This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Reduced TiO$_2$ rutile nanorods with well-defined facet and their visible-light photocatalytic activity

Zhao Zhao,$^{ab}$ Huaiqiao Tan,$^{a,*}$ Haifeng Zhao, Yang Lv,$^a$ Li-Jing Zhou,$^a$ Yujiang Song,$^c$ and Zaicheng Sun*$^{a,*}$

Abstract. Stable reduced TiO$_2$ rutile nanorods with well-defined facets was prepared by solvothermal route in the presence of Zn powder. The oxygen vacancy in the TiO$_2$ nanorods, which can be tuned by the amount of Zn, results in a narrow band gap and visible-light photocatalytic activity.

Titanium dioxide (TiO$_2$) has been extensively employed in many solar energy conversion applications such as photovoltaic, photocatalytic organic waste degradation, and water splitting for H$_2$ production and become a promising photocatalyst due to its good chemical, thermal and biological stability.¹ However, the large band gap of TiO$_2$ severely hinders its practical application because TiO$_2$ only absorbs UV light, which is lower than 5% of full solar spectrum. Many efforts have been proposed to make TiO$_2$ with visible-light response. For example, doped TiO$_2$ with metal or non-metal ions exhibited a broad visible light absorption and great performance.² Recently, reduced TiO$_2$ (TiO$_2$-3), incorporating Ti$^{3+}$ and/or oxygen vacancies in TiO$_2$, has emerged as an effective route to obtain visible-light photocatalytic activity.³ However, theoretical work has suggested that, in order to achieve an efficient activity in the visible spectrum, the concentration of Ti$^{3+}$ must be sufficiently high to induce a continuous vacancy band of electronic states just below the conduction band edge of TiO$_2$-3.⁴ Otherwise, a low Ti$^{3+}$ doping concentration only creates localized oxygen vacancy states that deteriorate the electron mobility and exhibit a negligible visible photo activity. This is due to the fact that the energy of the scattered doping states is largely (0.75–1.18 eV) below the conduction band edge of TiO$_2$ and the occupying photo-electrons are not adequately reactive and/or mobile for desired electrochemical reactions.⁵–²² Therefore, doping with a high concentration of Ti$^{3+}$ in TiO$_2$ is essential to enhance the photocatalytic activity in the visible region.

Several techniques have been reported to produce TiO$_2$-3, including thermal treatment under vacuum³,⁶–¹¹ reducing conditions,¹²–¹⁴ electron or Ar$^+$ ions¹⁵ bombardment, and hydrothermal treatment.¹⁶–¹⁸ Most reports start from TiO$_2$, from which a fraction of the Ti$^{4+}$ ions is reduced to Ti$^{3+}$ under harsh reducing conditions such as high temperature in reducing gas (H$_2$ or CO). Furthermore, since the reduction occurs mainly on the surface of TiO$_2$, the oxygen vacancies are usually not enough stable, even in air. The TiO$_2$-3 with surface oxygen vacancy (Ti$^{3+}$) could be easily oxidized to TiO$_2$ within a short period. Thus it is still a great challenge to develop a facile synthetic route to prepare stable reduced TiO$_2$ nanocrystals with well-defined facets.

In this report, we developed a simple and facile solvothermal strategy of preparing highly active and stable TiO$_2$-3 rutile nanorods exposed (110) facets and tunable oxygen vacancy. The key step is that TiCl$_4$ aqueous solution was employed as starting materials to make oxygen vacancy uniformly dispersed in the whole TiO$_2$ nanocrystals. Zn powder was added into the reaction to avoid the oxidation of Ti$^{3+}$, and tune oxygen vacancy concentration and crystalline phase. When the addition amount of Zn powder increases,
the color of reduced TiO₂ nanocrystals gradually turns into dark blue and rutile phase. That means reduced TiO₂ in rutile phase is more stable. The blue TiO₂ nanorods can be stored at room temperature over a year without activity-loss. The photocatalytic performance of TiO₂ nanocrystals just turned into rutile phase.

