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The Effect of Redox Cocatalysts Location on Photocatalytic Overall Water Splitting over Cubic NaTaO₃ Semiconductor Crystals Exposed with Equivalent Facets

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17 ABSTRACT

In the semiconductor photocatalyst system for overall water splitting, cocatalysts play crucial roles because they provide not only redox active sites but also charge separation function for photogenerated electrons and holes. In this work, we have investigated the cubic structured NaTaO₃ with six equivalent {001} facet exposure to address the following two important questions: if charge separation can occur among the equivalent facets, and how photogenerated charges can be separated on the equivalent surface for photocatalytic reactions. Photodeposition of noble metals and metal oxides show no preferential deposition, indicating that no spatial charge separation occurs among the six equivalent facets of NaTaO₃. However, observation of efficient overall water splitting reaction upon loading of well-known cocatalyst NiO on the NaTaO₃ clearly demonstrates that photogenerated electrons and holes could still be well-separated. In-situ formation of Ni and NiO cocatalysts during the water splitting process was revealed by XPS and XAFS analysis, confirming the role of dual cocatalysts Ni/NiO, where nickel serves as an electron trap (catalytic sites for water reduction) and NiO serves as a hole trap (catalytic sites for water oxidation). Such kind of vicinal charge separation by dual cocatalysts can also lead to efficient overall water splitting.

34 KEYWORDS: Charge separation, Equivalent facets, Dual Cocatalysts, Overall water splitting,

35 Photocatalysis, Hydrogen production

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39 INTRODUCTION

Photocatalytic splitting of water has been extensively studied in recent years since it is a viable means to harvest and store abundant solar energy in the clean chemical energy form of H₂.¹ In order to achieve efficient overall water splitting with sunlight, a photocatalyst or photocatalyst system must simultaneously meet the requirements of efficient light absorption, charge separation and catalytic reactions, which are the three key factors of photocatalytic water splitting reactions.² The crucial steps of charge separation and surface reaction can be principally tuned by semiconductor's interface and surface engineering. For example, fabrication of heterojunction,³ p-n junction,⁴ and phase junction⁵ have been well adopted for achieving efficient charge separation. Loading cocatalysts on the surface of a semiconductor is also a generally applied strategy for efficient charge separation and creating surface redox reaction sites.^{1a, 2b}

Recently, we reported that photogenerated electrons and holes can be spatially separated on the different facets of BiVO₄ semiconductor crystals,⁶ which opens up a new avenue for the assembly of crystal-based photocatalytic system by selectively loading redox cocatalysts on the different facets of a semiconductor crystal.⁷ Due to synergetic effect of facet charge separation and provision of redox active sites by cocatalysts spatially on the different facets, dramatic improvement of photocatalytic activity can be achieved.⁷ Though facet charge separation are now well accepted and studied on the different semiconductor crystals, such as TiO₂,⁸ BiVO₄,^{6-7,} 9 Cu₂WS₄, 10 Cu₂O, 11 BiOCl, 12 Sr₂Nb₂O₇, 13 BaTi₄O₇, 14 and BaLa₄Ti₄O₁₅, 15 etc, the mechanism of facet charge separation and its relation with the surface reaction sites as well as cocatalysts are not well understood.

NaTaO₃ is a typical n-type semiconductor for overall water splitting. It was reported that
NiO/NaTaO₃:La photocatalyst could achieve 56% apparent quantum efficiency (AQE) for

overall water splitting at 270 nm UV light irradiation.¹⁶ The high photocatalytic activity was ascribed to the separation of H₂ and O₂ evolution reaction sites by the unique nanostep structure of NiO ultrafine nanoparticles. Essentially, cocatalyst introduces two positive effects on the photocatalysis: (i) promotion of charge separation and (ii) construction of active sites for reduction and oxidation reactions.^{2b} However, the actual functional species of nickel oxide cocatalsyts is still under debate. It has been proposed that nickel oxide is a proton reduction cocatalyst for various n-type semiconductor photocatalysts, whereas water oxidation occurs at ntype semiconductor surface.¹⁷ And recently, this mechanism was revised to suggest that nickel oxide should be reformulated as Ni and NiO component, and the metallic Ni actually functions as proton reduction site and NiO functions as water oxidation site.¹⁸ These controversial mechanisms are rather bewildering and needs to be further addressed. It would be rather interesting to investigate further on how photogenerated electrons and holes are separated on the semiconductor crystals with equivalent facets, which is also a case of many semiconductors.

In this work, NaTaO₃ with six equivalent (100) crystal facets was synthesized and used as a model semiconductor photocatalyst to investigate the charge separation effect on equivalent facets and the methodologies for achieving efficient charge separation on semiconductors with equivalent facets. Photo-reductive deposition of noble metals and photo-oxidative deposition of metal oxides were used respectively for the probe of the preferential locations of photogenerated electrons (reduction sites) and holes (oxidation sites) on the surface of NaTaO₃. In the meantime, impregnation method for randomly distribution of noble metals and metal oxides on the surface were also applied for comparison as control experiments. Following these probe experiments for photogenerated electrons and holes, more detailed photocatalytic water splitting reactions were carried out by loading NiO or Ni/NiO cocatalysts. The existence of Ni and NiO dual cocatalysts

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was confirmed by combination of XPS and XAFS analyses, and their important functional roles
in achieving overall water splitting reactions on semiconductors with equivalent facets were also
investigated and discussed.

