

Water reduction and oxidation on Pt–Ru/Y₂Ta₂O₅N₂ catalyst under visible light irradiation

Meiying Liu,^a Wansheng You,^a Zhibin Lei,^a Guohua Zhou,^a Jianjun Yang,^a Guopeng Wu,^a Guijun Ma,^a Guoyou Luan,^a Tuyoshi Takata,^b Michikazu Hara,^b Kazunari Domen^{a,b,c} and Can Li^{*a}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning, 116023, China. E-mail: canli@dicp.ac.cn

^b Chemical Resource Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan. E-mail: kdomen@res.titech.ac.jp

^c Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation (CREST, JST), 2-1-13 Higashiueno, Taito-ku, Tokyo 110-0015, Japan

Received (in Cambridge, UK) 27th May 2004, Accepted 13th July 2004

First published as an Advance Article on the web 19th August 2004

Y₂Ta₂O₅N₂ is presented as a novel photocatalyst with high activity for water splitting under visible-light irradiation in the presence of appropriate sacrificial reagents; the activity for reduction to H₂ is increased by the incorporation of Pt or Ru as a co-catalyst, with a significant increase in production efficiency when both Pt and Ru are present.

Photocatalytic splitting of water using solar energy is a challenging and interesting topic of research with the potential to provide clean and renewable H₂ as an energy resource. To date, many mixed-metal oxides such as K₂La₂Ti₃O₁₀,¹ NaTaO₃,² and LnTaO₄ (Ln = La, Pr, Ce, Nd, Sm)³ have been studied for water splitting as a means of producing both H₂ and O₂, as such oxides have excellent stability and high activity. However, these catalysts are only active under ultraviolet (UV) light, which accounts for only a small fraction (5%) of the solar spectrum at the earth's surface. Therefore, the development of visible-light responsive photocatalysts for overall water splitting is currently attracting much attention as a potentially efficient utilization of solar energy.^{4–6}

Considerable effort has been made to extend the absorption edge of semiconductors with wide bandgaps into the visible-light region.^{7,8} The incorporation of non-metal atoms (C, N, F, P and S) into metal-oxide lattices is one way to narrow the bandgap of the parent oxide because of their p states mixing with O 2p states.^{9–11} A number of non-oxide photocatalysts have recently been reported to be promising candidates for overall water splitting under visible-light irradiation.^{6,12,13} Oxynitrides such as TaON and LaTiO₂N have been shown to exhibit absorption in the visible region and stable photocatalytic activity for water reduction and oxidation using appropriate sacrificial reagents. However, the range of oxynitride photocatalysts synthesized to date remains limited. Although platinum is already generally considered to be the best metal promoter for H₂ production from water due to its low overpotential, it has been recently shown to exhibit remarkably enhanced efficiency for H₂ evolution under visible light when Ru was deposited on TaON.¹⁴ This increased efficiency has been attributed to improved contact between the TaON and Ru. However, the simultaneous use of Pt and Ru as promoters of photocatalytic water reduction has yet to be reported.

This communication reports Y₂Ta₂O₅N₂ as a novel visible light-driven photocatalyst with high activity for oxidation of water in the presence of a sacrificial electron acceptor (Ag⁺). This catalyst also reduces water to H₂ in the presence of a sacrificial electron donor (ethanol) and Pt or Ru as a co-catalyst, with a significant enhancement of H₂ production efficiency in the presence of both Pt and Ru.

YTaO₄ was synthesized by a solid-state reaction method. Y₂O₃ and Ta₂O₅ powder were mechanically mixed in stoichiometric quantities, and then calcined at 1073 K for 2 h and 1473 K for 10 h in air. Y₂Ta₂O₅N₂ was obtained by nitriding YTaO₄ powder under a flow of ammonia gas (flow rate: 40 ml min⁻¹) at 1123 K for 15 h in a quartz tube. The Y₂Ta₂O₅N₂ powder was yellowish-green in

color and had an X-ray diffraction pattern consistent with that of pyrochlore-type Ln₂Ta₂O₅N₂.¹⁵

Energy-dispersive X-ray (EDX) spectroscopy combined with combustion analysis and thermogravimetric oxidation of Y₂Ta₂O₅N₂ samples gave a powder composition of Y : Ta : O : N = 1 : 1 : 2.47 : 1.09 (atomic ratio), indicating that the as-synthesized Y₂Ta₂O₅N₂ particles were in fact non-stoichiometric and defective. The BET surface area of the Y₂Ta₂O₅N₂ powder was 0.42 m² g⁻¹, as determined from the N₂ adsorption–desorption isotherm. Scanning electron microscopy (SEM) revealed that primary particles of about 20–100 nm in diameter had aggregated into large secondary particles of 0.5–4 μm. The formation of such large particles and the low surface area of the Y₂Ta₂O₅N₂ powder are attributed to the lengthy high-temperature sintering adopted in the synthesis process.