In typical, 1 mL of TiCl₄ (15-20%) aqueous solution was added into 30 ml isopropanol, and then Zn powder (0.5-2.5 mmol) was added into above solution. After stirring about 30 min, the mixture solution was transferred into a dried Teflon autoclave container. Then the reaction was placed into 180°C oven for 6 hours. The obtained solid was collected and washed with 100 ml of 4 mol/L HCl aqueous solution over 12 hours to remove excess Zn powder. After that, the solid was washed with distilled water 3 times, and then dried at 70°C. EDAX results (Fig. S1) indicate that no Zn signal is observed. That reveals the Zn has been totally removed by acid washing step.

When TiCl₄ aqueous solution was added into water, the color of solution turned from blue purple to transparent within a short period, indicating that the Ti⁺ is easily oxidized to Ti⁴⁺. Only white anatase TiO₂ nanocrystals are obtained after hydrothermal reaction (Fig. S2). Isopropanol is chosen as solvent instead of water due to Ti⁴⁺ can survive in the isopropanol solution. After solvothermal reaction, gray TiO₂ nanocrystals were obtained. X-ray diffraction (XRD) pattern (Fig. S3) indicate that the obtained TiO₂ is the mixture of anatase and rutile TiO₂ indicating that the most of Ti⁴⁺ is oxidized and forms TiO₂ in the solvothermal reaction. To avoid the oxidation of Ti⁴⁺, Zn powder is added into the solvothermal reaction. The as-prepared TiO₂ nanocrystals show a series color change from gray to dark blue with the addition of different amount Zn (Fig. 1C insets). The UV-Vis spectra of reduced TiO₂ nanocrystals, as shown in Fig. 1A, disclose that a broad absorption band appears in the visible region and it turns stronger with the addition amount of Zn powder. When the Zn powder amount increases to 1.5 mmol, the optical band gap of reduced TiO₂ changed to 2.93 eV (Fig. S4). Fig. 1B shows the XRD patterns of the reduced TiO₂ nanocrystals samples. The relative amount of rutile phase in the reduced TiO₂ gradually increases with increasing the amount of Zn powder. When 1.5 mmol Zn powder was added into the reaction, only rutile TiO₂ nanocrystals were obtained. Although Huang et al obtained the Ti⁺ self-doped TiO₂ through hydrothermal route with Zn powder and Ti⁴⁺, Zn⁺ was detected at the surface of TiO₂ nanocrystals.¹ In our case, no Zn signal is observed in the EDAX (Fig. S1) and X-ray photoelectron spectroscopy XPS full scan spectra (Fig. S5). High resolution XPS of Ti 2p, as shown in Fig. 1C, reveals that the peaks at 458.3 and 464.1 eV, attributed to Ti 2p 3/2 and Ti 2p 1/2, shift to low binding energy 457.8 and 463.5 eV, respectively. This shift indicates that the Ti⁺ doped TiO₂ forms and the oxygen vacancy concentration increases in the TiO₂ nanocrystals with the increase of Zn powder amount. Electron paramagnetic resonance (EPR) spectroscopy was employed to determine the presence of Ti⁷⁺. A strong EPR signal is observed at g=1.96 (Fig. 1D), which could be assigned to Ti⁷⁺, but the existence of the Ti⁷⁺ has no influence on the stability of our reduced TiO₂ nanorods.²³

Fig. 2 shows transmission electron microscopy (TEM) images of the reduced TiO₂ nanocrystals prepared by the solvothermal reaction with different amount of Zn powder. When the Zn powder amount is lower than 0.5 mmol, the TiO₂ nanocrystals are mainly in anatase phase and in truncated octahedron (Fig. 2A). High resolution TEM image (inset) also shows clear 0.35 nm lattice fringes, corresponding to (101) lattice plane of anatase TiO₂. When Zn powder amount increase to 1.0 mmol, there are two TiO₂ morphologies observed, truncated octahedron anatase TiO₂ and rutile TiO₂ nanorods with exposed of (110) facet. Further Zn powder amount increase to 1.5 mmol, only the rutile TiO₂ nanorods with 50 nm length and ~ 5 nm diameter were obtained. High-resolution TEM image disclose 0.32 nm lattice fringes, corresponding to (110) lattice plane of rutile TiO₂. Zn powder amount further increases, the TiO₂ morphology (Fig. 2D) has no obvious change. These TEM results indicate that all TiO₂ nanocrystals possess well-defined facet, for example, TiO₂ rutile nanorods exposed (110) facet. Small aggregation composed with a few TiO₂ nanorods can be observed in the SEM images (Fig. S6). The N₂ absorption was employed to evaluate the surface area of obtained TiO₂ nanocrystals. Fig. S7 shows the N₂ absorption curves, which exhibit typical type IV curves. The BET surface area of TiO₂ nanocrystals gradually decreases from 90 m²/g to 55m²/g for from anatase TiO₂ truncated octahedron to rutile nanorods, respectively.