88 EXPERIMENTAL SECTION

Preparation of NaTaO₃. Cubic NaTaO₃ was synthesized by a microwave-assisted hydrothermal method as reported in the previous literature.¹⁹ Ta₂O₅ (purchased from Amresco) and NaOH (AR) were employed as the starting materials. Firstly, 0.54 g (1.2 mmol) of Ta₂O₅ was added to 75 mL of 1.75 M NaOH solution to form a mixed suspension under magnetic stirring at room temperature for 30 min. The resultant reaction mixture was transferred to a 100 ml Teflon-lined vessel (model XP-1500, CEM Corp.), which was then placed in a MARS-5 microwave digestion system operated at 2.45GHz (EMCorp.). The reaction mixture was heated to 220°C in 60 min and maintained at 220°C for 3 hours. Then the products were simply collected by centrifugal separation and washed with deionized water for 4-5 times. Finally, the resultant samples was dried in an oven at 60 °C for overnight.

Deposition of metal and metal oxide nanoparticles. Photo-reductive deposition of noble metals (Pt and Ag) was carried out as follows. To a suspension of NaTaO₃ (0.3 g) aqueous solution containing 20 vol% methanol solution, a calculated amount (5 wt%) of Pt precursor H₂PtCl₆ or Ag precursor AgNO₃ were added. The resulting suspension was stirred and irradiated under a 450 W Hg lamp for 1 hour. For photo-oxidative deposition of MnO_x or PbO_x , a calculated amount (5 wt%) of the Mn precursor $Mn(NO_3)_2$ or the Pb precursor $Pb(NO_3)_2$ were added into the suspension of NaTaO₃ in the 500 mL NaIO₃ solutions (0.01M). The resulting suspension was stirred and irradiated under a 450 W Hg lamp for 1 hour. For metal and metal-oxide simultaneous photodeposition, H_2PtCl_6 (AgNO₃) and Mn(NO₃)₂ (Pb(NO₃)₂) were chosen

as precursors and reactions were carried out without any sacrificial reagent. After photodeposition, the final reaction mixture was well filtered, washed with deionized water for more than 3 times, and finally dried at 60 °C for overnight.

111 Deposition of NiO cocatalyst. NiO cocatalyst was loaded on the surface of cubic NaTaO₃ by
112 both photodeposition and impregnation methods.

In the photodeposition method, NaTaO₃ powder (0.3 g) suspension in 500 mL 20% methanol/water solution containing an appropriate amount of Ni(NO₃)₂.6H₂O was prepared in an inner irradiation cell made of quartz. The mixture was stirred while irradiation with a light source of a 450 W high-pressure mercury lamp (Ushio-UM452). After 3 hours reaction time, the suspension was filtered and washed with deionized water for more than 5 times. The sample was dried at 60 °C for overnight and further calcined at 543K for 2 hours. Thus prepared sample is denoted as NaTaO₃-NiO (*hv*).

For comparison, NiO was also deposited on the surface of NaTaO₃ by impregnation method. Typically, a suspension of NaTaO₃ powder in an aqueous solution (2~3 mL) containing an appropriate amount of Ni(NO₃)₂.6H₂O was prepared on a porcelain crucible. The suspension was then stirred at 100 °C using a glass rod during water evaporation. The dried powder was calcined at 543K for 2 hours. Such prepared sample is denoted as NaTaO₃-NiO (imp).

Photocatalytic Reactions. The photocatalytic activities of the prepared samples were carried out in a closed gas circulation and evacuation system under irradiation with a 450W high-pressure Hg lamp (Ushio-UM452). Typically, 0.3 g of sample (either NaTaO₃-NiO (imp) or NaTaO₃-NiO(*hv*)) was suspended in 500 mL deionized water. Before irradiation, the reaction system was thoroughly degassed by evacuation in order to drive off the air inside. The amounts of evolved

H₂ and O₂ gases were determined by an on-line gas chromatograph (Agilent, GC-7890, TCD, Ar
carrier).

Characterization. All samples were characterized by powder X-ray diffraction (XRD, Rigaku D/max-2500PC) equipped with a graphite-filtered Cu/K α (λ =0.154 nm) radiation source, and the applied current and voltage were 100 mA and 40 kV, respectively. The morphology of the samples were examined using a scanning electron microscope (SEM, FEI Quanta200F) operated at 20 kV, a transmission electron microscope (TEM, FEI Tecnai Spirit) and a high resolution transmission electron microscope (HRTEM, FEI TecnaiF30) operated at 120 kV and 300 kV, respectively. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VGESCALAB MK2 spectrometer with monochromatized Al/Ka excitation, and the C1s peak (284.6 eV) was used as the reference. ICP-AES analyses were carried out on an inductively coupled plasma atomic spectrometry (ICPS-8100 Shimadzu). The XAFS spectra of Ni K-edge were measured at beamline 14W station of Shanghai Synchrotron Radiation Facility (SSRF) equipped with 150 MeV linear accelerator, 3.5 GeV booster and 3.5 GeV storage ring. The output energy was tuned for Ni measurement using a Si(111) crystal monochromator. The samples were sealed with Kapton films in glove box and stored in argon atmosphere before measurements. The data were collected in fluorescence mode at room temperature using 32-element Canberra/XIA Ge detector system. Ni foil was also measured with the samples simultaneously using the third ionization chamber so that the energy calibration could be performed by scan. Athena software package was employed to process and analysis of the XAFS data.

