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Three-Dimensional Ruthenium-Doped TiO₂ Sea Urchins for Enhanced Visible-Light-Responsive H₂ Production

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Three-dimensional (3D) monodispersed sea urchin-like Ru-doped rutile TiO₂ hierarchical architectures composed of radially aligned, densely-packed TiO₂ nanorods have been successfully synthesized *via* an acid-hydrothermal method at low temperature without the assistance of any structure-directing agent and post annealing treatment. The addition of a minuscule concentration of ruthenium dopants remarkably catalyze the formation of the 3D urchin structure and drive the enhanced photocatalytic H₂ production under visible light irradiation, not possible on undoped and bulk rutile TiO₂. Increasing ruthenium doping dosage not only increases the surface area up to 166 m² g⁻¹ but also induces enhanced photoresponse in the regime of visible and near infrared light. The doping introduces defect impurity levels, *i.e.* oxygen vacancy and under-coordinated Ti³⁺, significantly below the conduction band of TiO₂, and ruthenium species act as electron donors/acceptors that accelerate the photogenerated hole and electron transfer and efficiently suppress the rapid charge recombination, therefore improving the visible-light-driven activity.

Introduction

Hydrogen generation from solar-driven water splitting using nanostructured semiconductor photocatalysts has become increasingly attractive due to the intensive demand for clean, renewable, abundant, cheap and sustainable energy sources.¹⁻⁴ Although TiO₂ has been widely investigated as a photocatalyst for H₂ production, it is almost inert under the irradiation of visible light because of its wide band gap (3.0 ~ 3.2 eV) and short diffusion length of photoinduced electron-hole pairs.¹⁻⁴ Several strategies have been employed to enhance the solar water splitting efficiency, including band structure engineering, surface and interface engineering, micro/nano engineering, co-catalyst engineering and bionic engineering.⁴ Great efforts have been made to extend the photoresponse to the visible regime, to re-align the band edge of TiO₂ and to improve the separation and transfer of photoinduced electron-hole pairs by introducing heteroatoms, *i.e.* transition metal ions. Suitable cationic dopants not only

easily tune the electron concentration, mobility and lifetime of the carriers, but also effectively alter the electronic structure and align the band levels of TiO₂ *via* the localized or delocalized nature of doping-induced states.^{1,3,4} Dopants may substitutionally locate in Ti(IV) lattice positions and/or locate at interstitial sites. Donor levels and/or acceptor levels, located above the valence band maximum (VBM) and/or below the conduction band minimum (CBM), respectively, can be formed, stemming from localized electronic states,^{1,3-5} thus inducing visible light absorption and hence improving the activity under visible light irradiation. Otherwise, the band of delocalized states in the middle of the band gap, also named as the intermediate band or mid-gap states, can be achieved in the case of heavy dopants, promoting the charge transport and photoconductivity, as well as prolonging the lifetime of charge carriers.^{1,3,4}

Among several metal dopants, ruthenium significantly promotes the separation of photogenerated electron-hole pairs and extends the photoabsorption toward the visible light regime arising from the formation of an intermediate energy level.⁶⁻⁸ Ruthenium doping not only causes the anatase-to-rutile transformation at lower temperatures^{6,7} but also enhances the electron conductivity, thus reducing the recombination probability of charge carriers.⁸ Furthermore, doping low concentration of ruthenium into TiO₂ nanotubes drastically enhances the photo-electrochemical water splitting performance compared to the decoration of RuO₂ nanoparticles on TiO₂ surface.^{9,10} Recently, the deposition of minute amount of RuO₂ in spherical, elongated and one-dimensional chain-like geometries onto TiO₂ nanorods

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remarkably improved the H₂ production from water upon visible light irradiation.¹¹ The formation of surface defects, band gap narrowing, enhanced visible photoresponse and favorable upward band bending at the RuO₂/TiO₂ heterointerface facilitated the transfer and separation of photoinduced electrons/holes pairs.¹¹

