Catalysis Communications 57 (2014) 115–118

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Influence of loading Pt, RhO_2 co-catalysts on photocatalytic overall water splitting over $H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta_2O_7$

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ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form 17 June 2014
Accepted 1 August 2014
Available online 10 August 2014

Keywords:
Photocatalyst
In situ photodeposition
Overall water splitting
Oxygen active site

ABSTRACT

Pt and Rh (oxides) were loaded on protonated layered pervoskite $H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta_2O_7$ by an in situ photodeposition method. It was found that, compared to Pt loading, the Rh loading facilitated the O_2 evolution and the ratio of H_2/O_2 was close to stoichiometric ratio (≈ 2). The HRTEM and XPS analysis indicated that the Rh species loaded on HKLBT were Rh^0 and RhO_2. The RhO_2 loaded on HKLBT could provide the active sites for O_2 evolution by means of reducing the overpotential of O_2 evolution.

1. Introduction

Photocatalytic water splitting has attracted much attention in the past decades for producing clean and renewable hydrogen energy [1–3]. To date, many photocatalytic materials such as NiO/Ta_2O_5 [4], Rutile–TiO_2 [5], NGO-QDs [6] have been reported to be active for overall water splitting. Currently, the water oxidation process is considered to be a key bottleneck in photocatalytic reactions [7]. The difficulty of water oxidation is due to the high overpotential of O_2 evolution, which originates from charge trapping by surface states and slow oxygen evolution kinetics [8–10]. This is also an explanation why some photocatalytic reactions in pure water only produce H_2 without O_2 (or $H_2/O_2 > 2$). Therefore, providing the active sites for O_2 evolution by reducing the overpotential is a key task for overall water splitting. It has been reported that co-catalysts such as NiO [11], RuO_2 [12], Mn_2O_3 [13] loaded on photocatalysts play a very important role on achieving overall water splitting by means of offering the active sites or inhibiting the occurrence of backward reaction. However, almost all loadings of metal oxides on photocatalytic materials need heat-treatment, which is harmful to some materials with less heat-resistance, such as protonated layered materials [14], metal (oxy)sulfide [15] and metal (oxy)nitride [16], etc. Recently, Kudo et al. [17] loaded PbO_2 from Pb^{2+} by a photodeposition method without heat-treatment, indicating that oxides could be loaded by oxidation of photogenerated holes, which will provide us with a feasible non-destructive way to load metal oxides on photocatalytic materials.

In our previous study, we found that, although protonated layered perovskite $H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta_2O_7$ showed high activity for overall water splitting, the ratio of H_2/O_2 was not stoichiometric [18,19]. In addition, $H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta_2O_7$ (HKLBT) possesses weak heat endurance and the heat-treatment would result in the collapse of layer structure. Herein, we report Rh oxide loaded on HKLBT by in situ photodeposition to function as active sites for oxygen evolution and enhance photocatalytic activity of water splitting. The chemical states of Pt and Rh loaded on HKLBT were investigated. The effects of co-catalysts on water splitting, especially on oxygen evolution, were also discussed.

2. Experimental

2.1. Preparation of materials

The protonated layered perovskite oxides $H_{1.9}K_{0.3}La_{0.5}Bi_{0.1}Ta_2O_7$ were prepared according to the method presented in our previous papers [18]. The detail processes are as follows:

(1) The layered compound $K_{0.5}La_{0.5}Bi_2Ta_2O_9$ was prepared by the polymerized complex method as follows. 60 ml methanol was used as a solvent to dissolve 0.006 mol of $TaCl_5$. A large excess of citric acid (CA, 0.09 mol) was added into the methanol solution with continuous stirring. After achieving complete dissolution, 0.006 mol $Bi(NO_3)_3 \cdot 5H_2O$, 0.0015 mol $La(NO_3)_3 \cdot nH_2O$, and 0.00825 mol K_2CO_3 were added to the solution. The mixture was then magnetically stirred for 1 h to afford a transparent solution and 0.36 mol of ethylene glycol (EG) was added to this solution. Then, the solution was heated at 130 °C to promote

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http://dx.doi.org/10.1016/j.catcom.2014.08.007
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esterification between EG and CA, yielding brown resin. The resin was then calcined at 350 °C for 1 h to form black solid mass. The resulting black powder was calcined on an Al_2O_3 plate at 650 °C for 2 h in air, and then calcined at 900 °C for 6 h to obtain $K_{0.5}La_{0.5}Bi_2Ta_2O_9$ (denoted as KLBT).

