlayer rGO nanosheets can transfer the photocarriers faster than a traditional p-n junction device without causing significant bulk recombination.

To demonstrate the enhanced photocatalytic property of the double-shelled NiO/rGO/TiO₂ heterostructured coaxial nanocable, hydrogen evolution was measured during the photocatalytic water-splitting process. As shown in Figure 6a, the rate of H₂ evolution for NiO nanofibers is around 3 μmol/h/g, while for NiO/rGO nanofibers, it is around 6 μmol/h/g. The flower-like TiO₂ nanowires have an activity of about 60 μmol/h/g, which is higher than that of P25 (19 μmol/h/g). By assembling TiO₂ nanowires on NiO nanofiber, the rate of hydrogen evolution reaches 160 μmol/h/g. This increased activity highlights the role played by the p-n junction in the design of the photocatalyst. For the hierarchical NiO/rGO/TiO₂ nanocables, H₂ generation drastically increases as it reaches 240 μmol/h/g. This value is significantly higher than the value for P25, which is considered as one of the best photocatalysts for hydrogen generation. This emphasizes the pivotal role played by the rGO layer at the interface between both semiconductors. More importantly, after four cycles of 10 h reaction, the hierarchical NiO/rGO/TiO₂ nanocables still retained high photocatalytic activity (Figure 6b). In addition, after the photocatalytic reaction the nanostructure of the catalyst is still intact, the SEM images are the same with Figure 2g and f. These results demonstrated the catalytic and morphology stability of these NiO/rGO/TiO₂ materials.

To further investigate the photoresponse of the various samples, the transient photocurrents of the electrode assembled with different samples were measured at a fixed bias potential of 0.2 V via several on-off cycles of white-light irradiation (Figure 7a). When the irradiation was interrupted, the photocurrent rapidly dropped to almost zero (steady-state value), and the photocurrent reverted to its original value once light was switched on again [49]. The transient photocurrent density of the NiO/TiO₂ heterostructures, flower-like TiO₂ nanowires and NiO/rGO nanofibers is less than 5.0 μA/cm², 3.0 μA/cm² and 0.2 μA/cm², respectively whereas it is more than 7.0 μA/cm² for NiO/rGO/TiO₂ under similar conditions. This enhanced transient photocurrent density can be attributed to the fact that the heterostructures are built so that the internal electrostatic field promotes the separation of photogenerated carriers [50]. As almost no photocurrent can be detected for pure NiO nanofibers (shown in Figure S6) under the same conditions, it can be inferred that the current from TiO₂ nanowires to the NiO nanofibers. In addition, when 0.2, 0.4, 0.6, 0.8 V bias is applied to the NiO/rGO/TiO₂ heterostructures, rapid and reversible photocurrent responses are observed, and the photocurrent densities reach an average of 7, 21, 27 and 31 μA/cm², respectively (Figure 7b). This result can be attributed to the fact that carrier separation is improved by creating an internal electrical field in the hybrid photocatalyst [51].

To gain deeper insight into the charge transport behaviors of the heterojunction system, we compared electrochemical impedance spectra (EIS) of NiO, NiO/rGO, NiO/TiO₂ and NiO/rGO/TiO₂ heterostructures (Figure 7c and d). Clearly, a smaller arc radius was observed for NiO/rGO/TiO₂ both in the dark and under illumination as compared to those of NiO, NiO/rGO and NiO/TiO₂. Upon irradiation, a semi-circle appears in the Nyquist diagram, suggesting that it is charge transfer resistance which controls the kinetics at the electrode interface [52,53]. The arc radii are much smaller under irradiation than in the dark, which is due to increased electron conductivity under irradiation [54]. The introduction of rGO sheets causes significant decrease of the arc radius, suggesting an increased electron transfer between the electrolyte and the electrode due to the excellent electrical conductivity and unique “bridge”-like structure of rGO. The radius of the double-shelled NiO/rGO/TiO₂ heterostructured coaxial nanocable is the smallest among all above NiO nanofibers based electrodes, which indicates that a more effective charge separation and faster interfacial charge transfer are occurring. Furthermore

![Figure 6](image-url) (a) Photocatalytic H₂ evolution from aqueous methanol solution over NiO nanofibers, rGO/NiO nanofibers, flower-like TiO₂, P25, NiO/TiO₂ and NiO/rGO/TiO₂ hierarchical heterostructures under white-light of Xe lamp. (b) Photocatalytic H₂ evolution in 4 repeated cycles (10 h/cycle) by the hierarchical NiO/rGO/TiO₂ nanocables.
the photoelectrochemical activity of the photoelectrode as a function of wavelength was quantitatively investigated by the incident photon-to-electron conversion efficiency (IPCE) curve (Figure S7). In the NiO/rGO/TiO2 composite, the rGO increases the energy conversion efficiency as a passive charge extraction layer. When a nanoscale p–n heterostructure is formed, the space charge layer creates a built-in electric field and separates the electrons and holes upon light illumination. Hence the p–n heterostructure changes the role of rGO from passive to active, further enhancing the charge separation.