The fabrication of 3D hierarchical TiO₂ photocatalysts at multiple length scales has received considerable attention as a means to improve the catalytic performance. Such complex superstructures are composed of lower dimensional nano-scaled building blocks (*i.e.* spheres, cubes, rods, tubes, sheets) so that they preserve the unique properties of individual components and induce a collective, synergistic effect to enhance the photoactivity. Several advantages over other geometries are larger surface-to-volume ratio, better mass-transfer properties of target molecular species, enhanced light absorption through multiple reflections, efficient charge carrier separation, faster charge transport, etc., thus improving the photocatalytic activity.¹²⁻²⁰ Particularly, 1-3D hierarchy consisting of one-dimensional (1D) nanostructures, such as nanorods, nanowires, nanotubes, nanofibers, assembling into 3D structures have been widely reported to be more appealing than zero-dimensional (0D) nanoparticles since 1D nanomaterials have superior electron lifetime, slow recombination time, fast electron transport and interfacial charge transfer rate, as well as effectively scatter visible light, thereby enhancing the overall light harvesting.^{16,19}

In this work, we concentrate on the combination of band gap engineering and micro/nano engineering in order to promote the optical absorption, improve charge separation and transfer of rutile TiO₂. We successfully synthesize 3D ruthenium-doped TiO₂ hierarchical architecture composed of radially aligned 1D nanorods in which the visible-light-driven H₂ generation from water is significantly enhanced.

Experimental

Synthesis of 3D Ru-doped TiO₂ urchins

All the reagents were analytical grade, purchased from Aldrich and used without further purification. In a typical procedure, 7 mL of titanium n-butoxide and 7 mL of hydrochloric acid (35 wt%) was mixed at room temperature for 30 min. Then a desirable amount of RuCl₃·xH₂O was added into the solution. The temperature was increased to 105 °C and the mixture was statically aged for further 11 h. The precipitate was washed several times with deionized water, thrice by aqueous 0.1 M NH₄OH solution, and finally with deionized water to entirely remove chlorine contaminants, and collected by high-speed centrifugation (20000 rpm). After drying at 80 °C overnight, the obtained product was denoted as 'Ru_xTi' where x represented the nominal doping dosage of ruthenium (x = 0.08, 0.4, 0.8 and 1.6 mol%). The undoped TiO₂ sample was synthesized by similar method without adding ruthenium precursor and labelled as 'TiO₂'.

Characterization

Synchrotron X-ray powder diffraction (XRD) patterns were collected at beamline 17-BM-B ($\lambda = 0.72768$ Å) of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Powder samples were loaded into a kapton capillary and two-dimensional diffraction patterns were collected by a Perkin Elmer amorphous silicon detector. The data acquisition was integrated by QXRD while the crystalline phase identification, composition and lattice parameters were subsequently analyzed by Rietveld refinement using GSAS-2 program.

High-resolution transmission electron microscopy (HR-TEM) images were recorded on a Tecnai G2 F20 S-TWIN transmission electron microscope equipped with a field emission electron source (200 kV). The powder samples were deposited from alcohol suspensions onto holey-carbon Cu grids. The Brunauer-Emmett-Teller (BET) specific surface areas (SSA) were determined by N₂ adsorption/desorption at -196 °C using an Altimira AMI-300ip instrument. The powders were outgassed at 120 °C to remove all surface-adsorbed contaminants prior to measurements.

High-resolution X-ray photoemission spectra (XPS) of each component were recorded on a laboratory-based monochromatized Al K α source with a hemispherical analyser (PHI 5000 Versa Probe, Physical Electronics). The core-level spectra were measured with pass energy of 23.5 eV, which corresponds to an instrumental resolution of 0.51 eV obtained from analyzing the adventitious hydrocarbon feature at 284.5eV, Au 4f_{7/2} and Fermi edge of Au foil. An electron neutralizer was used to compensate for charging, set to an energy of 1.2 eV with a current of 20 mA and a compensating Argon flood gun was also used with an energy of 107 eV.

Other characterization techniques were performed at the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 microscope. Raman spectroscopy was obtained on a WiTec Alpha combination microscope with 633 nm laser as an excitation source. UV-Vis diffuse reflectance (DRS) measurements were performed on PerkinElmer Lambda 950 spectrometer equipped with an integrating sphere assembly.

Table 1. BET surface areas and structural parameters obtained from Rietveld refinement of undoped and Ru-doped rutile TiO₂ series.

