Z-scheme overall water splitting on reduced graphene oxide modified Rh/$K_4Nb_6O_{17}$ nanosheets photocatalyst

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Abstract:

In this study, we develop a new Z-scheme photocatalysis system for overall water splitting which consists of reduced graphene oxide (RGO) modified Rh/$K_4Nb_6O_{17}$ nanosheets for H_2 evolution, Pt/WO_3 for O_2 evolution, and I^-/IO_3^- for an electron mediator under UV light irradiation. The H_2 evolution photocatalyst, Rh/$K_4Nb_6O_{17}$ nanosheets with a slit like framework, was prepared by exfoliation of and proton exchange reaction. Pt/WO_3 prepared via incipient-wetness impregnation method was used as O_2 evolution photocatalyst. The results show that RGO significantly influenced the photocatalytic activity. The combination of RGO and Rh/$K_4Nb_6O_{17}$ nanosheets with Pt/WO_3 achieves a high H_2 evolution rate (7039 μmol g^{-1} h^{-1}) and O_2 evolution rate (3289 μmol g^{-1} h^{-1}) at pH=12 in 6mM NaI solution.

Keywords: Rh/$K_4Nb_6O_{17}$ nanosheets, reduced graphene oxide, Z-scheme photocatalytic water splitting, hydrogen production

1. Introduction

Developing a photocatalyst system to generate hydrogen from water is a topic of great interest for fundamental and practical importance [1]. In this study, hydrogen production by a new Z-scheme photocatalysis water splitting system was examined over RGO modified Rh/$K_4Nb_6O_{17}$ nanosheets and Pt/WO_3 photocatalysts for H_2 evolution and O_2 evolution with I^-/IO_3^- electron mediator under UV light irradiation. The Rh/$K_4Nb_6O_{17}$ nanosheets photocatalysts were prepared by exfoliation of and proton exchange reaction, which lead to a slit like framework of $K_4Nb_6O_{17}$. Pt nanoparticles were deposited on WO_3 surface by incipient-wetness impregnation method to improve activity of photocatalytic O_2 evolution. Our results show that I^- concentration and pH of reaction solution significantly influenced the photocatalytic activity. The combination of 5wt% of RGO and Rh/$K_4Nb_6O_{17}$ nanosheets with Pt/WO_3 achieves a high H_2 evolution rate (7039 μmol g^{-1} h^{-1}) and O_2 evolution rate (3289 μmol g^{-1} h^{-1}) at pH=12 in 6mM NaI solution.

2. Experimental (or Theoretical)

The preparation of $K_4Nb_6O_{17}$ catalysts was accomplished by a two-step solid-state reaction method using K_2CO_3, and Nb_2O_5 with purities of 99.99%. The well-mixing K_2CO_3 and Nb_2O_5 (molar ratio 2.2: 3) were reacted in an aluminum crucible in air at 700°C for 2h then 1100°C for 5h. Proton-exchange $K_4Nb_6O_{17}$ (referred as $H_3KNb_6O_{17}$) was synthesized by suspending 1.5g $K_4Nb_6O_{17}$ in 150 cm^3 1M HCl solution for 3 days at room temperature, then washed and separated by centrifugation and dried at 60 °C overnight. The exfoliation of $H_3KNb_6O_{17}$ was carried out in an aqueous solution of tetrabutylammonium hydroxide (TBAOH). About 0.5g of $H_3KNb_6O_{17}$ and desired amount of $NaRhCl_6$ was suspended in 15ml of 6 wt% TBAOH aqueous solution at room temperature and stirred for 2 days. Subsequently, 100 ml of a 2M KOH was added to the solution and stirred for 1h. Then, the sample was washed several times with deionized water to remove residual TBA, separated by centrifugation and dried at 80 °C overnight. The final product, 1.5wt% Rh/$K_4Nb_6O_{17}$ nanosheets, was denoted as Rh-NSK.