The photocatalytic reaction was carried out in a closed gas circulation and evacuation system under a 300 W Xe lamp equipped with a cut-off filter (λ > 420 nm). Photocatalytic water reduction and oxidation were performed using an aqueous solution of 20% (v/v) ethanol and 0.01 M AgNO₃. Pt and Ru were photodeposited on the Y₂Ta₂O₅N₂ catalyst *in situ* from precursors of H₂PtCl₆·6H₂O and RuCl₃·3H₂O to evaluate the potential of these elements as H₂ evolution promoters. La₂O₃ (0.2 g) was added to maintain the pH of the solution at 8.5. H₂ and O₂ evolution was measured by on-line gas chromatography with thermal conductivity detector. UV-vis diffuse reflectance spectra were recorded using a Jasco V-550 spectrophotometer.

Figure 1 shows the UV-vis diffuse reflectance spectra of YTaO₄ and Y₂Ta₂O₅N₂. YTaO₄ exhibits strong absorption in the UV region with an absorption edge at about 330 nm, corresponding to a bandgap energy of 3.8 eV. The absorption band threshold of Y₂Ta₂O₅N₂ occurs at 560 nm, shifted about 230 nm from that of YTaO₄, and corresponds to an estimated bandgap energy of 2.2 eV. The smaller bandgap energy of Y₂Ta₂O₅N₂ is attributed to the partial replacement of O²⁻ by N³⁻ in the crystalline matrix of

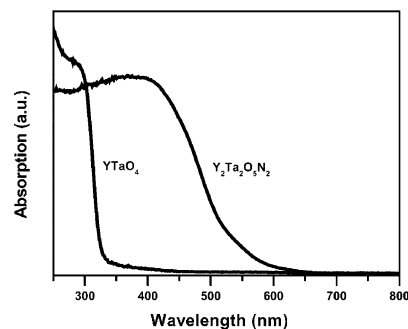


Fig. 1 UV-vis diffuse reflectance spectra of YTaO₄ and Y₂Ta₂O₅N₂.

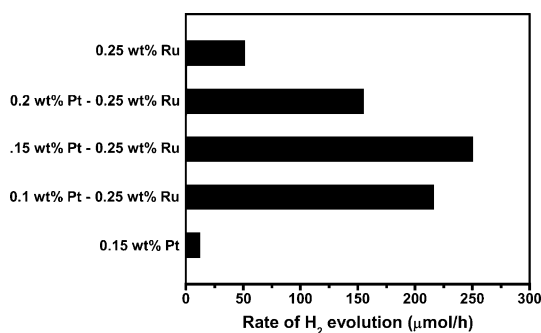


Fig. 2 Dependence of the rate of H₂ evolution from an aqueous ethanol solution on the atomic ratio of Pt to Ru on Y₂Ta₂O₅N₂ catalyst under visible-light irradiation. Catalyst, 0.3 g; ethanol solution (20% v/v), 200 ml; light source, 300 W Xe lamp ($\lambda > 420$ nm).

YTaO₄, where the energy level of the N2p orbital is higher than that of the O2p orbital, and the predominant population of the valence band of Y₂Ta₂O₅N₂ by a hybrid orbital between N2p and O2p.