Based on the above experimental results, the enhanced photocatalytic activity of double-shelled NiO/rGO/TiO2 heterostructured coaxial nanocable can be attributed to the combined effects of several factors. First, the TiO2 nanowires are homogeneously distributed in a non-aggregated fashion at the surface of the NiO/rGO.

Figure 7  (a) Transient photocurrent density vs. time for NiO/rGO, TiO2, NiO/TiO2 and NiO/rGO/TiO2 under white light irradiation (bias voltage 0.2 V). (b) Photocurrent densities vs. time for NiO/rGO/TiO2 with various applied bias potentials under white light irradiation in 1 M NaOH (pH=13.6) electrolyte. (c, d) EIS Nyquist plots of the NiO nanofibers (1, 5), NiO/rGO nanofibers (2, 6), NiO/TiO2 (3, 7) and NiO/rGO/TiO2 (4, 8) at a bias of 0 V under dark and white light irradiation.

Scheme 1  Schematic diagrams for (a) formation of p–n nanojunction, and (b) formation of nano-heterostructured coaxial nanocable.
nanofibers, leading to an optimal access to active surface area. Second, TiO2 can absorb UV light, and visible light can pass through the shell and reach NIO nanofibers which are photoactive in the visible range, leading to a more efficient use of light. Third, the p–n junction leads to a better separation of photogenerated charge carriers due to the presence of an internal electrical field. Scheme 1 shows the band structure of (a) NIO/TiO2 and (b) NIO/rGO/TiO2 heterojunctions. The energy bands of the NIO and TiO2 bend downward when contacting with the rGO to form metal-semiconductor contact. NIO Fermi level shifts downward $qV_{1}=W_{s-NIO}−W_{m-rGO}$ (Figure S8b), TiO2 Fermi level shifts upward $qV_{2}=W_{s-TiO2}−W_{m-rGO}$ (Figure S8c), barrier height increase $qV_{1}+qV_{2}=W_{s-NIO}+W_{s-TiO2}−2W_{s-rGO}>0$ [55–57]. The built-in electric field enhancement and the space charge region increase because of the barrier height increase. Although the rGO interlayer does not contribute to the generation of photoexcited electron-hole pairs, because it does not have an energy gap [58], rGO nanosheets effectively increased the barrier height by lowering the Fermi level of the NIO nanofiber core and increasing the Fermi level of the TiO2 nanowire shell. The electrons ultimately transfer to the solution to reduce water into H2. The layer of rGO prohibits the saturation of the internal electric field, because the accumulated electrons at the NIO edge cross the barrier of the internal field and reach the opposite side through the rGO layer, just as if going through a “bridge”. We believe that the combined effects of the introduction of rGO nanosheets and the formation of the core/shell heterostructure contribute to the enhancement in the efficiency of water splitting.

**Conclusions**

In summary, double-shelled NiO/rGO/TiO2 heterostructured coaxial nanocables were successfully fabricated for the first time by coating rGO nanosheets on electrospun NIO nanofibers, and then by assembling a layer of TiO2 nanowires on top. The enhanced light harvesting, efficient separation of photogenerated electron-hole pairs and rapid charge transfer at the interface contribute to the excellent photocatalytic activity for water splitting. During the enhanced photogenerated carrier separation process, the effective internal electric field at the interface between p-type NIO and n-type TiO2 and the bridging effect of rGO play important roles. This work has demonstrated the unique advantages of double-shelled NiO/rGO/TiO2 heterostructured coaxial nanocables for photocatalytic water splitting and opened promising avenues for the design and fabrication of novel rGO-based core/shell heterojunction arrays for other electronic nanodevices.