Graphite oxide (GO) was prepared by graphite power (Showa) using modified Hummers' method [2]. About 0.5g graphite powder and 2.5g $NaNO_3$ was added to 115 ml 18M H_2SO_4 in an ice-bath. Then, 15g $KMnO_4$ was added to the solution under stirring. 230ml of deionized water was added to the mixture which was stirred at 35°C for 4h. After that, 360 ml of water was introduced to the suspension and stirred for 1 h. The reaction was terminated by adding 12ml H_2O_2 under stirring. Finally, the product was washed 3 times with 500ml deionized water. A GO suspension was achieved through a simple centrifugation.

The Pt/WO_3 was by loading 0.5wt% Pt on the photocatalyst powders using an aqueous H_2PtCl_6 solution. The WO_3 were used as purchased from Alfa Aesar. Following the impregnation, the samples were dried at 80

°C overnight. The Pt species would be reduced to metallic Pt nanoparticles during photocatalytic water splitting, therefor no further calcination was required.

The characterization methods included Powder X-ray diffraction (XRD, Cu-Kα radiation, λ= 1.54178Å), UV-vis (Varian Lary 5E diode array spectrometer), Scanning Electron Microscopy (SEM, Hitachi S-3500H) and transmission electron microscopy (TEM, JEOL JEM-2000FX Π microscope). The photocatalytic reaction was carried out in a reactor equipped with an inner irradiation quartz cell with a cooling water jacket. A 400 W medium pressure halide lamp (Phillips HPA400, λ_{max} = 360 nm, irradiation 150 mW/cm^2) was mounted inside the quartz cell. The photocatalytic H_2 evolution and O_2 evolution of water splitting was performed in 550 ml aqueous 6mM NaI solution containing about 0.2 g Rh-NSK, Pt/WO_3 and desired amount of RGO (0.002g – 0.02g) at 43 °C. The pH value of reaction solution was adjusted to pH= 12 by NaOH. The gas product was analyzed by a gas chromatography (China Gas Chromatography 9800) with a packed column (MS-5A, 3.5m in length) and thermal conductivity detector.

3. Results and discussion

The appurtenance diffraction peak at 2Θ= 14.8° in Fig. 1(a) and no diffraction peak at 2Θ= 26.5° was observed indicated that that GO was synthesized successfully. The XRD pattern showed in Fig. 1(c) and (d) indicated $K_4Nb_6O_{17}$ nanosheets with Rh nanoparticles and GO cocatalyst remained single phase $K_4Nb_6O_{17}$ (JCPDS 76-0977) crystal structure. No reflection peak corresponded Rh or GO appeared in XRD spectra of Rh-NSK or 1wt% GO/Rh-NSK samples, suggesting that the cocatalysts were well dispersed and difficult to be detected by XRD. Furthermore, the Rh-NSK or 1wt% GO/Rh-NSK samples the much broad diffraction peak (040) at about 2Θ= 10° than the bulk $K_4Nb_6O_{17}$ (Fig. 1(b)) indicated that the smaller crystalline size of $K_4Nb_6O_{17}$ nanosheets.

Fig. 2 shows the UV-vis spectra of the Rh-NSK and GO modified Rh-NSK samples. The Rh-NSK catalyst was orange color with a band gap about 3.54 eV estimating form UV-vis spectra (Fig. 2(a)). Fig. 2(b) showed the UV-vis spectra of GO which exhibited a brown color in water suspension and had a band gap about 4 eV, this result was well consisted with Yeh et al [3]. The band gap of GO modified Rh-NSK samples was similar to Rh-NSK with an increase absorption in long wavelength (Fig. 2(b) and (c)).

The TEM images of 5wt% GO/Rh-NSK photocatalysts shown in Fig. 3 revealed clearly that Rh nanoparticles (2~9 nm) were well dispersed on the $K_4Nb_6O_{17}$ nanosheets surface which was curved like a tube roll and well attached with a GO nanosheets with an larger size of 1-2 µm.