Photocatalytic water splitting H₂ production was used to evaluate the photocatalytic activity of as-obtained TiO₂ nanocrystals. Fig. 3A shows typical time course of H₂ evolution under full solar spectrum (Xeon lamp 300W). Normal rutile nanoparticles (~ 30 nm in diameter purchased from Aladdin Reagent, Inc.) shows very weak photocatalytic activity. Rutile TiO₂ nanorods prepared from reduced TiO₂ nanorods calcined at 450 °C for 30 min, shows ~ 0.14 mmol/h per 0.1 g photocatalyst. For the reduced TiO₂, the H₂ evolution amount at same time period increases with the increase of rutile ratio in mixture reduced TiO₂ nanocrystals. H₂ production amount reach maximum ~ 0.6 mmol/hour for 0.1 g reduced TiO₂ when reduced TiO₂ completely transfer into rutile phase. After that, the H₂ evolution amount decreases, indicating that the photocatalytic performance decrease in the case of too high oxygen vacancy concentration, which produced by the over-reduction of excess amount Zn powder. Under visible light (λ > 420 nm, Xeon lamp with a 420 nm cut-off filter), the H₂ evolution curve is exhibited in Fig. 3B. The reduced TiO₂ rutile nanorods show a stable H₂ release rate of ~ 8 μmol/hour per 0.1 g photocatalyst. The normal Rutile TiO₂ nanoparticles and TiO₂ nanorods with defined facets show no H₂ production under visible light (λ > 420 nm). The probably
mechanism is that the oxygen vacancy narrow the band gap of TiO$_2$ and promote the charge separation of photo generated charge carriers (Fig. S9). The photocatalytic activity is still kept without noticeable decrease after five times recycles (Fig.3D), demonstrating the excellent stability of the reduced TiO$_2$.

Fig. 3 Time courses of H$_2$ production from reduced TiO$_2$ loaded with 0.5% Pt in 20% methanol/water under Xeon lamp (300W) without (A) and with (B) UV-420 cut-off filter illumination. (C) H$_2$ production rate for reduced TiO$_2$ prepared from different amount of Zn powder under visible light (λ>420nm). (D) Cycling tests of photocatalytic activity of reduced TiO$_2$ prepared from 1.5 mmol Zn powder under visible light (λ>420nm). Rutile NPs is TiO$_2$ nanoparticles with ~30 nm in diameter. Rutile NRs was prepared reduced TiO$_2$ calcined at 450°C for 30min.

In conclusion, we have developed a simple one-step method to synthesize reduced TiO$_2$ rutile nanorods with well-defined facets. The as-prepared reduced TiO$_2$ exhibits high stability in air and water with light irradiation. The reduced degree (oxygen vacancy concentration) can be tuned by the addition amount of Zn powder. Experimental results show good conversion efficiency in both full solar spectrum and visible light (λ>420nm), which support that it is the introduced oxygen vacancy that accounts for the extension of the photocatalytic activity from the UV to the visible light region. Excess amount of oxygen vacancy will result in a decrease of photocatalytic performance. The present study demonstrates a simple and economical method for narrowing the band gap and for the development of a highly active photocatalyst under visible light.

Financial support from the National Natural Science Foundation of China (No. 21201159, 61176016, and 21104075), the Science and Technology Department of Jilin Province (No. 20121801), “Hundred Talent Program” CAS and open research fund of Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University).

**Notes and references**

Enhanced visible-light photocatalytic performance for water splitting H\textsubscript{2} evolution is obtained from reduced TiO\textsubscript{2} rutile nanorods with well-defined facets.