151 RESULTS AND DISCUSSION

Crystal structure of NaTaO₃. As shown in SEM images of Fig. 1a, the synthesized NaTaO₃ samples are cubic morphology crystals. The particle size ranges from 130-430 nm with the mean value of ca. 270 nm. The normally seen crystalline structures of NaTaO₃ are: (a) the cubic phase; (b) the monoclinic phase; (c) the orthorhombic phase. The 2θ positions of the principal diffraction peaks for these three phases are nearly identical, which leads to difficulty in identifying the different phase structures of the synthesized NaTaO₃ To identify phase structure of the synthesized NaTaO₃, we have conducted the XRD measurement at slow scanning rate of 0.02° /min and the spectra are shown in Fig 1b. Some principal peaks, such as those designated as A, B and C, were identified to be comprised of several sub-peaks. By comparing with the standard JCPDS, we concluded that the NaTaO₃ materials prepared in this work are the orthorhombic phase (Pcmn a=5.5319 Å, b=7.8054 Å and c = 5.4943 Å).²⁰ The full TEM images (Figure 1c) in 100 nm resolution shows that the synthesized NaTaO₃ are cubic morphology crystals, which is consistent with the result of the SEM images. The SAED patterns (Figure 1d) of the area shown with a circle in Figure 1c further indicates that the synthesized NaTaO₃ belongs to an orthorhombic phase with space group *Pcmn*. The calculated lattice parameters of a_0 b₀ and c₀ are 5.5319 Å, 7.8054 Å and 5.4943 Å, respectively. However, the main exposed crystallographic planes are not the typical orthorhombic phase of (100) and (001), because it shows six crystallographic planes with four equivalent crystallographic planes of (101), (10-1), (-101), and (-10-1) indexed by {101} set together and two equivalent crystallographic planes of (010) and (0-10) indexed by {010} set together. It should be noted that the six crystallographic planes are actually corresponding to the cubic {100} facet of NaTaO₃. Furthermore, HRTEM image (Figure 1e) shows that the crystal features with lattice distances of 3.92 Å and 7.84Å calculated from FFT analysis, which are corresponding to the crystal planes of (101) and (010),

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respectively. Therefore, it is clear that the synthesized $NaTaO_3$ is a standard cubic crystal with six equivalent {100} facets exposed on the surface.



Figure 1 (a) SEM image, (b) XRD patterns, (c) TEM image, (d) SAED pattern, and (e) HRTEM ofsynthesized cubic crystals of NaTaO₃.

Probing electron and hole sites on the facets. Excitation of a semiconductor with an appropriate light source can generate photoexcited electrons and holes, which may migrate to some particular sites of the semiconductor surface to participate in the surface redox reactions. Thus, photo-reductive deposition of metals or photo-oxidative deposition of metal oxides are convenient methods to probe the surface electron sites or hole sites, respectively.

The six facets of the cubic NaTaO₃ are smooth as revealed by the SEM image shown in Figure 2a. Photo-oxidation deposition of Mn^{2+} ions on NaTaO₃ was performed with IO_3^- as the electron acceptor. It can be seen from the SEM image of the Figure 2b that the MnO_x nanoparticles are deposited randomly on the six facets of NaTaO₃ without any facet selectivity. This demonstrates

 H^+

(1)

that there is no preferential facet to capture the photogenerated holes upon photo-irradiation. The
 photodeposition reactions can be described as follows:⁶

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$$Mn^{2+} + xH_2O + (2x-2)h^+ \longrightarrow MnO_x + 2x$$

$$(2x-2)H^{+} + (x-1)/3IO_{3}^{-} + (2x-2)e^{-} \longrightarrow (x-1)/3I^{-} + (x-1)H_{2}O$$
 (2)

Photodeposition of Pt was carried out using H_2PtCl_6 as Pt precursor in the presence of methanol as hole sacrifice agent. It can be seen from the SEM image of Figure 2c that Pt particles are also randomly deposited on the six faces of NaTaO₃ without any facet selectivity. This demonstrates that there is no preferential facet to host the photogenerated electrons upon photo-irradiation. The photo-reduction of metal ions into metal nanoparticles can be described as follows:^{1b}

$$PtCl_6^{2^2} + 4e^2 \longrightarrow Pt + 6Cl^2$$
(1)

$$2/3CH_3OH + 2/3H_2O + 4h^+ \longrightarrow 2/3CO_2 + 4H^+$$
 (2)

Simultaneous photodeposition of Pt and MnO_x was also carried out without using sacrificial agents. The SEM image (Fig. 2d) shows that Pt and MnO_x are also randomly distributed on each facet of NaTaO₃. To demonstrate the universality of the observed non-facet selective deposition phenomena, photodepositions of other metals (e.g., Ag) and metal oxides (e.g., PbO₂) were also tested. And again the SEM images (Fig. S1) revealed that these metals and metal oxides were also randomly deposited on the surface of NaTaO₃, suggesting non-facet selectivity is not due to some particular properties of deposited metals or metal oxides but is due to the intrinsic nature of the NaTaO₃ crystal with six equivalent facets.