Samples	SSA / m ² g ⁻¹	Rutile weight percentage / %	Lattice constants		Calculated d ₍₁₁₀₎ - spacing / Å
			a = b / Å	c / Å	
TiO ₂	65	97.2	4.596(3)	2.943(9)	3.250
Ru _{0.08} Ti	112	100	4.616(4)	2.956(0)	3.264
Ru _{0.4} Ti	125	100	4.618(7)	2.956(2)	3.266
Ru _{0.8} Ti	147	100	4.608(9)	2.957(5)	3.259
Ru _{1.6} Ti	166	100	4.617(5)	2.956(5)	3.265

Visible light-driven H₂ evolution

The photocatalytic hydrogen production was carried out in a gas-closed circulation and evacuation system at 293 K. 3 mg of

powder catalyst was dispersed in 3 mL aqueous solution containing 20 vol% methanol in a sealed quartz cell. After evacuation and degassing by Ar flow, the cell was side-irradiated by a 150 W Xenon arc lamp equipped with a CuSO₄ filter and 400 nm long pass filter (400 nm < λ < 625 nm) under vigorous stirring. The amount of hydrogen gas was determined by gas chromatography (GC Agilent 6890N) equipped with FID and TCD detectors using Ar as the carrier gas.

Results and discussion

The crystal structures of bulk rutile TiO₂ and rutile RuO₂ are shown in **Figure 1A**. The similarity in tetragonal bulk unit cells of both structures is observed where either Ti or Ru atoms prefer a coordination number of 6 with nominal charge of +4. The lattice parameters $a=b$ of RuO₂ are slightly smaller and c is greater than those of TiO₂. The effective ionic radius of Ru(IV) is slightly larger (62 pm) than that of Ti(IV) (60.5 pm) in the six coordination site of the rutile structure.²¹ The solid solubility limits are approximately 5% of each oxides in the other and Ru impurities in rutile TiO₂ retain their electrons as Ru⁴⁺ ions.²² Therefore, the segregation of ruthenium oxide during the anatase-to-rutile phase transformation is less probable in our present study since the maximum nominal concentration of ruthenium is 1.6 mol%.

Figure 1. (A) Crystal structure of rutile TiO₂ and rutile RuO₂; (B, C) SXPD patterns; and (C) Raman spectra of Ru-doped TiO₂ series.

On the basis of model crystal structures for 0.925% and 1.39% Ru-doped rutile TiO₂ (closed to nominal doping concentrations) in **Figure S1** (ESI), the simulated diffraction patterns reveal that there is almost no difference in rutile TiO₂ can be found after doping ruthenium, although small differences in the peak positions between the two bulk oxide references are well established (**Figure S2**, ESI). **Figure 1B** displays the experimental XRD patterns of the undoped and Ru-doped TiO₂ with different Ru doping concentrations. The crystal phase composition and lattice parameters achieved

from Rietveld refinement is presented in **Table 1** and **Figure S3** (ESI). Tetragonal rutile phase of TiO₂ with a space group $P4_2/mnm$, lattice constants of $a = b = 4.596(3)$ Å and $c = 2.943(9)$ Å were observed in all samples *via* the presence of (110), (101), (111) and (211) diffraction peaks at $2\theta = 12.9$, 16.9, 19.2 and 24.9°. A small fraction of the anatase phase (*ca.* 2.8 wt%, $a = b = 3.794(5)$ Å and $c = 8.751(1)$ Å with a space group $I4_1/amd$ was observed in undoped TiO₂ only. Houšková et al.⁷ stated that ruthenium can assist the anatase-to-rutile phase transformation at much lower temperatures, compared to bare TiO₂, owing to the so-called strong-metal-support interaction. Due to the comparable lattice parameters of RuO₂ and rutile TiO₂, no new diffraction features associated with any ruthenium-related species was found regardless of Ru doping concentration. It could be ascribed to the very low dopant concentration, the inclusion of Ru species into the host TiO₂ matrix and/or the formation of ultra-small, sub-atomic RuO_x particles/clusters (< 1 nm) highly dispersed within TiO₂.

