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Water reduction and oxidation on Pt–Ru/$Y_2Ta_2O_5N_2$ 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*[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, Midoni-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*

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$Y_2Ta_2O_5N_2$ 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 H_2 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 H_2 as an energy resource. To date, many mixed-metal oxides such as $K_2La_2Ti_3O_{10}$,[1] $NaTaO_3$,[2] and $LnTaO_4$ (Ln = La, Pr, Ce, Nd, Sm)[3] have been studied for water splitting as a means of producing both H_2 and O_2, 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 $LaTiO_2N$ 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 H_2 production from water due to its low overpotential, it has been recently shown to exhibit remarkably enhanced efficiency for H_2 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 $Y_2Ta_2O_5N_2$ 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 H_2 in the presence of a sacrificial electron donor (ethanol) and Pt or Ru as a co-catalyst, with a significant enhancement of H_2 production efficiency in the presence of both Pt and Ru.

$YTaO_4$ was synthesized by a solid-state reaction method. Y_2O_3 and Ta_2O_5 powder were mechanically mixed in stoichiometric quantities, and then calcined at 1073 K for 2 h and 1473 K for 10 h in air. $Y_2Ta_2O_5N_2$ was obtained by nitriding $YTaO_4$ powder under a flow of ammonia gas (flow rate: 40 ml min^{-1}) at 1123 K for 15 h in a quartz tube. The $Y_2Ta_2O_5N_2$ powder was yellowish-green in color and had an X-ray diffraction pattern consistent with that of pyrochlore-type $Ln_2Ta_2O_5N_2$.[15]

Energy-dispersive X-ray (EDX) spectroscopy combined with combustion analysis and thermogravimetric oxidation of $Y_2Ta_2O_5N_2$ samples gave a powder composition of Y : Ta : O : N = 1 : 1 : 2.47 : 1.09 (atomic ratio), indicating that the as-synthesized $Y_2Ta_2O_5N_2$ particles were in fact non-stoichiometric and defective. The BET surface area of the $Y_2Ta_2O_5N_2$ powder was 0.42 $m^2\ g^{-1}$, as determined from the N_2 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 $Y_2Ta_2O_5N_2$ 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 ($\lambda > 420$ nm). Photocatalytic water reduction and oxidation were performed using an aqueous solution of 20% (v/v) ethanol and 0.01 M $AgNO_3$. Pt and Ru were photodeposited on the $Y_2Ta_2O_5N_2$ catalyst *in situ* from precursors of $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3 \cdot 3H_2O$ to evaluate the potential of these elements as H_2 evolution promoters. La_2O_3 (0.2 g) was added to maintain the pH of the solution at 8.5. H_2 and O_2 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 $YTaO_4$ and $Y_2Ta_2O_5N_2$. $YTaO_4$ 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 $Y_2Ta_2O_5N_2$ occurs at 560 nm, shifted about 230 nm from that of $YTaO_4$, and corresponds to an estimated bandgap energy of 2.2 eV. The smaller bandgap energy of $Y_2Ta_2O_5N_2$ is attributed to the partial replacement of O^{2-} by N^{3-} in the crystalline matrix of

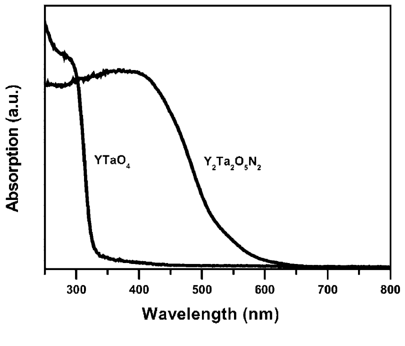

Fig. 1 UV-vis diffuse reflectance spectra of $YTaO_4$ and $Y_2Ta_2O_5N_2$.

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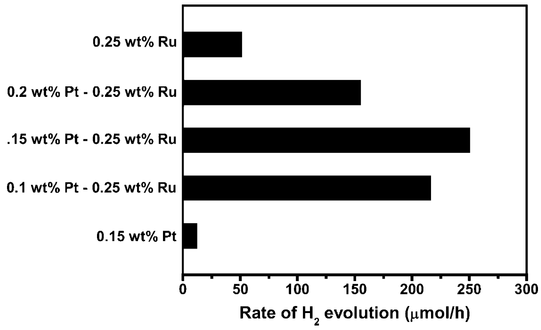

Fig. 2 Dependence of the rate of H_2 evolution from an aqueous ethanol solution on the atomic ratio of Pt to Ru on $Y_2Ta_2O_5N_2$ catalyst under visible-light irradiation. Catalyst, 0.3 g; ethanol solution (20% v/v), 200 ml; light source, 300 W Xe lamp (λ > 420 nm).

