Efficient Photocatalytic Hydrogen Generation by Pd Modified La-NaTaO$_3$ Nanoparticle

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Abstract. The advantage of palladium modified La-doped NaTaO$_3$ (Pd/La-NaTaO$_3$) semiconductor photocatalyst for enhanced hydrogen generation under irradiation at the ultraviolet range has been investigated. The La-NaTaO$_3$ has been synthesized by sol-gel technique. The palladiums are loaded by impregnation of aqueous palladium nitrate solution. The palladiums supported of NaTaO$_3$ composites are characterized by transmission electron microscopy (TEM), high-resolution HRTEM (HRTEM), and X-ray absorption spectroscopy (XAS). The HRTEM images indicate that Pd nanoparticles (NPs) are deposited on the surface of La-NaTaO$_3$. Most of the Pd deposits have diameters ranging from 3 to 4 nm. XAS spectra shows that the Pd-La-NaTaO$_3$ absorbance profiles of the pristine and used samples are overlaped with the Pd foil, indicating that oxidation of the fresh and used cocatalyst was identical in nature with that of the palladium foil. Hydrogen production from pure water irradiation with ultra violet (UV) light source is 1.1 mmol g$^{-1}$h$^{-1}$ on La-NaTaO$_3$ photocatalysts. The activity of the La-NaTaO$_3$ up to 8.9 mmol g$^{-1}$h$^{-1}$ H$_2$ from an aqueous methanol solution are obtained. The hydrogen evolution on the La-NaTaO$_3$ sample can be further increase of 36.49 mmol g$^{-1}$h$^{-1}$ or 4.1 times higher by depositing nanosized Pd as a cocatalyst on the surface photocatalyst. The highest hydrogen generation is observed at 0.15 wt% Pd loading. The higher activity of the Pd/tantalates from aqueous methanol solution is attributed to an important suppressing in the electron–hole pairs recombination due to the effect produced by the presence of La in the NaTaO$_3$ structure as well as by the role of methanol acts as hole-trap and Pd like electron-trap.

Keywords: Palladium, cocatalyst, nanoparticles, La-NaTaO$_3$, photocatalyst, hydrogen.

Introduction

Hydrogen is considered as an ideal fuel for the future. Hydrogen fuel can be produced from clean and renewable energy sources and, thus, its life cycle is clean and renewable. Solar and wind are the two major sources of renewable energy and they are also the promising sources for renewable hydrogen production. However, presently, renewable energy contributes only about 5% of the commercial hydrogen production primarily via water electrolysis, while other 95% hydrogen is mainly derived from fossil fuels (Balat and Kirtay, 2010). Renewable hydrogen production is not popular yet because the cost is still high. Photovoltaic water electrolysis may become more competitive as the cost continues to decrease with the technology advancement. Photocatalytic water-splitting using NaTaO$_3$ for hydrogen production offers a promising way for clean and environmentally friendly production of hydrogen by solar energy.

The photocatalytic efficiency of photocatalyst is limited due to the recombination rate of photo-generated electron-hole pairs. To resolve this issue and enhance the photocatalytic activity, methods like deposition of transition metals and their oxide particles, metal doping, and chemical modification have been proposed (Kato et al., 2003; Huang et al., 2008; Husin et al., 2011a; Husin et al., 2011b). Noble metals and some transition-metal oxides are able to be used as cocatalysts for H$_2$ evolution from aqueous solutions containing electron donor species (Sathish et al., 2006; Chen et al., 2010; Ma et al., 2010). As the number of electrons on the noble metal particles increases, the Fermi level shifts toward NaTaO$_3$ conduction band generating more energy levels for electron transfer. The Fermi level of the photocatalyst-noble metal composite should be more negative than the H$_2$ evolution level the H$^+/H_2$ (Subramanian et al., 2003) to enable...
effective transfer of the accumulated electrons to the protons adsorbed on the noble metal-
photocatalyst interfaces and noble metal surfaces. Noble metals have found to be effective
and they act as catalyst for the hydrogen evolution, by reducing the activation energy of
water reduction (Baba et al., 1985).

Various techniques such as evaporation, irradiation, thermal decomposition, chemical
reduction, and impregnation have been adopted for cocatalyst loading (Jakob et al., 2003).
The impregnation method is excellent for depositing small loading amounts (Husin, 2012).
This technique is arguably the greenest, simplest, and most direct method of deposition.
In the present study, crystalline La-NaTaO₃ were fabricated by hydrogen peroxide-water
based solvent system by a facile sol–gel technique and loaded with Pd(NO₃)₂.6H₂O via
impregnation methods. The samples were then characterized using TEM and XAS
apparatus. The H₂ generation rates from Pd/ La-NaTaO₃ suspension in methanol-water
mixture upon ultra violet (UV) light irradiation were investigated.