Figure 2 correlates the rate of H₂ evolution over Y₂Ta₂O₅N₂ with the ratio of photodeposited Pt to Ru in the reaction solutions. In the initial stage of the reaction, H₂PtCl₆ and RuCl₃ were reduced to Pt and Ru, which serve as H₂-evolution promoters. It was confirmed by X-ray photoelectron spectroscopy (XPS) that H₂PtCl₆ and RuCl₃ in the solution were deposited as metallic Pt⁰ and Ru⁰ particles, with no oxidized noble metals present. The rate of H₂ evolution was examined after reaction for 1 h. Although Pt generally functions as an excellent promoter for photocatalytic water reduction to H₂, 0.15 wt% Pt/Y₂Ta₂O₅N₂ exhibited very low H₂-evolution activity (37 μmol h⁻¹ g⁻¹). In contrast, H₂ reduction was remarkably enhanced by the addition of 0.25 wt% Ru to Y₂Ta₂O₅N₂, reaching 170 μmol h⁻¹ g⁻¹. The activity of H₂ evolution was further increased by co-depositing both Pt and Ru on the Y₂Ta₂O₅N₂ catalyst, increasing with the amount of Pt to a maximum of 833 μmol h⁻¹ g⁻¹ over a catalyst of Y₂Ta₂O₅N₂ with 0.15 wt% Pt and 0.25 wt% Ru. This rate is 22 times greater than that for 0.15 wt% Pt/Y₂Ta₂O₅N₂. Deposition of more than 0.15 wt% Pt lowered the activity from this peak.

The remarkably high activity for photocatalytic water reduction (H₂ evolution) achieved by the presence of both Pt and Ru as noble metal co-catalysts is attributable to facile electron migration from the conduction band of Y₂Ta₂O₅N₂ to the Pt–Ru co-catalysts, thereby retarding the possibility of electrons recombining with holes in the valence band and improving the charge separation efficiency. This promoting effect is much greater when both Pt and Ru are present as co-catalysts compared to one or the other alone.

Figure 3 shows the results for photocatalytic O₂ evolution from 0.01 M AgNO₃ solution over Y₂Ta₂O₅N₂. No reaction took place in the absence of light. Upon irradiation, O₂ was produced at an initial rate of 140 μmol h⁻¹. With prolonged irradiation, the rate of O₂ evolution decreased, due to a decrease in the Ag⁺ concentration in solution and the deposition of reduced metallic Ag⁰ on the catalyst surface, shielding the catalyst from irradiation. During the first 10 h of reaction, Ag⁺ ions in the solution (2000 μmol) were almost entirely consumed to produce 470 μmol of O₂. Only a small amount of N₂ (< 2% of the evolved O₂) was detected in the early stage of the reaction (1–3 h), demonstrating that photodegradation of the catalyst is negligible in this reaction. No noticeable differences were observed in the X-ray diffraction patterns of the catalyst before and after reaction, except for the emergence of a diffraction

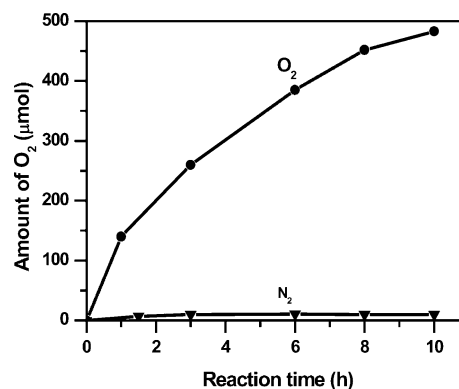


Fig. 3 O₂ production from an aqueous AgNO₃ solution over Y₂Ta₂O₅N₂ catalyst under visible-light irradiation. Catalyst, 0.3 g; La₂O₃, 0.2 g; 0.01 M AgNO₃ solution, 200 ml; light source, 300 W Xe lamp ($\lambda > 420$ nm).

peak attributable to the metallic Ag⁰ deposited on the Y₂Ta₂O₅N₂, further confirming that the photocatalyst is essentially stable.

In summary, Y₂Ta₂O₅N₂ catalyst synthesized by nitriding YTaO₄ under ammonia flow has a small optical bandgap energy of 2.2 eV and functions as an efficient photocatalyst for water oxidation to O₂ in the presence of a sacrificial electron acceptor (Ag⁺). This catalyst also exhibits activity for water reduction to H₂ in the presence of a sacrificial electron donor (ethanol) and Pt or Ru as a co-catalyst. This activity is significantly enhanced by the presence of both Pt and Ru.

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 90210036, 20273070), the National Key Basic Research and Development Program (Grant No. 2003CB214500), the Core Research for Evolutional Science and Technology (CREST) Program of the Japan Science and Technology Corporation (JST), and the Innovation Program of the Chinese Academy of Sciences (Grant No. DICP K 2002 F1). The authors also gratefully acknowledge the China Petroleum & Chemical Corporation (Grant No. X503019) for financial support.

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