**Experimental section**

**Materials**

All the reagents in this work are of analytic grade and commercially available. Titanium oxalate $K_2TiO(C_2O_4)2$, diethylene glycol (DEG), urea (H2NCONH2), ethanol (CH3CH2OH), nickel (II) acetate (C7H4O2Ni·4H2O), acetic acid (CH3COOH), potassium persulfate (K2S2O8), phosphorus pentoxide (P2O5), potassium permanganate (KMnO4), hydrochloric acid (HCl), sulfuric acid (H2SO4), and sodium hydroxide (NaOH) were purchased from China National Medicines Corporation Ltd., and the polyvinylpyrrolidone (PVP, $M_w=1,300,000$), graphite, and titania P25 (TiO2; ca. 80% anatase, and 20% rutile) were purchased from SigmaAldrich. All chemicals were used as received without further purification.

**Synthesis**

**Preparation of NiO nanofibers**

Polyvinylpyrrolidone powder (PVP, 1.05 g, $M_w=1,300,000$ g/mol) was added to a mixture of 6.0 g of absolute ethanol and 19 g of acetic acid in a capped bottle. The mixture was stirred for 1 h to generate a homogeneous solution. Then 3.0 g of nickel acetate (II) was added to the solution, and the mixture was continuously stirred for another 1 h to make a precursor solution. Then 1 mL of the precursor solution was placed in a 5 mL syringe equipped with a blunt metal needle of 0.8 mm diameter. A stainless steel plate covered with a sheet of aluminum foil was employed as the collector. The distance between the needle tip and collector was 25 cm, and the voltage was set at 22 kV. The as-collected nanotubes were calcined at 500 °C for 2 h to form NiO nanofibers.

**Fabrication of NiO/rGO hierarchical nanostructures**

The graphene oxide was first synthesized through chemical exfoliation of graphite via a modified Hummers' method (see the Supporting information). The NiO/rGO nanofibers were synthesized by assembling GO sheets on the surface of the NiO nanofibers followed by the hydrothermal method. In a typical procedure, 20 mg of NiO nanofibers were added to 70 mL of deionized water. Then 125 μL of 8 mg/mL GO solution was added. After stirring for 2 h, this solution was transferred to a 100 mL autoclave and heated at 120 °C for 9 h. The collected solid was washed with distilled water 3 times, and dried at 80 °C for 12 h resulting in the formation of the NiO/rGO nanofibers.

**Fabrication of NiO/rGO/TiO2 hierarchical nanostructures**

In a typical experiment, 0.42 g of $K_2TiO(C_2O_4)2$ was added to 5 mL of deionized water and 15 mL of diethylene glycol (DEG). After vigorously stirring for 30 min, 100 mg NiO/rGO nanofibers were added and the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave. The hydrothermal synthesis was conducted at 180 °C for 9 h to allow the growth of TiO2 nanowires. The wet products were then thoroughly washed with ethanol and dried in an oven at 80 °C overnight. Finally, the thermal decomposition process was performed by heating the dried samples in Ar at 500 °C for 2 h, 1 °C min⁻¹.

**Materials characterization**

The H2 evolution experiments were carried out in a gas-closed circulation system. In a typical reaction, the 50 mg catalyst powder was dispersed by using a magnetic stirrer in CH3OH aqueous solution (80 mL of distilled water + 20 mL of CH3OH). A commercial solar simulator (300 W) equipped with a Xenon lamp as the light source for photocatalytic H2...
generation. The power density of the incident light was about 100 mW/cm². The H₂ evolution was measured with an on-line gas chromatograph (GC-7900).

Photoelectrode fabrication: 50 mg of photocatalyst sample was mixed with 20 ml of terpineol and stirred with a magnetic stirrer for 10 h. The suspension was dip-coated onto the fluorine-doped tin oxide (FTO) glass substrate. A doctor blading technique was employed to ensure the same thickness for each photoelectrode. The photoelectrode was dried on a hot plate at 80 °C, and then heated in a quartz tubular furnace in Ar at 500 °C for 2 h. A Cu wire was then connected to the FTO substrate with the silver colloid paste. Finally epoxy was solidified to cover the FTO substrate, the Cu paste and wire to avoid short current in the measurement.

Photoelectrochemical measurement: photoelectrochemical analyses were carried out using a standard three-electrode cell with Ag/AgCl as reference electrode and Pt sheet as the counter electrode in the NaOH solution (1 M). The electrolyte was bubbled with N₂ for 2 h to remove O₂.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jnanoen.2015.06.028.

References

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