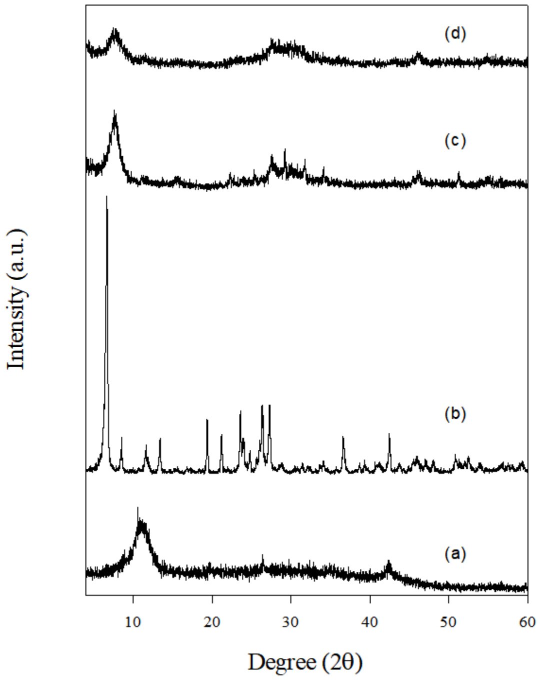

Fig.1 XRD specra of (a) GO (b) $K_4Nb_6O_{17}$ (c) Rh-NSK (d) 3 wt% GO/Rh-NSK

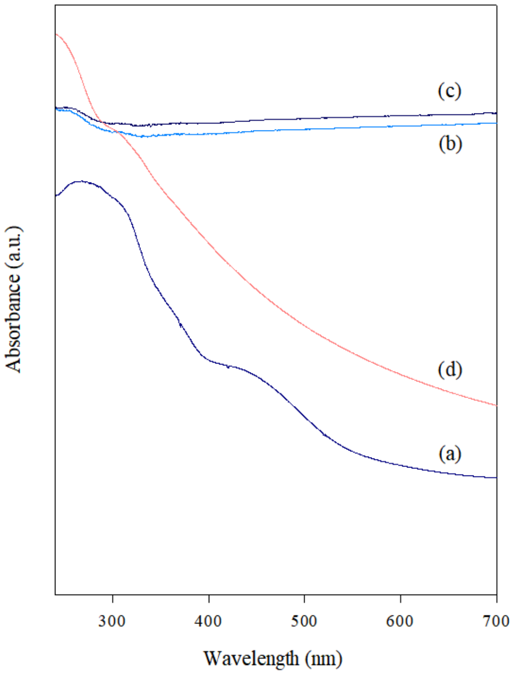

Fig.2 UV-vis specra of (a) Rh-NSK (b) 1 wt% GO/Rh-NSK (c) 3 wt% GO/Rh-NSK and (d) GO