Materials and Methods

Materials

Analytical grade TaCl₃ (Acros Organics; 99.9%), NaOH (Acros Organics; 99.9%),
La(NO₃)₃·2H₂O (Acros Organics; 99.9%), Citric acid anhydrous (C₆H₆O₇, 99.5%): Acros
Organics, Ammonia solution (NH₃, 35%): Fisher Scientific, Palladium nitrate hydrate
(Pd(NO₃)₂.6H₂O, 99.0%): UR Biotech, Hydrogen peroxide (H₂O₂, 35%): Showa Chemical
Co. Ltd, Methanol (CH₃OH, 99.5%) solution: Acros Organics, Hydrogen gas (H₂ 20%, Ar
80%), Argon gas (Ar 99.99%), were used without further purification. All solutions were
prepared using high purity DI water.

Catalyst preparation

The La-NaTaO₃ samples were synthesized by a sol-gel procedure using a hydrogen
peroxide-water based solvent system. The synthesis procedure used was analogous to a
previously reported protocol (Husin et al., 2011a; Husin et al., 2011c). Palladium co-
catalyst was loaded on the photocatalyst powder to promote H₂ production. The
photocatalyst powder was immersed into an aqueous solution containing the required
amount of Pd(NO₃)₂.6H₂O (e.g. 0.15 wt% as a Pd) by the impregnation method. The Pd-
loaded photocatalysts were firstly calcined at 300 °C for 1 h under air flow and reduced in
H₂ atmosphere at 250 °C for 2 h to obtain Pd metal.

Catalyst characterization

To investigate the morphology of the structure, transmission electron microscope
(TEM) and high-resolution HRTEM images of the final nanosized NaTaO₃ were recorded by a
Philips/FEI Tecnai 20G2 S-Twin TEM apparatus. For TEM analysis, the Pd/La-NaTaO₃ was
suspended ultrasonically in an ethanol solution and the samples were applied to a carbon-
coated copper grid, after which the solvent was evaporated in an oven at 80 °C. X-ray
absorption spectra (XAS) were recorded at beam line 17C, National Synchrotron Radiation
Research Center (NSRRC), Hsinchu, Taiwan. The electron storage ring was operated at 1.5
GeV with a current of 300 mA. A Si (111) double-crystal monochromator was employed for
energy selection with a resolution ΔE/E better than 2×10⁻⁴ at the Pd K-edge. After
photocatalytic reaction, the samples were removed from the solution by rotating
evaporator. Then the sample powders were collected in an Ar-purged glove box to prevent
oxidation in air.

Photocatalytic reaction

Photocatalytic reactions were carried out in an inner irradiation cell under UV
irradiation for H₂ evolution. The photocatalyst powder (0.5 g) was dispersed in a solution (1
L of aqueous solution, 10% v/v of methanol and pure water) using a magnetic stirrer. The
irradiation source was a 400 W high-pressure Hg lamp (λ ≥ 250 nm). Prior to irradiation,
the air inside the reactor was purged by Ar gas. To investigate the photocatalytic stability
for hydrogen production from an aqueous methanol solution, the Pd-loaded La-NaTaO₃, with 0.15 wt% of Pd was used in 6 h reaction. The amount of H₂ produced was measured by YANGI-LiN gas chromatograph (column porapax N and Molecular sieve 5A, PDHID detector, with Helium carrier).

Results and Discussion
Photocatalyst characterizations

TEM images of La-NaTaO₃ and Pd/La-NaTaO₃ are shown in Figure 1. As shown in Figure 1a, the La-NaTaO₃ samples have a cubic morphology, with particle sizes of approximately 75 nm, indicating that La-doping can effectively inhibit the agglomeration of the La-NaTaO₃ nanoparticles. Interestingly, the sample shows more regular particles with smooth crystal surfaces, indicating the higher crystallinity were observed. The high crystallinity and fineness of semiconductor particles might be efficient in suppressing the recombination, resulting in increasing conversion efficiency.

Figure 1b depicts the particle size distribution of the as-prepared Pd nanoparticles. This was derived by measuring the dimensions of visible palladium particles in a large number of TEM micrographs. It should be pointed out that Pd particle size distribution data were measured using several TEM images. In TEM image for Pd/La-NaTaO₃ sample, a Pd layers coating is anchored on the surface of La-NaTaO₃ particles. All spherical Pd metal nanoparticles were produced with narrow size ranges and high dispersion. We note that about >50% of Pd particles were in the size range of approximately 3-4 nm.