However, as shown in **Figure 1C**, the intensities of all diffraction peaks became weaker along with broader peaks with increasing ruthenium concentration up to 0.8%, possibly indicating the decrease in crystallite size of TiO₂ because of restrained crystal grain growth *via* the formation of Ru-O-Ti bonds, and the formation of defects after Ru doping into the host lattice. The full width at half maximum (FWHM) of Ru_{1.6}Ti was much smaller than other samples, indicating either induced internal stress or increase in grain size. Furthermore, a slight positive shift of 0.06° for the (110) peak was observed in the Ru_{0.8}Ti sample whereas other peaks were unchanged. Such a shift, which is associated with compressive residual stress, defects, or the change in electronic configuration or atomic structure, was also not detectable in other samples. It is quite consistent with the smaller expansion of a (4.608(9) Å) and the larger c (2.957(4) Å) that solely occurs on Ru_{0.8}Ti superstructure. As summarized in **Table 1**, Rietveld refinement shows the relaxation of the cell parameters upon Ru doping. The calculated d -spacings of rutile the (110) plane clearly indicate an increment on all doped samples compared to undoped TiO₂ (3.250 Å). The substitution of ruthenium ions into the TiO₂ lattice might be responsible for larger lattice constants and d -spacing values due to slightly larger effective ionic radius of Ru⁴⁺ than that of Ti⁴⁺ in the hexa-coordination of the rutile structure.²¹ The structural relaxation follows the Vegard's law^{23,24} where the lattice of metallic substitutional solid solution is expanded with increasing solute concentration as the atomic radius of solute atoms (Ru, 178 pm) is bigger than that of solvent atoms (Ti, 176 pm), and it is reversed in case of the smaller atomic size of the solute atoms. Similar phenomena were reported by several groups working on doped TiO₂ system.³⁻¹⁰ In this study, if Ru³⁺ ions exist in the system, they are not able to substitute for titanium ions due to their much larger ionic radius (68 pm),²¹ instead they enter the lattice by interstitial means, resulting in a lattice distortion energy; meanwhile the shrinkage of the TiO₂ lattice possible occurs for substitutional Ru⁵⁺ sites (56.5 pm).²¹ Therefore, a small amount of Ru⁵⁺ species in Ru_{0.8}Ti is probably suggested to co-exist with Ru⁴⁺ and Ru³⁺.

The crystal structure is consistent with the molecular structure proven by Raman spectroscopy. As indicated in **Figure 1D**, two characteristic bands centered at 449 and 611 cm^{-1} correspond to E_g and A_{1g} modes, respectively, for rutile TiO_2 . These Raman-active modes comprise motions of anions with respect to stationary central cations, either perpendicular to the c axis (Ti-O stretch, mode A_{1g}), or along the c axis (planar O-O-vibration, mode E_g).²⁵⁻²⁷ Additionally, an anomalously broad band at 252 cm^{-1} was attributed to the multiple photon scattering process.²⁵⁻²⁷ The lack of features attributable to ruthenium species, *i.e.* RuO_2 , was evident in all of the doped TiO_2 materials, further confirming the lattice substitution. It is worth noting that increasing the Ru doping dosage induced the broadening and the increment in relative intensities of both characteristic modes, as well as an obvious red-shift of E_g toward lower wavenumbers (*i.e.*, up to 418 cm^{-1} for $\text{Ru}_{1.6}\text{Ti}$). Such a change in the Ru-doped TiO_2 series could be explained by the changes in internal stress or strain upon doping leading to the lattice distortion of TiO_2 and the imbalance oxygen stoichiometry, possibly due to the formation of oxygen defects or Ru-O-Ti linkages. The structural effect can be crucial for the photocatalytic performance which will be discussed later.

Figure 2. (A-C) SEM images and (D) HR-TEM micrograph of 0.8 mol% Ru-doped TiO_2 . Inset of D is corresponding FFT pattern.