211 Figure 2 SEM images of (a) NaTaO₃; (b) MnO_x-NaTaO₃; (c) Pt-NaTaO₃; (d) Pt-MnO_x-NaTaO₃.

Overall, the probing of electron and hole sites on NaTaO₃ revealed that the photogenerated electrons and holes cannot be spatially separated on the equivalent $\{100\}$ facets of NaTaO₃, which is quite different compared with the results of spatial separation of photogenerated electrons and holes on the nonequivalent $\{001\}$ and $\{101\}$ facets of BiVO₄. The present work adequately demonstrates that the prerequisite of the facet charge separation in semiconductor crystals is the existence of nonequivalent facets.

Overall water splitting by loading NiO cocatalyst. Since the key process of charge separation cannot be achieved by facet charge separation on NaTaO₃ with six equivalent facets, question then remains on how to achieve efficient charge separation on crystals with equivalent facets for overall water splitting. Since NiO is a known cocatalyst matching with NaTaO₃ in energy level for water splitting,¹⁶ it was used as a cocatalyst for the investigation of charge separation on NaTaO₃ with six equivalent facets during photocatalytic overall water splitting.

For comparison, NiO was loaded by both photodeposition (Fig. 3a) and impregnation (Fig. 3b) methods. Firstly, the photocatalytic water splitting activities of NaTaO₃-NiO (hv) and NaTaO₃-NiO (imp) samples with highest amount of NiO (2 wt%) were subject for the investigation. Under the same experimental conditions, these two photocatalysts showed similar photocatalytic activity for overall water splitting as shown in the photocatalytic reaction time courses in Fig. 3c and Fig. 3d. The fact of the similar photocatalytic activities is a strong indication that the NiO cocatalyst might be randomly deposited on each facets of NaTaO₃ in a similar manner in spite of the different cocatalyst loading methods. This is not surprising since the synthesized $NaTaO_3$ with six equivalent facets has no facet charge separation effect as confirmed in the previous sections. Nevertheless, the successful splitting of water demonstrates that the photogenerated electrons and holes indeed could be efficiently separated once NiO were loaded on the surface of $NaTaO_3$ either by photodeposition or impregnation method, implying that the cocatalyst plays an important role in achieving efficient charge separation for overall water splitting.

To know the nature of the NiO species in these two samples, ICP-AES, XPS, TEM and XRD patterns analyses were performed. Per ICP-AES, the amount of Ni in NaTaO₃-NiO (hv) and NaTaO₃-NiO (imp) is 1.05 wt % and 1.12 wt %, respectively, which are nearly the same within the experimental error. XPS spectra (Figure S2) show two main peaks at 855.4 and 872.7 eV and shoulder peaks at 861.2 and 879.4 eV, which correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. All peaks are the distinctive feature of oxidized nickel, i.e. NiO. However, a small shoulder peak at ca. 853.0 eV in NaTaO₃-NiO (hv) is relevant to the metallic Ni species. Despite this, observation of almost identical binding energies of Ni $2p_{3/2}$ and $2p_{1/2}$ for both of the samples demonstrates that the similar NiO species were formed on the surface of NaTaO₃ though different deposition methods were applied.²¹ The morphology and the particle size of NiO

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particles deposited by different methods are also guite similar, as visualized by the almost complete coverage of NiO on the surface of NaTaO₃ in TEM images (Fig. 4). The XRD patterns of NaTaO₃ with and without doped NiO are shown in Fig. S3. We found that the 20 values of the most intense peak at 32.5° did not change before and after NiO loading, which means that loading of NiO co-catalysts on the surface of NaTaO₃ did not obviously change the crystal structure of NaTaO₃. These results demonstrate that there is no significant difference of the NiO species in terms of loading amount, valence state and morphology for the NaTaO₃ samples with 2 wt% NiO loading either by photodeposition or impregnation methods. It can be tentatively concluded that achievement of overall water splitting is not due to charge separation in a way of spatial facet charge separation in this system. Efficient charge separation for overall water splitting might be related to the presence of the NiO cocatalyst species.



Figure 3 The scheme of NaTaO₃ with NiO cocatalyst deposited by (a) photodeposition and (b) impregnation methods, and (c, d) the time courses of the photocatalytic water splitting activity over NaTaO₃-2% NiO(hv) and NaTaO₃-2% NiO(imp), which are corresponding to (a) and (b), respectively.



Figure 4 The TEM images of (a,b) NaTaO₃-NiO(hv) and (c,d) NaTaO₃-NiO(imp) with 2 wt% NiO loading.