(2) Proton exchange reaction: KLBT (0.8 g) was performed in 250 ml of 3 M HCl solution for 72 h at room temperature with replacement of the acid every 24 h, and then the product was washed with deionized water and dried at 60 °C for 3 h to remove the water on the surface of photocatalyst to obtain HKLBT.

2.2. Characterizations

The UV–vis diffuse reflection spectra (DRS) were determined by a UV–vis spectrophotometer UV-2450 (Shimadzu, Japan) and were converted to absorbance by the Kulbelka–Munk method. The high resolution transmission electron microscopy (HR-TEM) measurements were conducted using a JEM-2100F (Japan). The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu-Kratos, Axis Ultra ^{DLD}, Japan). All the binding energy (BE) values were calibrated by using the standard BE value of contaminant carbon (C1s = 284.6 eV) as a reference.

2.3. In situ photodeposition and photocatalytic reaction

The in situ photodeposition and photocatalytic reactions were carried out in a 350 ml top irradiation reaction Quartz cell at room temperature and a 250 W high-press Hg lamp was used as the light source. The catalyst powder (50 mg) was suspended in 60 ml aqueous solution containing a certain amount of $(NH_3)_4PtCl_2$ and $Rh(NO_3)_3$ solution by magnetic stirring. The reaction cell was deaerated by a vacuum pump before reactions. At initial stage (about 2 h), Pt or Rh species were gradually deposited and loaded on the surface of HKLBT (denote as Pt/HKLBT, Rh/HKLBT). After 2 h, generated gases were analyzed by an on-line GC with a TCD detector (Huaai, GC9160, China, MS-5A, argon as carrier gas).

3. Results and discussion

3.1. UV–vis DRS

The UV–vis diffuse reflection spectra (DRS) of naked HKLBT and Pt (Rh)/HKLBT photocatalysts are shown in Fig. 1. The absorption edges of HKLBT are near 320 nm, which should be attributed to the electron transition from valence band to conduction band in HKLBT, namely from O 2p to Ta 5d, and have no notable change even after Pt or Rh loading. However, after in situ photodeposition, the spectra longer than 320 nm exhibit new weak absorptions, which should be ascribed to the absorption of Pt or Rh (oxides) on the surface of HKLBT. The result indicates that the co-catalysts are loaded on photocatalyst successfully.

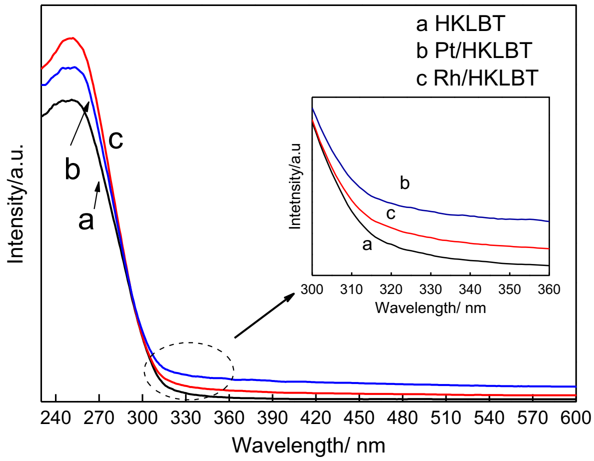

Fig. 1. UV–vis diffuse reflectance spectra of naked HKLBT, Pt/HKLBT and Rh/HKLBT.

