



Evaluation of photocatalyst using binary transition metal phosphide for their Hydrogen production & Economic Values

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Abstract

Water decomposition hydrogen, which is expected to replace fossil fuels, has a problem in that it is difficult to commercialize due to its high cost. To lower the hydrogen production cost, this project produced hydrogen by CdS/g-C₃N₄/CoNiP, using one of binary TMPs instead of platinum, and the result was evaluated by comparing it with the literature. As a result, the catalyst with CoNiP performed better than the catalyst with nickel phosphide or platinum used as a cocatalyst, so it was concluded that the catalyst using binary TMPs was economical.

Introduction

Because of climate change, Carbon neutral has emerged as an important topic, and accordingly, fossil energy conversion is major task in the future society. One of the alternatives to fossil fuel is hydrogen which can be made by water splitting through photocatalysts. However, since most photocatalysts use platinum as cocatalyst, the price of photocatalysts is quite expensive. To make lower the photocatalyst price, studies for substituting platinum cocatalyst with TMPs already have been progressed and recently, research using binary TMPs have been reported. In this project, CdS, which has a narrow band gap but easily generate electron hole recombination, and g-C₃N₄, which has a wide band gap but outstanding electrical performance, formed heterojunction, compensating for the shortcomings of each component. Furthermore, after conjugating CoNiP to CdS/g-C₃N₄ the H₂ production rate, absorbance, and bandgap were measured and calculated, and the results were compared with other literature to evaluate catalyst performance and economic feasibility.

Experiment

Cadmium chloride(CdCl₂), cobalt (II) chloride hexahydrate(CoCl₂·6H₂O), nickel (II) chloride hexahydrate(NiCl₂·6H₂O), sodium hypophosphite (NaH₂PO₂) thiourea, urea, melamine, sodium sulfide(Na₂SO₃), sodium sulfide nonahydrate(Na₂SO₃·9H₂O), ethylene diamine, ethylene glycol, acetone were purchase from Sigma-Aldrich.

1. Synthesis nanorod CdS

Cadmium chloride 9.26g and thiourea 9.26g were dissolved in in a 120mL of ethylene diamine and stirred for 1 hour. The solution was then poured into a 120mL Teflon-lined autoclave, heated to 160°C and maintain for 36 hours for solvothermal synthesis. After heating, yellow precipitate was washed with DI water and ethanol for several times, and then dried at oven to get cadmium sulfide.

2. Synthesis g-C₃N₄

5g of melamine was put in a mortar and ground finely. Afterwards, put the ground melamine in the crucible and calcin at 550°C for 4 hours at a heating rate 5°C/min. Thereafter, after cooling to room temperature, the product was ground to obtain fine particles of g-C₃N₄.

3. Synthesis CoNiP

1mmol of cobalt (II) chloride hexahydrate, 1mmol of nickel (II) chloride hexahydrate and 0.2g of urea were dissolved in 20mL DI water and 20mL of ethylene glycol mixed solution. The solution was then poured into a 100ml Teflon-lined autoclave, heated to 140°C and maintain for 10 hours. After heating, precipitate was washed with DI water and ethanol for several times, and then dried at oven. Thereafter, the product was calcined in air at 400°C for 2 hours to obtain black cobalt nickel oxide. After mixing with excess sodium hypophosphite, the mixture was heated at 250°C for 2 hours and washed with DI water and ethanol for several times to get CoNiP

4. Synthesis CdS/g-C₃N₄ Composite

0.06g of previously synthesized g-C₃N₄ was homogeneously dispersed in 20mL acetone. 1.5g of cadmium sulfide was added to the solution and stirred for 24 hours. Acetone was evaporated in the stirred solution using a rotary evaporator, and then the remaining yellow solids were gathered. Finally, the solid was dried in and oven to obtain CdS/g-C₃N₄ heterojunction catalyst.