It should be noted that the H₂ and O₂ rates in Fig. 3c and Fig. 3d are not in stoichiometric ratios. Such kind of deviation may be related to many factors, including the reactions with sacrificial reagents, adsorption of the evolved gases on the catalyst, consumption of the evolved gases by impurities, etc. But in most cases, it reflects that the photogenerated electrons and holes are not equally consumed by water splitting reaction, which may be related to the nature of the surface redox active sites for H₂ and O₂ evolution. To better understand the non-stoichiometric ratio of H₂ and O₂ evolution, the effect of the NiO cocatalyst was further examined by varying its loading amount from 0 wt% to 2 wt%. The reaction rates of evolved H₂ and O₂ are shown in Fig. 5. It can be seen that the photocatalytic water splitting activities are quite different for $NaTaO_3$ -NiO(imp) and NaTaO₃-NiO(hv). The NaTaO₃-NiO (imp) samples show a kind of volcanic trend. At high NiO loading, the H_2/O_2 ratio is much higher than 2. And the highest activity with H_2/O_2 ratio approximately to 2:1 can be reached when NiO loading was 0.2 wt%. Further decrease of the NiO loading decreases the O₂ evolution rate, and no O₂ evolution was observed without NiO

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loading. On the other hand, the NaTaO₃-NiO ($h\nu$) also showed that the highest photocatalytic water splitting activity with H₂/O₂ ratio more than 4 was reached when the NiO loading was ca. 1.6 wt%. Further decrease of the NiO loading decrease the O₂ evolution rate and no oxygen evolution was observed. It can be seen that the NiO loading amount largely affects the photocatalytic activities in both cases. Especially the O₂ evolution rate was largely inhibited when low amount of NiO was loaded by photodeposition method. This implies that though the same amounts of NiO cocatalysts were loaded on the surface of NaTaO₃, the photodeposition method may give much less O₂ evolution sites to consume the photogenerated holes, especially when NiO was in low amount loading.



Figure 5 Photocatalytic water splitting into H_2 and O_2 over (a) NaTaO₃-NiO (imp); (b) NaTaO₃-NiO(hv) with different amounts of NiO loading.

To gain a deep insight into the effect of NiO loading, the typical samples of NaTaO₃-NiO (imp) (which shows both H_2 and O_2 evolution activity) and NaTaO₃-NiO (hv) (which shows only H_2 evolution activity) with the same amount of NiO loading (0.2 wt%) were also subject to ICP-AES, XPS, HRSEM investigations. The ICP-AES analyses show that the actual amounts of Ni in NaTaO₃-NiO (imp) and NaTaO₃-NiO (hv) are similar, which are 0.15 wt% and 0.13 wt%,

respectively. HRSEM and SEM images (Fig. 6) show that the NiO particles with size ranging from 7 to 9 nm are all randomly distributed on the surface of each sample. XPS (Fig. S3) spectra show almost identical binding energies of Ni $2p_{1/2}$ and Ni $2p_{3/2}$ for both samples. The shoulder peaks at ca. 852.5 eV is due to the metallic Ni, which is more intense in NaTaO₃-NiO (hv) than that in NaTaO₃-NiO (imp). Ni and NiO are the main component of the Ni species in both samples though the relative ratio of Ni and NiO may be different. Further, to address the questions whether the cocatalysts change the facial orientation of NaTaO₃, we have carefully analyzed the TEM and HRTEM images of NaTaO₃-NiO (imp) and NaTaO₃-NiO (hv) with 0.2 wt% NiO loading. It can be seen from Figure 7 that the lattice fringe distance of NiO (111) plane was kept same, no matter what kinds of the loading methods were employed. This provides sound base for the comparison of NiO effects on different loading methods. Furthermore, HRTEM images of NaTaO₃ also clearly show that the synthesized NaTaO₃ crystals always keep the lattice distances of crystal planes of (101) to be 3.92 Å in the presence and absence of NiO. From these observation, we concluded that the presence of NiO cocatalyst does not change the facial orientation of NaTaO₃. All of these characterization results indicate that there is no great difference of the originally loaded NiO species in NaTaO₃-NiO (imp) and NaTaO₃-NiO (hv). This is a little hint that certain amount of H₂ or O₂ evolution sites may not present at the initial stage of the photocatalytic reaction but be derived in-situ during the photocatalytic reaction.



before and after photocatalytic water splitting reaction by XPS (Fig.8), EXAFS (Fig. 9) diffuse
reflectance spectra (Fig. S5).

