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## Development photocatalyst reduce graphene oxide (RGO) composited with (Zn,Ni)(O,S) for photocatalytic hydrogen production

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**Abstract.** Hydrogen is being considered as the green and renewable fuels in the near future to replace the high global energy demands on fossil fuels. In this work, the photocatalyst reduce graphene oxide (RGO) composited (ZnNi)(O,S) with different amount of RGO has been developed for photocatalytic hydrogen production. X-ray did not show any characteristic peak of RGO due to a little amount in nanocomposite catalyst. However, elemental mapping clearly exhibited the presence of carbon as the element constituent of RGO. Based on the EIS result, RGO could decrease the charge transfer resistance to let the photogenerated electrons-holes easily migrate on the surface of catalyst for executing oxidation and reduction reactions. The optimum amount of RGO was 5 mg to provide the highest hydrogen production rate of 8100  $\mu\text{mol/gh}$ . The enhanced hydrogen production rate was investigated and explained in this paper.

### 1. Introduction

Development new alternative energies with green and sustainable resources are currently devoting by researcher, scientist and engineer to reduce the high global energy demands on fossil fuels. Hydrogen has become one of the important consideration since it has high efficiency and green energy carriers in the near future. However, most of hydrogen production method at this present time is unsustainable due to utilization of unrenewable such as methane and coal as hydrogen source[1]. Moreover, the final product by that method is not only hydrogen but also carbon dioxide or carbon monoxide as the side product. Hydrogen also can be produced from water by green technology so-called photocatalytic water splitting. However, its efficiency is quite low because of rapid electrons and holes recombination after photoexcitation process. Therefore, the great efforts have been conducted in improving the efficiency for hydrogen production[2].

In previous works, we have successfully developed the Zn(O,S) and (Zn,Ni)(O,S) for **hydrogen evolution** reaction from the mixture of water and ethanol[3, 4]. On the other side, reduce graphene oxide (RGO), as important 2D material, has excellent properties such as high surface area, conductive material and so on [5]. Several studies have reported the photocatalytic improvement after being composited with RGO. Take as an example, RGO/ Zn<sub>x</sub>Cd<sub>1-x</sub>S, its activity for hydrogen production improved about four times after adding 0.25 wt% RGO to Zn<sub>x</sub>Cd<sub>1-x</sub>S[6]. Another recent work by Zhao and co-workers have success synthesized RGO-wrapped Pt/TiO<sub>2</sub> for CO<sub>2</sub> reduction to CH<sub>4</sub>[7]. Its photocatalytic activity improved by 31 times compared to TiO<sub>2</sub> due to high electrons-holes separation



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efficiency. Therefore, based on above consideration, we investigate the effect of RGO contents on hydrogen production rate of RGO/(Zn,Ni)(O,S) nanocomposite.

## 2. Experimental section

The RGO/(Zn,Ni)(O,S) photocatalyst was prepared by a simple chemical precipitation method as follows. A certain amount of RGO (2.5, 5.0 and 10 mg) was dispersed in 100 mL DI water. Then, 5 mmol of zinc acetate, 0.5 nickel chloride and 2.5 mmol thioacetamide were dissolved into above solution under magnetic stirring for 30 min. After that, the solution was kept stirring and heating for another 4h. Finally, the obtained solid precipitation was dried at 80°C in a vacuum oven after washing process. The catalysts with 2.5, 5.0 and 10 mg-RGO composited with (Zn,Ni)(O,S) were assigned as RZ-2.5, RZ-5.0 and RZ-10, respectively.

The as-prepared catalyst was characterized by several instruments including X-ray diffractometer (D2-Phaser), field emission scanning electron microscope (JEOL 6500), electrochemical impedance spectra (Biologic 1000) and gas chromatography (GC-1000). To evaluate the hydrogen production, each catalyst was dispersed in 450 mL mixture solution of 10 vol% ethanol and 90 vol% water. Then, the solution was transferred into a reactor and connected to a gas-closed system consisting of GC, reactor and argon tank. The measurement was done every 30 min for 5h. The amount of hydrogen from the reaction was determined by GC that equipped with thermal conductivity detector (TCD) and Chroma software.