In addition, Ru doping induces a significant alteration in the textural characteristics of TiO_2 . As shown in **Table 1**, the specific surface areas increase with Ru concentration which is consistent with the decrease in crystallite size and lattice expansion concluded from XRD results. Such an enlargement might be attributed to the presence of ultra-small, sub-atomic RuO_x particles and/or clusters (< 1 nm). **Figure 2** shows the morphology and structure of 0.8% Ru-doped TiO_2 material by means of electron microscopy. 3D sea urchin-like superstructures constructed by radially aligned, densely-packed nanorods were observed as shown in **Figure 2A and 2B**. The average size of hierarchical microstructures ranged from 2-3 μm and the typical lengths of these rods were 0.5-1.5 μm . Rectangular and/or cubic facets of the rod subunits with an average size of 5-10 nm are observed in the top view image

in **Figure 2C**. It should be noted that without Ru doping, such unique hierarchical structure was not obtained and further increasing the Ru doping concentration gradually improves the sea urchin-shaped geometry as shown in **Figure S4** (ESI). It is clear that apart from its dopant function, Ru possibly acts as a structure-directing agent to enable the rod-like building blocks to radially grow so that the uniform urchin-like superstructure becomes more obvious. As mentioned above, the hierarchical architecture assembled from low-dimensional building blocks is always favourable to the (photo)catalytic activity, compared to lower dimensional nanostructures.¹²⁻²⁰ Herein, the high acidic media not only prefers the selective adsorption of Cl^- on to {110} crystal plane of rutile, but also allows the edge sharing of $[\text{TiO}_6]$ octahedral along the crystallographic c -axis, followed by corner-shared bonding.^{19,28,29} As a result, the formation of 3D urchin-shaped superstructure in the layout of 1-3 hierarchy is governed by an aggregation mechanism, namely Ostwald ripening, or a surface-energy-driven self-assembly to reduce the total surface energy of the whole system.^{13-15,19}

Due to the dense structure of such a hierarchical architecture (**Figure S5**, ESI), it is very difficult to observe the local structure of a single nanorod. HR-TEM image of a fragment in **Figure 2D** visibly implies the poor-crystallinity of a rod-like pieces and the presence of a high number of structural defects. No other individual metallic Ru and/or RuO_x are unequivocally identifiable. The corresponding FFT pattern in the inset clearly shows several spots at 2.32 and 2.52 Å, representing a slight enlargement of lattice spacing with respect to the nominal values of the rutile TiO_2 structure at 2.30 and 2.49 Å, respectively corresponding to the interplanar distance of (200) and (101) crystallographic planes. Such a lattice expansion is in good agreement with XRD results and theory. Taking into account that (i) the effective ionic radius of Ru(IV) is slightly larger than that of Ti(IV) in the VI-coordinated environment,²¹ (ii) the lattice spacings recorded are slightly larger than those of rutile TiO_2 structure, and (iii) no isolated Ru-containing nanoparticles are visible at the surface of the rods, it is possible to tentatively conclude that Ru is likely incorporated into the rutile structure in $\text{Ru}_{0.8}\text{Ti}$ sample.

Furthermore, XPS measurements were performed to clarify the electronic structure and chemical states of each component in undoped, 0.8% and 1.6% Ru-doped TiO_2 . The survey spectrum confirms the complete removal of chlorine in undoped and doped samples (not shown here). As presented in **Figure 3A**, the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ binding energies at 458.8 and 464.5 eV correspond to octahedrally coordinated Ti^{4+} state (with the spin-orbit splitting Δ of 5.7 eV). Ruthenium doping induces blue-shifts toward the lower binding energies (458.4 and 458.2 eV, $\Delta = 5.9$ eV), which might indicate a higher electron charge density for titanium atoms and the non-stoichiometric bonding of titanium atoms to oxygen atoms *via* the substitution of Ru ions into the TiO_2 lattice and/or the formation of reduced state, *i.e.* Ti^{3+} , owing to the electron transfer to adjacent Ti^{4+} . The existence of interstitial donor Ti^{3+} species may lead to the generation of under-coordinated oxygen species, particularly oxygen vacancies, to preserve the electrostatic balance. The result is consistent with XRD and

Raman observations. Valentin et al.³⁰ reported that the bridging oxygen vacancy on rutile TiO₂ introduces localized Ti³⁺ 3d¹ states about 1 eV below the conduction band minimum (CBM). The Ru 3d core level spectrum was also obtained to confirm the existence of Ru species. As seen in **Figure 3B**, the

Figure 3. High resolution XPS core-level spectra of TiO₂, 0.8% and 1.6% Ru-doped TiO₂: (A) Ti 2p + Ru 3p and (B) C 1s + Ru 3d.