We have measured the XPS of NiO only (Figure 8a), and compared it with XPS data of NaTaO₃-NiO(imp) with 0.2wt% loading before (Figure 8b) and after (Figure 8c) water splitting reactions. The XPS spectrum of NiO obtained by calcination of Ni(NO₃)₃ at 270 $^{\circ}$ C for 4 h (Figure 8a) shows similar XPS spectrum as the commercial NiO (Fig. S6). First, the peaks centered at 853.7 eV and 855.5 eV as well as those at 872.9 eV and 870.9 eV can be ascribed to two multiplet-split peaks of Ni2p3/2, and the broad peaks centered at 860.9 eV and at 879.1 eV can be ascribed to the other two satellite peaks of NiO. However, it can be seen from Figure 8b that metallic Ni is formed after photocatalytic water splitting reactions, as evidenced by the clear observation of Ni 2p1/2 and Ni 2p3/2 at 855.5 eV and 872.9 eV in addition to the shoulder peaks at 861.0 eV and 879.1 eV, respectively. From Figure 8b, it can be seen that NiO is the main component for NaTaO₃-NiO(imp) with 0.2wt% loading before water splitting reaction, as evidenced by the clear observation of Ni 2p1/2 and Ni 2p3/2 at 855.5 eV and 872.9 eV with the shoulder peaks at 861.0 eV and 879.1 eV, respectively. However, after photocatalytic water splitting, the peak at 855.5 eV was dramatically broadened, and appearance of additional peak at low binding energy of 852.4 eV is a strong indication that reduced Ni species, mostly probably metallic Ni species, were formed (Fig. 8c). So it is reasonable to deduce that the actual cocatalyst during photocatalytic reaction is Ni and NiO dual cocatalysts, where Ni was in-situ formed by photoreduction of NiO during photocatalytic reactions.

Figure 8: The Ni 2p XPS spectra of NaTaO₃-NiO(imp) with 0.2 wt% NiO loading (a) before, (b) after water splitting reaction and (c) NiO.

In order to further elucidate the oxidation state changes of the Ni species, EXAFS spectra were recorded for Ni foil, NiO, and the NaTaO₃-NiO(imp) before and after photocatalytic water splitting reactions (Figure 9a). In the XANES spectra, the position of the K-edge corresponds to the oxidation state of the measured elements, the higher energy position it is, the higher oxidation state of the elements, and vise versa. Though the high energy shift of the K-edge of the NiO species compared to the metallic Ni can be directly visualized, the K-edge spectra of the NaTO₃-NiO(imp) before and after photocatalytic water splitting reaction look rather similar, indicating that NiO on NaTaO₃ were well reserved after photocatalytic water splitting reaction. The K-edge positions of these samples were further analyzed using the derivative spectra as shown in the inset of Figure 9b, since the K-edge positions can be more clearly judged by the peak positions in the derivative spectra. Compared to the pure NiO, the Ni K-edge position of

360 NaTaO₃-NiO(imp) before photocatalytic water splitting reaction was slightly shifted toward low 361 energy compared to pure NiO, indicating that some reduced Ni species might be present. After 362 photocatalytic water splitting reaction, the Ni K-edge was further shifted toward the low energy 363 position, indicating that more reduced Ni species might be formed.

The Ni K-edge K³ weighted EXAFS spectra as well as the Fourier-transformed relative radial distance spectra are shown in Fig 9c and Fig. 9d, respectively. It can be seen that the Ni species in NaTaO₃-NiO (imp) before and after photocatalytic water splitting reaction were mainly in the form of NiO states, because all of the peak positions are all well correlated with those of pure NiO in both spectra. However, careful inspection on the Fourier-transformed relative radial distance spectra shows some minor but clearly detectable changes of the Ni species after photocatalytic water splitting reaction. Firstly, the second shell of Ni-Ni was slightly shifted (ca. 0.02 Å) toward the first shell of the metallic Ni, while the peaks of the third and the fourth shells were also simultaneously shifted (0.06Å and 0.13Å, respectively) toward the peak positions of the third and forth shells of the metallic Ni. This is a strong indication that there must be some reduced Ni species formed.¹⁶ Combining with the XPS results, we can infer that the in-situ formed metallic Ni by photoreduction of NiO is not stable, which can be readily oxidized back to NiO. The reduced Ni species deduced from the EXAFS analysis might be some stable metallic Ni species randomly distributed on NiO or surface of NaTaO₃.

Figure 9: (a) Ni K-edge spectra of Ni foil, NiO, NaTaO₃-NiO(imp) before photocatalytic water splitting reaction; NaTaO₃-NiO(imp) after photocatalytic water splitting reaction. (b) corresponding derivative spectra for the clarify of the Ni K-edge shift. (c) Ni K-edge K3 weighted EXAFS spectra and (d) Fourier Transformed spectra of Ni foil, NiO, NaTaO₃-NiO(imp) before photocatalytic water splitting reaction; NaTaO₃-NiO(imp) after photocatalytic water splitting reaction.

This infers that the actual cocatalyst during photocatalytic reaction is dual cocatalyst, Ni and NiO. At the initial stages of the photocatalytic water splitting reactions, the photogenerated electrons might reduce NiO in-situ to Ni at reduction sites instead of the reduction of proton to H_2 . Before reaching the balance, non-stoichiometric amounts of H_2 and O_2 was generated, as observed in Fig. S8 that the ratio of H_2 and O_2 was ca. 3.2 at a reaction time of 15 min. With the reaction proceeds, more NiO was reduced to metallic Ni, and finally reach the reaction balance to give H_2 and O_2 evolution ratio in 2:1. Diffuse reflectance spectrum of the NaTaO₃-NiO (imp)

with 0.2wt% NiO loading (Fig. S5) was similar to that of the naked NaTaO₃ before photocatalytic water splitting reaction because of the small amount of NiO loaded. After water splitting, the spectrum of NaTaO₃-NiO (imp) became similar to that of the NaTaO₃-Ni photocatalyst with 5wt% Ni loading by photoreduction. The additional absorption at ca. 400~800 nm was observed after reaction which is consistent with the color change from white to grey, indicating that the metallic nickel fine particles were formed in situ when NaTaO₃-NiO (imp) photocatalyst was photoirradiated. These in-situ photoreduced Ni species may play important role in photocatalytic water splitting reaction.