## 3. Results and discussion

### 3.1 X-ray diffraction Analysis (XRD)

Figure 1 shows the X-ray diffraction pattern of RGO/(Zn,Ni)(O,S) nanocomposite with different amount of RGO. There are three peaks appear for each sample that located at 29.09, 48.82, and 57.56°. Those peaks correspond to the characteristic peaks of (Zn,Ni)(O,S) with peak shifting to the higher 2θ. It is reasonable since nickel with a smaller ionic radius of 69 pm partly replace of side zinc with a larger ionic radius of 74 pm[8]. The detail for this phenomena had been well explained in our early work[4]. The X-ray does not show any peak of RGO due to its little amount that cannot be detected by X-ray diffractometer.

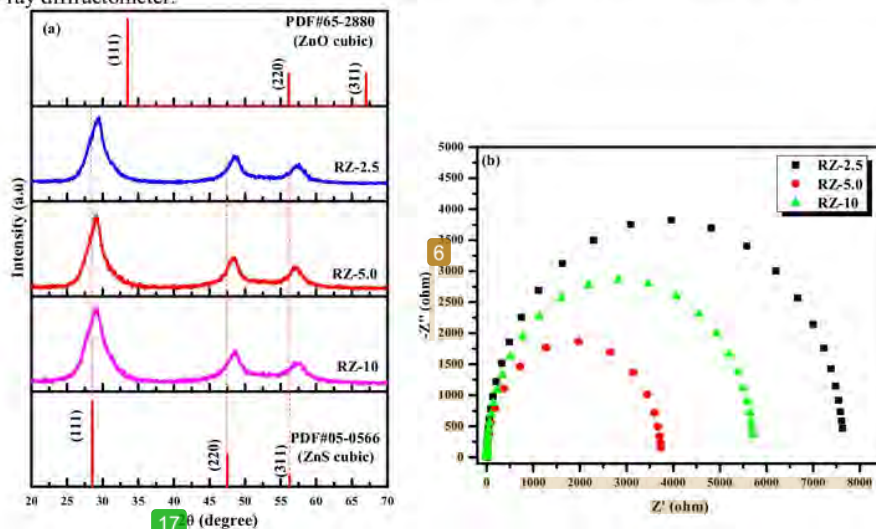


Figure 1. (a) XRD patterns and (b) Electrochemical impedance spectra (EIS) of RZ-2.5, RZ-5.0 and RZ-10



### 3.2 Electrochemical impedance spectroscopy (EIS) analysis

To investigate the effect of RGO against charge transfer resistance, the EIS measurements were conducted in 0.1M KCl solution at a frequency range of 100mHz to 200kHz. Figure 1b shows the EIS of RGO/(Zn,Ni)(O,S) nanocomposite with different amounts of RGO. After fitting with a Randle circuit, the charge transfer resistance of RZ-2.5, RZ-5.0 and RZ-10 could be determined as 7,620, 3,730, and 5,700  $\Omega$ , respectively. The catalyst RZ-5.0 has the lowest charge transfer resistance among of as-prepared catalyst which represents the easiest of electrons and holes in moving on the surface of its catalyst. This catalyst might have higher photocatalytic hydrogen production than other catalysts.

### 3.3 Morphology and microstructure

The morphology of as-prepared RGO/(Zn,Ni)(O,S) was recorded by FE-SEM at accelerating voltage of 15 kV. Figure 2a shows the FE-SEM image of RGO before combining with (Zn,Ni)(O,S) and exhibits the layers of graphene. However, after forming the RGO/(Zn,Ni)(O,S) the FE-SEM images do not clearly show the thin layers of RGO. It can be explained because the thin layers are covered by the (Zn,Ni)(O,S) nanoparticle during the particle growth. From the Figure 2b-d, can be clearly seen that all sample have the nanoparticle morphologies with an average grain size of several nanometers. It seems that by increasing the amount of RGO from 2.5 to 10 mg the grain size slightly decreases. The reason is that RGO can inhibit the grain growth of (Zn,Ni)(O,S) during the synthesis process.