$YTaO_4$, 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 $Y_2Ta_2O_5N_2$ by a hybrid orbital between N2p and O2p.

Figure 2 correlates the rate of H_2 evolution over $Y_2Ta_2O_5N_2$ with the ratio of photodeposited Pt to Ru in the reaction solutions. In the initial stage of the reaction, H_2PtCl_6 and $RuCl_3$ were reduced to Pt and Ru, which serve as H_2-evolution promoters. It was confirmed by X-ray photoelectron spectroscopy (XPS) that H_2PtCl_6 and $RuCl_3$ in the solution were deposited as metallic Pt^0 and Ru^0 particles, with no oxidized noble metals present. The rate of H_2 evolution was examined after reaction for 1 h. Although Pt generally functions as an excellent promoter for photocatalytic water reduction to H_2, 0.15 wt% Pt/$Y_2Ta_2O_5N_2$ exhibited very low H_2-evolution activity (37 μmol h^{-1} g^{-1}). In contrast, H_2 reduction was remarkably enhanced by the addition of 0.25 wt% Ru to $Y_2Ta_2O_5N_2$, reaching 170 μmol h^{-1} g^{-1}. The activity of H_2 evolution was further increased by co-depositing both Pt and Ru on the $Y_2Ta_2O_5N_2$ catalyst, increasing with the amount of Pt to a maximum of 833 μmol h^{-1} g^{-1} over a catalyst of $Y_2Ta_2O_5N_2$ with 0.15 wt% Pt and 0.25 wt% Ru. This rate is 22 times greater than that for 0.15 wt% Pt/$Y_2Ta_2O_5N_2$. Deposition of more than 0.15 wt% Pt lowered the activity from this peak.

The remarkably high activity for photocatalytic water reduction (H_2 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 $Y_2Ta_2O_5N_2$ 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 O_2 evolution from 0.01 M $AgNO_3$ solution over $Y_2Ta_2O_5N_2$. No reaction took place in the absence of light. Upon irradiation, O_2 was produced at an initial rate of 140 μmol h^{-1}. With prolonged irradiation, the rate of O_2 evolution decreased, due to a decrease in the Ag^+ concentration in solution and the deposition of reduced metallic Ag^0 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 O_2. Only a small amount of N_2 ($<$ 2% of the evolved O_2) 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 peak attributable to the metallic Ag^0 deposited on the $Y_2Ta_2O_5N_2$, further confirming that the photocatalyst is essentially stable.

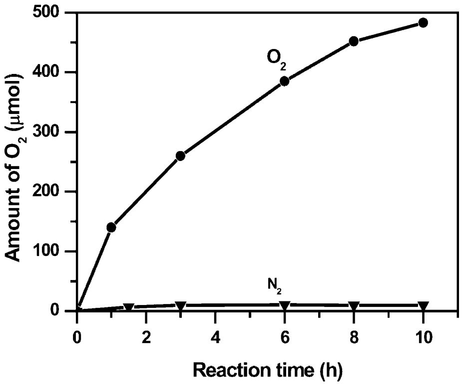

Fig. 3 O_2 production from an aqueous $AgNO_3$ solution over $Y_2Ta_2O_5N_2$ catalyst under visible-light irradiation. Catalyst, 0.3 g; La_2O_3, 0.2 g; 0.01 M $AgNO_3$ solution, 200 ml; light source, 300 W Xe lamp (λ > 420 nm).

In summary, $Y_2Ta_2O_5N_2$ catalyst synthesized by nitriding $YTaO_4$ under ammonia flow has a small optical bandgap energy of 2.2 eV and functions as an efficient photocatalyst for water oxidation to O_2 in the presence of a sacrificial electron acceptor (Ag^+). This catalyst also exhibits activity for water reduction to H_2 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.

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