peak location of C 1s and Ru 3d_{3/2} appear overlapped. The signal of Ru 3d_{5/2} was solely detected in the region of 279-282 eV for the Ru_{1.6}Ti sample, implying the presence of oxidized Ruⁿ⁺ states ($n = 2 \sim 5$), whereas no peak was found for Ru_{0.8}Ti possibly stemming from the miniscule amount of ruthenium dopant. The oxidation state of Ru species is crucial in the charge of the overall photocatalyst. For instance, as Ti⁴⁺ sites are substituted by Ru³⁺ and/or Ru²⁺, an electron donor level can be formed whereas Ru⁴⁺ and/or Ru⁵⁺ species might induce an acceptor level in the band gap of TiO₂ to keep the charge balance, resulting in a visible light response as well as affecting the charge transport and transfer pathway.

It is well known that the photocatalytic activity highly correlates with the light absorption behaviour and the subsequent photoexcitation to induce charge carriers which further migrate to the reaction sites on the surface for the surface chemical reactions. UV-Vis diffused absorption spectroscopy is a useful tool to understand the optical characteristics that correlate with the visible-light-activated performance. **Figure 4A** shows the digital photographs of Ru-doped TiO₂. With increasing Ru dopant dosage, the color of powders changed from light yellow to dark orange, in clear contrast to white undoped TiO₂. Herein, the colorization can

be likely associated with the dopant itself and the presence of defects, *i.e.* oxygen vacancies.

The UV-Vis-DRS spectra of all the samples are shown in **Figure 4B**. The intense absorption feature in the range of 200 nm ~ 408 nm is characteristic of the O 2p-Ti 3d transition (from valence band to conduction band) of titania and the onset located at 408 nm corresponds to the direct band gap energy of 3.09 eV (**Figure S6**, ESI). Ru doping obviously alters the octahedral environment of Ti species. Moreover, the absorption beyond 408 nm up to the visible and near infrared range ($\lambda = 408 \text{ nm} \sim 900 \text{ nm}$) significantly enhances with the increment of Ru doping concentration. It can be attributed to low-energy photon and/or thermal excitations of trapped electrons in localized states of the defects, *i.e.* oxygen vacancies or Ru-substitution related Ti³⁺, that locate below the CBM.^{27,31} Triggs and Lévy³² ruled out the cause of internal *d-d* transition of Ru⁴⁺ ions for the visible absorption band from 2 to 3 eV, therefore, the strong absorption band extending from 410 nm to 620 nm can be assigned to charge transfer transition of the donor (Ru⁴⁺ → Ru⁵⁺ + e⁻, Ru³⁺ → Ru⁴⁺ + e⁻) or acceptor (Ru⁴⁺ → Ru³⁺ + h⁺) type. It is also supported by photoelectrochemical measurement that the creation of carriers (electrons and holes) in Ru-doped TiO₂ occurred for $h\nu > 2 \text{ eV}$ ($\lambda < 620 \text{ nm}$).^{32,33} The weaker tail in range of 650 nm ~ 900 nm might be arisen from internal *d-d* transition of Ruⁿ⁺ and the excitation of an electron from one ruthenium ion to another on a neighbouring cation site.³² Ohno et al.⁶ considered that the formation of defects in the TiO₂ lattice by the inclusion of Ru³⁺ in the lattice is most plausible for the visible absorption. A small red-shift of the absorption onset occurred in excess doping sample, indicating the band gap narrowing to 2.91 eV due to the introduction of mid-band or impurity levels that are located between the valence band (VB) and conduction band (CB) of TiO₂. Such an optical improvement predicts good visible-light-driven H₂ evolution

Figure 4. (A) Digital photographs of undoped and Ru-doped TiO₂ powders with different Ru doping contents; and (B) UV-Vis diffused absorption spectra of Ru_xTi series.

activity over hierarchical Ru-doped TiO_2 system. The XPS valence band spectra in **Figure S6C** (ESI) show a downshift of VB edge from 1.84 eV (TiO_2) to 1.98 eV of representative $\text{Ru}_{0.8}\text{Ti}$. The band structure of $\text{Ru}_{0.8}\text{Ti}$ was roughly calculated on the basis of VBM and band gap (**Figure S6D**, ESI). Despite the band level of doped photocatalyst is slightly re-aligned, such a band structure involving defect impurity level and localized dopant levels located beyond the VB and below the CB expects to facilitate the water splitting reaction.