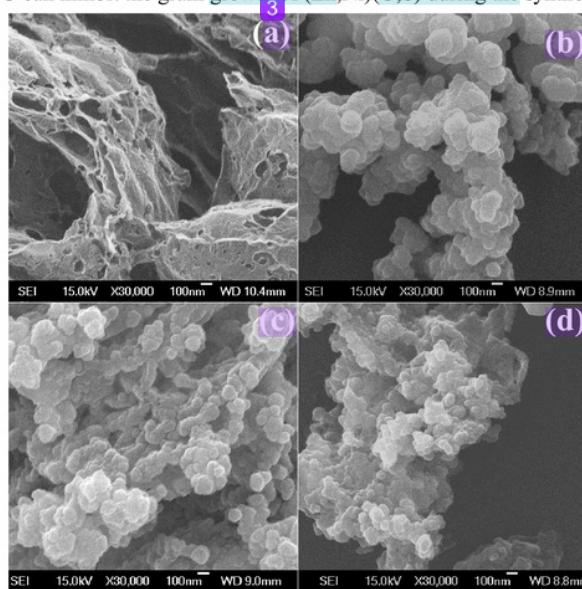
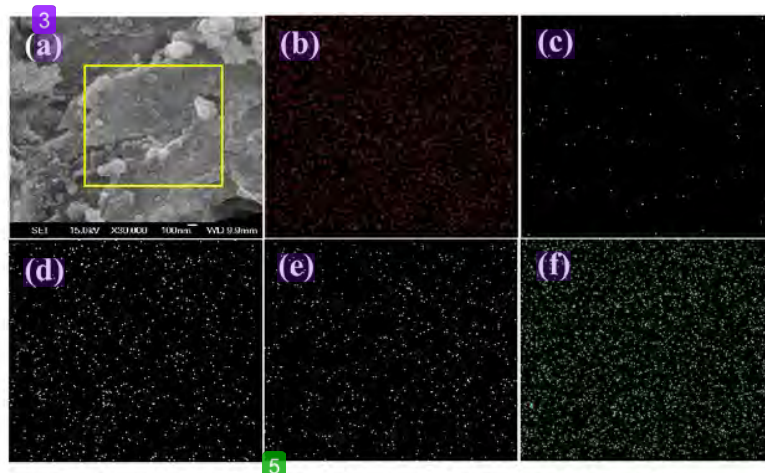


Figure 2. FE-SEM images of (a) RGO (b) RZ-2.5, (c) RZ-5.0 and (d) RZ-10

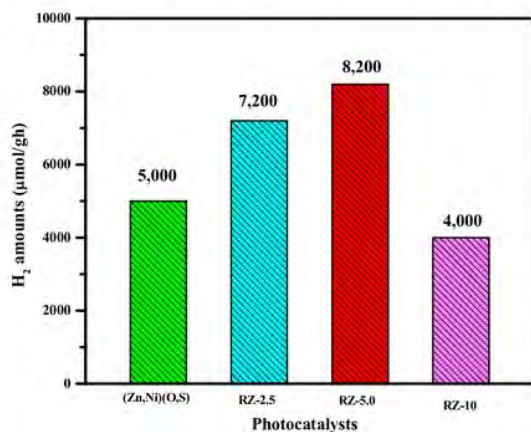
To further understand the distribution of each element in the catalyst, the EDX elemental mapping was performed and shown in Figure 3. All element constituent of catalyst RZ-2.5 appears in the elemental mapping including zinc, nickel, oxygen, sulfur and carbon. It can be seen that nickel concentration is much lower than zinc concentration. It is reasonable since nickel is a dopant with concentration 10% in the preparation, however, the actual amount is only about 2% based on EDX analysis. The element mapping of carbon in Figure 3f depicts its good distribution in the whole area. This reveals the presence of RGO in the nanocomposite catalyst.



**Figure 3.** (a) FE-SEM image and elemental mapping of (b) Zn, (c) Ni, (d) O, (e) S and (f) C of catalyst RZ-5.0

### 3.4 Photocatalytic activity for hydrogen production

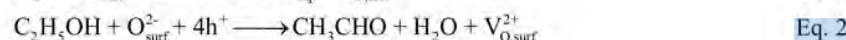
Figure 4 shows the hydrogen production rate of RGO/(ZnNi)(O,S) with different amount of RGO. The photocatalytic hydrogen production of a single (Zn,Ni)(O,S) is 5,000  $\mu\text{mol/gh}$ . After adding a little amount of 2 mg-RGO(RZ-2.5) the hydrogen production rate improves to 7,200  $\mu\text{mol/gh}$ . By further increasing the amount of RGO to 5 mg (RZ-5.0) the hydrogen production rates continuously increases to 8,200  $\mu\text{mol/gh}$ . Eventually, the hydrogen production rate sharply decreases to 4,000  $\mu\text{mol/gh}$  when the amount of RGO elevate to 10 mg. The reason for this degradation might be caused by too much RGO in the catalyst that inhibits the light absorption. The similar results also can be found in previous reports[9, 10]. Therefore, the optimum amount of RGO is 5 mg to provide the highest hydrogen production rate with an improvement of 64 % compared to without RGO or single (Zn,Ni)(O,S).