401 The Illustration of dual cocatalysts in overall water splitting reaction on the Ni/NiO 402 NaTaO₃ photocatalyst.

Based on the above experimental results, Scheme 1 describes the promotion of the photocatalytic
water splitting reaction by the formation of Ni and NiO dual cocatalysts on the cubic NaTaO₃
with equivalent facets.

In the assembly of the semiconductor photocatalyst system for overall water splitting, the energy level matching between light absorbing semiconductor photocatalyst and the cocatalysts is vitally important. As shown in Scheme 1a, the energy diagram shows that photogenerated electrons on NaTaO₃ could reduce NiO to metallic Ni, since the conduction band level of the NaTaO₃ photocatalyst is roughly estimated to be -1.06 eV, which is more negative than that of NiO (-0.96 eV).²² This is quite different compared with the behavior of the NiO on the surface of SrTiO₃, which showed no reduction of NiO to metallic Ni, because the lower conduction band level of SrTiO₃ is more positive than that of the NiO.^{17d, 18b} In case of NaTaO₃, in-situ photoreduced metallic Ni species may also involve in the photocatalytic water splitting reaction, and the balance between Ni and NiO as well as their location sites are crucial factors influencing

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the overall water splitting activity (Scheme 1b). Scheme 1c and 1d give the illustration of two possible processes for the evolvement of the Ni and NiO dual cocatalysts in the water splitting reaction and the overall water splitting on the dual cocatalysts. The early stage of the progresses in the Scheme1c and 1d are the same, photogenerated electrons on NaTaO₃ could reduce NiO to metallic Ni. The difference is that situation between NiO and in-situ formation of Ni dual cocatalyst in the following stage for overall water splitting, and Scheme 1c and 1d give two possible illustrations.

In the synthesis of NaTaO₃-NiO (hv) with low Ni content (e.g., 0.2 wt% NiO), the Ni precursor $Ni(NO_3)_3$ was photoreduced to metallic Ni by photogenerated electrons, and then oxidized to NiO at 270 °C. In such processes, the NiO should mainly reside at the reduction sites of NaTaO₃. Because it is at the reduction sites that such deposited NiO could be reduced to metallic Ni (highly efficient proton reduction cocatalyst) again by photoirradiation during the photocatalytic water splitting reactions, hence greatly enhance the hydrogen evolution activity to give non-stoichiometric ratio of H_2 and O_2 evolution during the photocatalytic water splitting reaction. As for the NaTaO₃-NiO (imp) with same low Ni content (e.g., 0.2 wt% NiO), though the synthesis procedure was same as that of the NaTaO₃-NiO(hv), but NiO cocatalyst may be located randomly on both reduction and oxidation sites of NaTaO₃. The deposition of NiO on NaTaO₃ by impregnation method is simply by physical adsorption thus no redox site selectively. Thus, photoirradiation of NaTaO₃-NiO (imp) during photocatalytic water splitting reaction may also reduce partial NiO on the reduction sites to metallic Ni while still maintaining large amount of NiO on the oxidation sites. Metallic Ni species produced at the reduction sites serves as efficient proton reduction cocatalyst and the NiO reserved at the oxidation sites serves as water oxidation cocatalyst. This may be the reason for that the NaTaO₃-NiO (imp) with 0.2 wt% NiO loading can

evolve stoichiometric amounts of H₂ and O₂. The similar photocatalytic water splitting activities of NaTaO₃-NiO (hv) and NaTaO₃-NiO (imp) with high Ni loading (2 wt% NiO) may also be easily understood. Because of high NiO loading, prolonged time is needed for the reduction of NiO to metallic Ni till reaching the balance between Ni and NiO. However, due to relatively high NiO loading in both cases, well balance between Ni and NiO could be reached which may ensure both H₂ and O₂ evolution effectively, leading to stoichiometric generation of H₂ and O₂. Meanwhile, we have performed additional O₂ and H₂ evolution experiments on bare NaTaO₃, NiO/NaTaO₃, and NiO only in the presence of sacrificial agents, and the results are summarized in Table S1. It can be seen that NiO itself showed negligible O₂ or H₂ evolution activities, but both O2 and H2 evolution reactions were promoted over NaTaO3-0.2 wt% NiO (imp) compared to those of the bare NaTaO3. It should be noted that ratio of the separate H2 and O2 evolution rates in the presence of sacrificial agents were increased approximately 4.7 and 2.7 times, respectively. Since both H₂ and O₂ evolution reactions can be promoted by NiO loading, and considering the synergetic effects of redox reactions (promotion of oxidation reaction by promoting the corresponding reduction reaction, vise versa), it is difficult to determine whether NiO is a proton reduction cocatalyst or water oxidation cocatalyst directly by separate oxygen evolution experiments. However, because water oxidation is the rate-determining step in overall water splitting reaction, and the enhancement of water oxidation activity by NiO cocatalyst loading was indeed observed by the separated water oxidation reaction experiment, we tentatively prefer that NiO on NaTaO₃ more likely serves as a water oxidation cocatalyst in overall water splitting in our work. Thus, it is believed that they must be at the vicinity of the NiO on the surface of NaTaO₃ since major part of the metallic Ni are originated from the reduction of NiO in-situ by photoirradiation.