Figure 2 show the HRTEM images of the palladium-loaded La-NaTaO₃ with Pd nanoparticles (NPs). From the micrograph indicates that Pd NPs clearly deposit on the surface of La-NaTaO₃ photocatalyst. From HRTEM observation revealed that Pd metal with an average particle size about 3-4 nm could be successfully produced and deposited on the surface of La-NaTaO₃. Figure 3 shows Pd K-edge X-ray absorption near-edge structure (XANES) spectra for Pd-loaded La-NaTaO₃. Although the activity of Pd (0.15 wt %)/La-NaTaO₃, for the photocatalytic decomposition of H₂O was higher than that for Pd (3 wt %)/LaNaTaO₃, the latter sample was used for the measurements of XANES because of the low sensitivities of these spectroscopic techniques. After 6 h photocatalytic reaction, the samples were removed from the solution by rotary evaporator. The absorbance of Pd/La-NaTaO₃ as-prepared sample (Figure 3A.a) was overlapped with the Pd-foil (Figure 3A.c), indicating the oxidation of the fresh cocatalyst was identical with the Pd foil. There was no evident change even after the photocatalytic reaction (Figure 3A.b).
Figure 2. HRTEM micrograph of Pd deposited on La-NaTaO$_3$ photocatalyst

![HRTEM micrograph of Pd deposited on La-NaTaO$_3$ photocatalyst](image1)

Figure 3. (A) Pd K-edge X-ray absorption near-edge structure (XANES) spectra of Pd/La-NaTaO$_3$ dan (B) Magnification: a) Pd (fresh) and b) Pd (used); c) Pd foil and d) PdO as references.

![Pd K-edge X-ray absorption near-edge structure (XANES) spectra of Pd/La-NaTaO$_3$ and Magnification spectra](image2)

**Photocatalytic H$_2$ production activity**

Figure 4 depicts the effect of Pd loaded La-NaTaO$_3$ on the extent of rate of H$_2$ evolution from pure water and an aqueous methanol solution. It is note that the photocatalytic activity of pure La-NaTaO$_3$ for hydrogen evolution from pure water was as low as 1.1 mmol g$^{-1}$h$^{-1}$. When 10 vol.% of methanol was added as sacrificial reagent in the reaction solution, the H$_2$ evolution rate increased to 8.9 mmol g$^{-1}$h$^{-1}$. The enhanced evolution of H$_2$ from aqueous methanol solution was attributed to the effective charge separation as well as the improved light absorption property. Interestingly, when the La-NaTaO$_3$ was loaded with 0.15 wt.% Pd (Figure 4.a), the hydrogen evolution rate increased dramatically (36.49 mmol g$^{-1}$h$^{-1}$). This result indicates that by adding even small amounts of Pd, the activity of La-NaTaO$_3$ from an aqueous methanol solution increases significantly. It is believed that the cocatalysts provide reaction sites and decrease the activation energy for gas evolution. As the Fermi levels of Pd noble metals are lower than that of La-NaTaO$_3$, photo-excited electrons can be transferred from CB to metal particles deposited on the surface of La-NaTaO$_3$, while photo-generated VB holes remain on the La-NaTaO$_3$. These
activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions (Ni et al., 2007; Priya et al., 2009). The stability of the Pd/La-NaTaO$_3$ photocatalyst during 6 h is quite stable for H$_2$ evolution, as shows in Figure 4.b.

![Figure 4.](image)

**Figure 4.** Hydrogen evolution on La-NaTaO$_3$ (A) from pure water, (B) from an aqueous methanol solution 10% vol of methanol, (C) with Pd cocatalyst deposited Pd 0.15 wt%. (a) Average H$_2$ evolution and (b) Hydrogen evolution as a function of time (1.0 L reaction solution; catalyst 0.5 g) under UV-light, 400W Hg lamp.

Furthermore, the La-NaTaO$_3$ loaded with Pd metal as cocatalyst showed negligible activity for H$_2$ production from pure water (Husin, 2012). This phenomenon can be explained by the fact that H$_2$ and O$_2$ react immediately to form H$_2$O, on the surface of the Pd, before they are removed from the suspension to the gas phase. Noble metals such as Pd and Pt are excellent promoters for H$_2$ evolution but can also catalyse a backward reaction, forming water from H$_2$ and O$_2$, limiting their usefulness as cocatalysts for photocatalytic overall water splitting.

**Conclusions**

Pd nanoparticle has been successfully synthesized by impregnating of Pd nitrate solution on to La-NaTaO$_3$ crystalline. Pd/La-NaTaO$_3$ possessed enhanced light absorption ability and a lower recombination rate of photogenerated electrons-holes pairs, thus exhibited higher photocatalytic activity toward the hydrogen evolution from aqueous methanol solution. The highest photocatalytic activity was observed at 0.15 wt% of Pd loading. The photocatalysts are promising candidates for photocatalysis hydrogen production.

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References