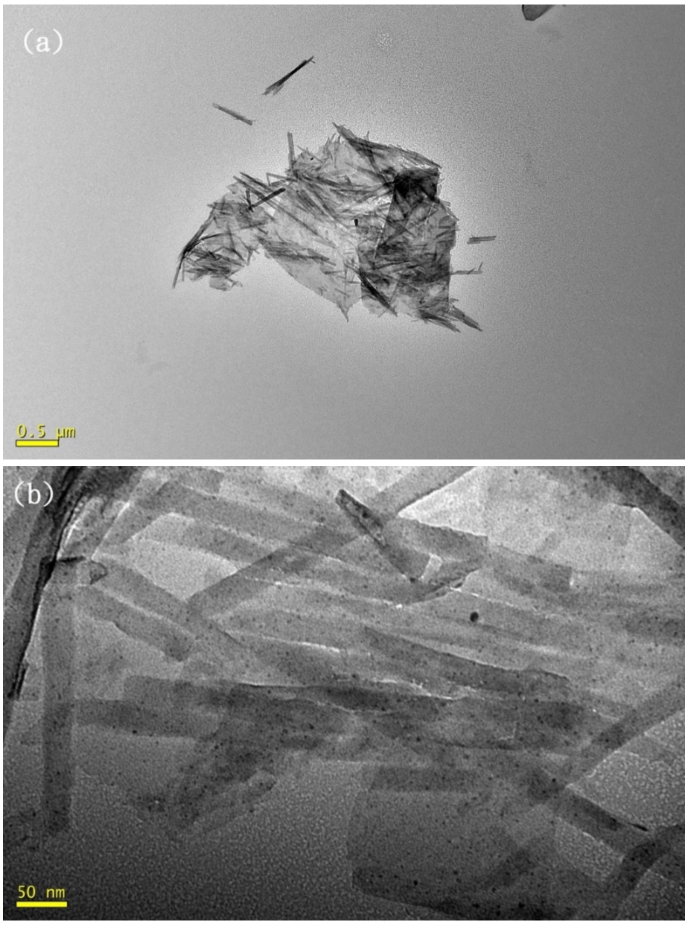

Fig.3 TEM images of (a) 5 wt% GO/Rh-NSK and (b) enlarged TEM image of 5 wt% GO/Rh-NS

Table 1. Photocatalytic H_2 evolution rates and on O_2 evolution rates GO/Rh-NSK and Pt/WO_3 photocatlysts

Catalyst	H_2 (μmole h^{-1} g^{-1})	O_2 (μmole h^{-1} g^{-1})
Rh-NSK	2929	997
Rh-NSK - Pt/WO_3	4240	1622
5 wt% GO/Rh-NSK	3500	1312
10 wt% GO/Rh-NSK	3926	1243
1 wt% GO/Rh-NSK - Pt/WO_3	3060	1571
3 wt% GO/Rh-NSK - Pt/WO_3	6098	2459
5 wt% GO/Rh-NSK - Pt/WO_3	7039	3289
10 wt% GO/Rh-NSK - Pt/WO_3	6867	4079

As shown in Table 1, the photocatalytic activity of GO/Rh-NSK-Pt/WO_3 was significantly influenced by the loading amount of GO. The results demonstrated that Rh-NSK photocatalyst could produce H_2 and O_2 at the same time, the reaction rate of O_2 evolution was limited to the valance band edge of Rh-NSK where the O_2 evolution rate was lower than H_2 evolution rate. The O_2 evolution rate was increase by introducing GO to Rh-NSK surface, however, the H_2 evolution rate was slightly decreased. This might attributed to the photo excited electron transferred from Rh-NSK to GO and O_2 evolution rate was increased by the enhanced charge separation.

On the other hand, the H_2 evolution rate was decreased by the competition reaction of $IO_3^- + e^- > I^-$ on GO surface. With combination of Pt/WO_3, the photocatalytic GO/Rh-NSK - Pt/WO_3 was significantly improved. The combination of 5wt% of RGO and Rh/$K_4Nb_6O_{17}$ nanosheets with Pt/WO_3 achieved a very high H_2 evolution rate (7039 μmol g^{-1} h^{-1}) and O_2 evolution rate (3289 μmol g^{-1} h^{-1}) at pH=12 in 6mM NaI solution which was very close to the stoichiometric ratio of water.

4. Conclusions

Our results show that the photocatalytic activity of GO/Rh-NSK-Pt/WO_3 was significantly influenced by the loading amount of GO. The combination of 5wt% of RGO and Rh/$K_4Nb_6O_{17}$ nanosheets with Pt/WO_3 exhibited a very high H_2 evolution rate (7039 μmol g^{-1} h^{-1}) and O_2 evolution rate (3289 μmol g^{-1} h^{-1}) at pH=12 in 6mM NaI solution.

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