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Scheme 1: Schematic description of overall water splitting over Ni/NiO dual cocatalyst loaded cubic NaTaO₃ with equivalent facets. (a) Energy diagram showing in-situ formation of Ni/NiO dual cocatalysts at the initial stage of the photocatalytic water splitting reaction. (b) Energy diagram showing the functional role of Ni and NiO in photocatalytic water splitting reactions. Metallic Ni serves as proton reduction site and NiO serves as the water oxidation site. (c, d) Illustration of two possible processes for the evolvement of the Ni and NiO dual cocatalysts in the water splitting reaction and the overall water splitting on the dual cocatalysts.

Dual cocatalysts play important roles in the achievement of overall photocatalytic water splitting activity. The concept of the dual cocatalysts is now well accepted and applied. ^{1a, 2b, 18b, 23} But the optimal distance of spatial separation of reduction and oxidation cocatalysts is still not clear. For example, Domen's group designed a core/shell structure photocatalysts with spatially separated reduction and oxidation sites to block the reverse reaction. The high photocatalytic water splitting activity was attributed to the core/shell structure and spatially separated reduction and oxidation cocatalysts assisting separation and collection of photogenerated electrons and holes at

 the respective cocatalysts.^{23a} The dual cocatalysts on the different facets of BiVO₄ were also rationally designed and prepared. The separation of reduction and oxidation sites and the synergetic effect of dual cocatalysts lead to significantly enhanced photocatalytic performances in water oxidation.⁶⁻⁷ However, recent experimental results also show that the closely intimate location of the reduction and the oxidation cocatalysts may also lead to efficient charge separation for promoting photocatalytic reactions. For example, the PdS/CdS photocatalyst was found to be more active than Pt/CdS for H₂ production in Na₂S–Na₂SO₃ aqueous solution. The TEM study clearly showed that Pd reduction cocatalyst and PdS oxidation cocatalyst were connected to each other at the atomic level.²⁴ In Pd-IrO₂/TiO₂ photocatalytic system, it was also found that the intimate contact between the Pd reduction cocatalyst and the IrO₂ oxidation cocatalyst can lead to the enhancement of photocatalytic activity of H₂ production.^{23b} Present work further demonstrated that efficient charge separation can also occur even on the same facets of the cubic NaTaO₃ semiconductor photocatalyst with the equivalent facets instead of spatial separation of reduction and oxidation cocatalysts on the different facets. Presence of the dual cocatalysts might be a prerequisite for promoting the redox reactions on the same surface.

493 CONCLUSIONS

Using cubic NaTaO₃ with six equivalent $\{001\}$ facets as a model semiconductor photocatalyst, no preferential deposition of noble metals (Pt and Ag) and metal oxides (MnO₂ and PbO₂) on a particular facet confirms that it could not be the facet charge separation that lead to photocatalytic overall water splitting. However, observation of efficient overall water splitting upon loading of well-known cocatalyst NiO clearly demonstrates that photogenerated electrons and holes could still be well-separated. Impregnation and photoreduction methods were used respectively for random (reduction and oxidation sites) and selective (reduction sites) deposition Page 27 of 32

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of various amounts of NiO cocatalyst on the surface of NaTaO₃, which suggest that the location of cocatalyst affects the charge separation. XPS and XAFS analyses of the samples before and after photocatalytic water splitting reactions revealed that reduced Ni species (metallic Ni) were formed in-situ by photoreduction of NiO during the photocatalytic water splitting reactions, demonstrating that the actual efficient water splitting cocatalysts are metallic Ni and NiO located on the same facets. The enhancement of the overall photocatalytic water splitting activity upon NiO loading on the NaTaO₃ with equivalent facets is due to the synergetic effect between NiO and metallic Ni, which are derived during the photocatalytic reaction. The metallic nickel serves as an electron trap for proton reduction and NiO serves as a hole trap for water oxidation. Presence of the dual cocatalyst Ni/NiO is a prerequisite for the promotion of the photocatalytic overall water splitting, specially for the semiconductors, like NaTaO₃ crystal with equivalent facets exposed. ASSOCIATED CONTENT The Supporting Information is available free of charge on the Internet at http://pubs.acs.org. AUTHOR INFORMATION **Corresponding Author** *(Can Li). Email: canli@dicp.ac.cn, Tel: 86-411-84379070; Fax: 86-411-84694447; Homepage: http:// www.canli.dicp.ac.cn *(Hongxian Han). Email: hxhan@dicp.ac.cn, Tel: 86-411-84379760

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