3.2. TEM and XPS analysis

The representative HR-TEM images of Rh/HKLBT and Pt/HKLBT are shown in Fig. 2. Fig. 2a shows that the size of the Rh on HKLBT is about 5–10 nm. The lattice fringes of Rh and HKLBT can be observed clearly, suggesting the well-defined crystal structure. The lattice fringes with *d* spacing of ca. 0.251 nm and 0.184 nm can be assigned to the (101) lattice plane of RhO_2 and (002) lattice plane of Rh metal (Rh^0) based on the data of JCPD 21-1315 and JCPD 05-0685, respectively. The result indicates that Rh particles photodeposited on HKLBT contain two different Rh species. As seen from Fig. 2b, the lattice fringe with d value of ca. 0.197 nm corresponds to the (200) lattice plane of metallic Pt (Pt^0) (JCPD 65-2868), suggesting that Pt^{2+} was photo-reduced to Pt metal by photogenerated electrons instead of being oxidized by holes.

The chemical states of Rh and Pt species on HKLBT photocatalysts were investigated by XPS. Fig. 3 shows the Rh 3d (a) and Pt 4f (b) binding energy spectra of Pt/HKLBT and Rh/HKLBT. As shown in Fig. 3a, the Rh $3d_{5/2}$ XPS spectrum displays broad peaks and has been fitted to two overlapped peaks at ca 307.2 eV and 309.2 eV. The low binding energy at 307.2 eV is attributed to the Rh^0 [20], and the high binding energy at 309.2 eV is ascribed to RhO_2 [21]. There are many reports that photocatalytic materials with layer structures have the ability to assemble electrons and hole at different sites. So it is probable that Rh cations adsorbed on HKLBT are reduced to Rh^0 and oxidized to RhO_2, respectively. The result is also in good agreement with the HR-TEM. The spectrum for the $Pt_{7/2}$ (Fig. 3b) exhibits two major peaks with binding energies of ca. 70.8 and 72.3 eV, which are assigned to Pt^0 and Pt^0 with adsorbed oxygen (Pt^0–O_{ads}) based on the previous report by Kim et al. [22].

3.3. Photocatalytic water splitting activities

Table 1 lists the rates of H_2 and O_2 on HKLBT loaded with different amounts of Pt-cocatalyst and Rh-cocatalyst by a photodeposition

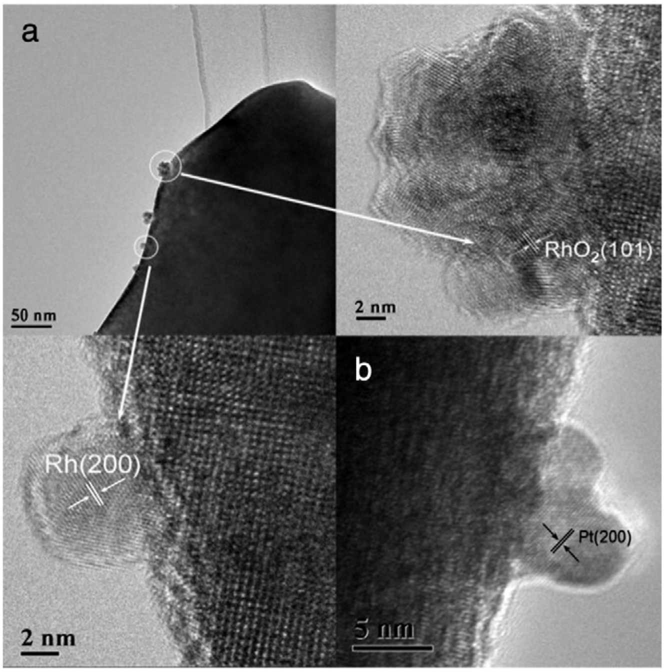

Fig. 2. HR-TEM images of Rh/HKLBT (a) and Pt/HKLBT (b).