5. Synthesis CdS/g-C₃N₄/CoNiP Composite

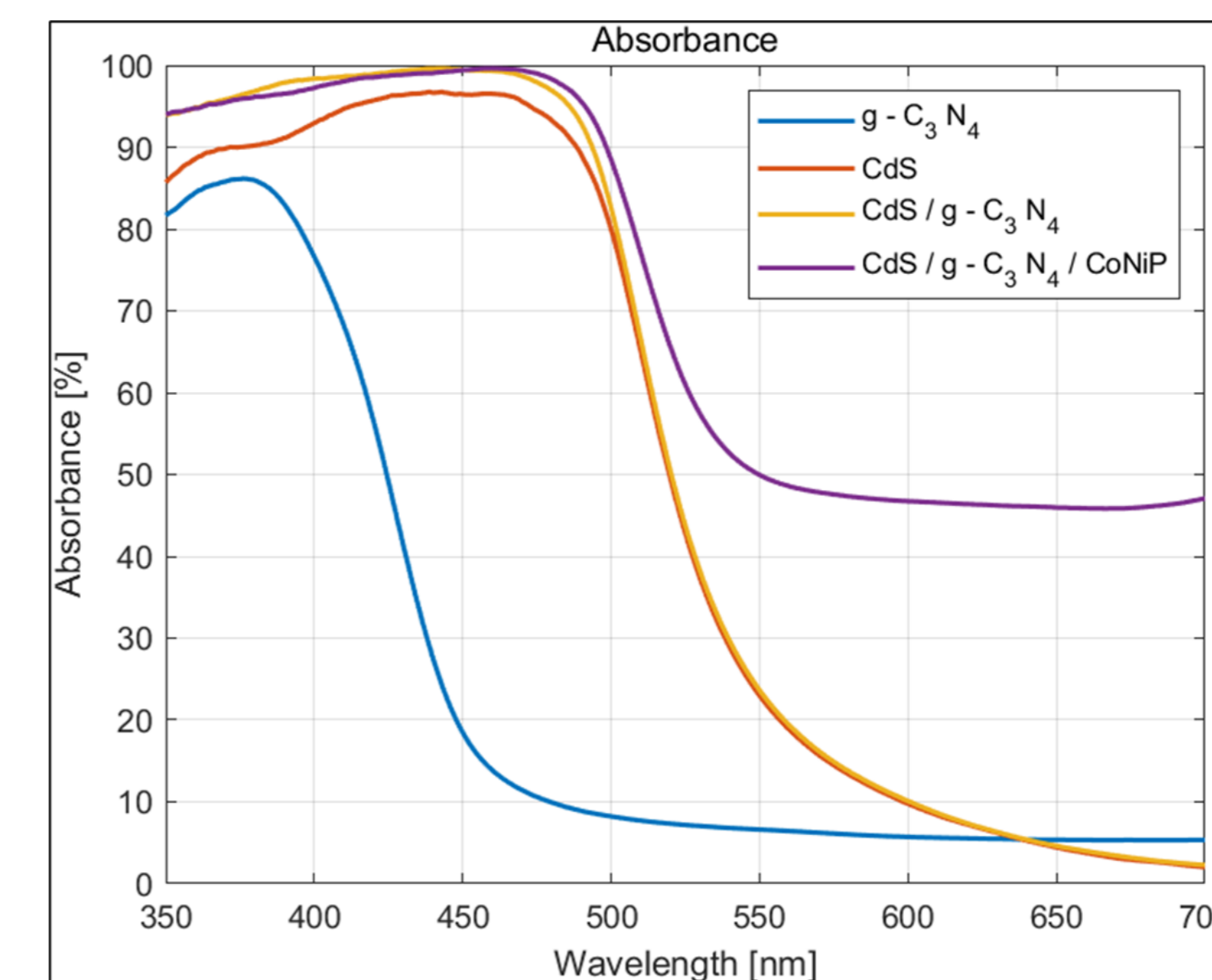
0.2g of CdS/g-C₃N₄ was dissolved in a solvent blended with 20mL of ethanol and 12.5mL of DI water, and 0.015g of synthesized CoNiP was added. The solution stirred for 10 minutes, then the solution was poured into a 100mL Teflon-lined autoclave, heated to 160°C and maintain for 6 hours. After hydrothermal synthesis was completed, the products were collected and washed with water several times.