The visible-light-driven H_2 evolution was measured in the presence of methanol as a hole scavenger, where bulk rutile TiO_2 was used as a reference. The time courses of photocatalytic reaction using different photocatalysts are shown in **Figure 5A** where stable, constant amounts of H_2 are generated during 5 h of visible light illumination, indicating that the hydrogen evolution is a persistent and continuous process. Negligible amount of hydrogen gas was produced while employing bulk rutile TiO_2 ; and compared to undoped rutile TiO_2 , hierarchical Ru-doped rutile TiO_2 systems exhibit much better photocatalytic activity, implying the pivotal role of Ru dopants. The activity improvement can be assigned to the increase in surface area, 3D geometry, enhanced absorption of visible-light regime, and the modification of the electronic structure after Ru doping. It is apparent that 0.8 mol% is the optimal Ru doping concentration to produce 92 $\mu\text{mol H}_2$ per gram of catalyst per hour, which is 15-times greater than TiO_2

sample (**Figure 5B**). This photocatalyst is robust, remaining the H_2 evolved rate of 89 $\mu\text{mol g}^{-1} \text{h}^{-1}$ after 3 cycles as shown in **Figure S7** (ESI). However, it is noteworthy that further increasing Ru doping dosage resulted in lower photocatalytic hydrogen evolution. In spite of the coloration of doped samples, larger surface area and enhanced visible-light absorption behaviour, excessive doping can extend the lifetime of charge carriers by trapping them transiently and shallowly, and the formation of recombination centers for photogenerated electrons and holes under band gap excitation drastically decreases the activity.^{1,6,8}

On the other hand, the post treatments under ambient air, vacuum annealing and hydrogen reduction have been demonstrated to be efficient ways to improve the photocatalytic activity.³⁴ The oxidation significantly increase the crystallinity of TiO_2 , meanwhile, an oxygen-deficient atmosphere not only colorizes TiO_2 but also introduces defects such as oxygen vacancies and reduced $\text{Ti}^{3+}/\text{Ti}^{2+}$. The influence of post treatment on the photocatalytic activity was also investigated for TiO_2 sample doped with 0.8 mol% Ru, which was subsequently annealed at 200 $^{\circ}\text{C}$ for 2 h in ambient air (named $\text{Ru}_{0.8}\text{Ti@air}$) and in the flow of pure H_2 (as $\text{Ru}_{0.8}\text{Ti@H}_2$). As shown in **Figure S8** (ESI), it is obvious that the calcination strongly inhibits the production of H_2 from water. It is evident that either an oxygen-rich or hydrogen-rich environment not only strongly crystallizes rutile TiO_2 inducing larger grain size but also facilitates the formation of rutile RuO_2 on the surface of TiO_2 . The complete oxidation induces mostly Ru^{4+} ions and possible re-population of oxygen vacancies (or, restoration of lattice oxygen) by oxygen atoms, thus leading to no charge compensation. The higher the crystalline quality is, the smaller the amount of defects is.¹ Previous reports observed that the calcination in ambient air at 300 $^{\circ}\text{C}$ or below inhibited the photocatalytic activity since Ru ions are not effectively incorporated into the TiO_2 lattice at low calcination temperature.^{6,8} Otherwise, reducing the Ru-doped rutile TiO_2 system in hydrogen can form ruthenium species with lower valence states, *i.e.* Ru^{2+} , Ru^{1+} , and even Ru^0 , *via* the formation of structural defects and the introduction of interstitial hydrogen donors.³² These species can act as trapping sites, encouraging the charge recombination and thereby diminishing the photocatalytic activity.