**Figure 4.** Photocatalytic hydrogen production of (Zn,Ni)(O,S), RZ-2.5, RZ-5.0 and RZ-10

### 3.5 Photocatalytic mechanism

The mechanism of catalyst RGO/(Zn,Ni)(O,S) nanocomposite to produce hydrogen is illustrated in Figure 6. The similar chemical reaction for Zn(O,S)-based material is proposed in this work, as shown in equation 1 to 4. Under the UV-light illumination, electrons ( $e^-$ ) are excited from the valence band to the conduction band of the (Zn,Ni)(O,S) semiconductor and then transfer into carbon atoms on the reduce graphene oxide layers. At the same time, holes ( $h^+$ ) are also formed in the valence band of Zn,Ni)(O,S). Then, photogenerated holes execute the oxidation reaction of surface oxygen anion and water/ethanol to form the oxygen vacancies according to Equation 1 and 2, respectively. These oxygen vacancies will trap the water molecules and weaken its O-H bonding. After breaking the O-H bonding of water, it releases protons ( $H^+$ ) as shown in equation 3. These protons will be reduced to form the hydrogen by the presence of photogenerated electron based on the reduction reaction in equation 4.



The enhanced photocatalytic hydrogen production rate of RGO/(ZnNi)(O,S)-5.0 compared to the bare (ZnNi)(O,S) is contributed from the lowering charge transfer resistance after the incorporation of RGO as proven by the EIS results in Figure 1b. This low charge transfer resistance assists the easiness for electrons and holes in diffusing on the surface of the catalyst to effectively carry out both oxidation and reduction reactions. Besides this, RGO also has another important role as the electron collector. After the photo-excitation process, the electrons from the conduction band of (ZnNi)(O,S) is transferred to RGO layers. This process is very helpful in separating electrons and holes instead of recombination each other[11]. Then RGO layers become electron-rich and provide more active area for carrying out the reduction reaction in order to generate more hydrogen. The lower hydrogen production rate of bare (Zn,Ni)(O,S) may be contributed to the rapid electrons-holes recombination. Therefore, after incorporation of RGO in (Zn,Ni)(O,S) to form the nanocomposite the electrons-holes recombination can be suppressed by graphene layers then its hydrogen production rate is significantly increased.

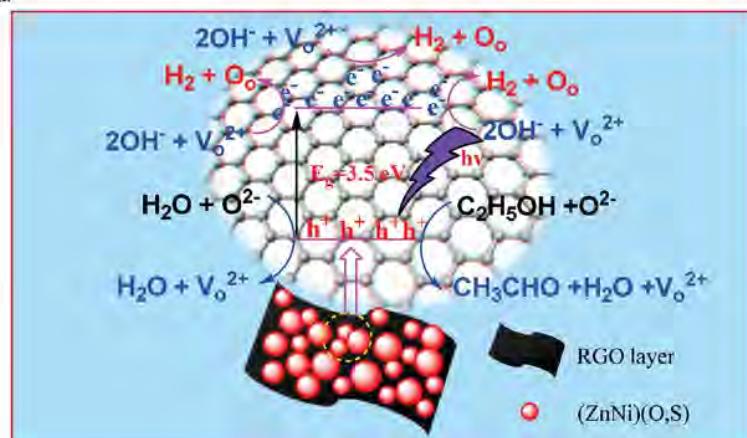


Figure 5. Photocatalytic mechanism of RGO/(ZnNi)(O,S) for hydrogen generation



#### 4. Conclusions

In summary, the photocatalyst RGO/(Zn,Ni)(O,S) with different RGO contents had been successfully developed for photocatalytic hydrogen production under low power UV illumination. XRD did not show any diffraction pattern of RGO due to a small amount in the as-prepared catalyst. However, elemental mapping clearly proved the presence of carbon as the element constituent of RGO. Based on the EIS result, RGO could decrease the charge transfer resistance to let the photogenerated electrons-holes easily migrate on the surface catalyst. The highest hydrogen production rate reached to 8,200  $\mu\text{mol}\cdot\text{h}^{-1}$  by catalyst RZ-5.0 which was about 64% higher than the single (Zn,Ni)(O,S). The enhanced hydrogen production was contributed by the low charge transfer resistance after the incorporation of RGO in (Zn,Ni)(O,S) semiconductor. It assisted the easiness for electrons and holes in diffusing on the surface of the catalyst to effectively carry out both oxidation and reduction reactions. The RGO layers was also proposed as electron collector and provide more active area for executing the reduction reaction in order to generate more hydrogen.

#### 4. Acknowledgments

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