The schematic illustration in **Scheme 1** describes the proposed charge-transfer mechanism over TiO_2 in the presence of the ruthenium dopant. It has been reported that although a more positive conduction band edge potential and slower electron transport are often seen as detracting features of rutile TiO_2 , this may lead to higher electron densities within the conduction band, subsequently increasing the quasi Fermi-level, and mitigating the aforementioned concern.¹⁹ The enhanced photocatalytic activity of doped systems may be ascribed to the role of ruthenium dopant species as effective electron donors and acceptors that drive the fast transfer of photoinduced electrons from the CB of TiO_2 to dopant sites, subsequently reacting with water and/or protons to produce H_2 . It is known that the VB of TiO_2 is composed of oxygen 2p orbitals (O 2p π states) and the CB is mainly constituted by Ti

Figure 5. (A) Time profiles and (B) mass specific rate of H_2 evolution over Ru-doped TiO_2 with different Ru dopant dosages under visible light irradiation (aqueous methanol 20 vol% as sacrificial agent, at 293 K, $\lambda = 400\text{--}625$ nm).

3d states, and each Ti^{4+} is surrounded by an octahedron of oxygen ions. According to Triggs and Lévy,³² the acceptor transitions of Ru^{4+} ($\text{Ru}^{4+} \rightarrow \text{Ru}^{3+} + h^+$) associated with a strong visible absorption band is considerably stronger than donor transitions ($\text{Ru}^{4+} \rightarrow \text{Ru}^{5+} + e^-$, $\text{Ru}^{3+} \rightarrow \text{Ru}^{4+} + e^-$).³² The acceptor state is located slightly above the donor state and the acceptor levels are placed above the VB edge of TiO_2 , i.e. Ru^{4+} acceptor level lies ~ 1.9 eV above the VB,³² allowing the electrons to excite from the VB of TiO_2 to these levels rather than directly to the conduction band of TiO_2 . As proposed in Scheme 1, the holes remaining on the VB of TiO_2 can be consumed by methanol simultaneously. As a consequence, the electron transfer is facilitated and the recombination opportunity with

Scheme 1. Illustration proposing the charge-transfer mechanism of rutile TiO_2 in the presence of Ru dopant to facilitate the visible-light-driven activity by introducing the electron donor/acceptor level of ruthenium and the mid-band energy level of defects between the conduction band minimum and valence band maximum of TiO_2 .

minority carriers is significantly retarded. In addition, the formation of coordinatively unsaturated species, i.e. oxygen vacancy and Ti^{3+} defects, due to the charge imbalance may work as efficient hole- and electron-trapping centers. The mid-band energy levels associated with these defects located below the CBM of TiO_2 may enhance the electron migration and thus, lengthening the lifetime of excited electrons and holes. Another possibility is the capture of photogenerated holes by $\text{Ru}^{(n-1)+}$ state, i.e. Ru^{3+} , and oxidize methanol afterwards, leaving large amount of electrons toward the surface for proton reduction. Furthermore, the optimization of the dopant concentration plays an essential role in the performance since the active surface of TiO_2 can be shielded by higher coverage of overloaded RuO_x aggregates that might be formed in case of heavy doping, weakening the light penetration and subsequent photo-activation.^{8,11} Miniscule amount of RuO_x onto rutile TiO_2 not only induced unique geometries of RuO_x on 1D rod-like host structure^{11,35} but also generated special optical, electronic and chemical properties of heterostructures systems.¹¹ However, higher loading amounts (beyond 0.1 wt%) had adverse effects on the photocatalytic H_2 evolution. Excessive ruthenium species can become recombination centers to trap a large number of electrons and neutralize the holes, decreasing the separation efficiency of charge carriers,^{1,6,11,32} hence being deleterious to H_2 evolution activity. Therefore, doping with 0.8 mol% of ruthenium produces the largest amount of H_2 evolved gas in this report.

Conclusions

We have successfully fabricated 3D urchin-like Ru-doped TiO_2 hierarchical architectures by a facile one-pot hydrothermal method without the use of a template or structure-directing agent. The pivotal role of a miniscule quantity of ruthenium dopant in enhanced visible-light-driven H_2 production has been unravelled. Notably, 0.8 mol% doping concentration produces the largest H_2 amount. Combined with a unique 3D geometry and surface area enhancement, the introduction of defect impurity energy levels and the function of ruthenium species as electron donors/acceptors are suggested to be responsible for the improved photocatalytic activity due to both the facilitation of electron transfer/migration and the suppression of electron-hole recombination.

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