6. H₂ production measurement

Solar simulator and gas chromatography were used to measure hydrogen production. 0.1 g of the catalyst to be measured was put in 40 mL of DI water and sonicated for 1 hour. A solution of which ultrasonic treatment was completed was added to a solution of adding 1.8906g of sodium sulfide and 5.0438g of sodium sulfide nonahydrate to 20mL DI water and then stirred in a measurement container. The measuring container was nitrogen purged for 5 minutes, installed under the solar simulator, and immediately collected 1 ml of gas and measured by gas chromatography. Thereafter, hydrogen production was measured through gas chromatography up to 4 hours at hour intervals.

Result and Discussion

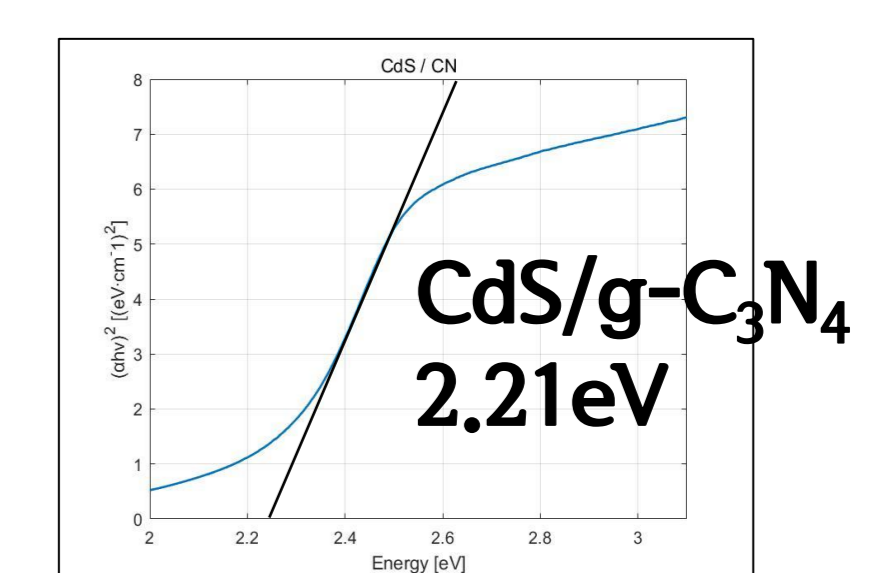
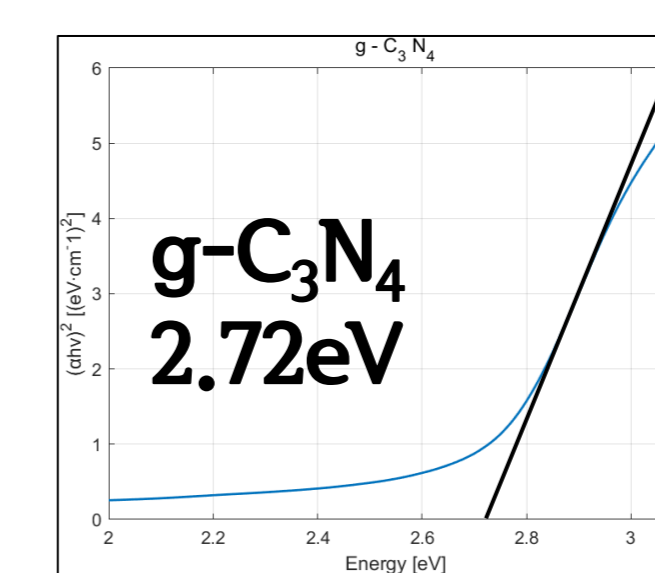
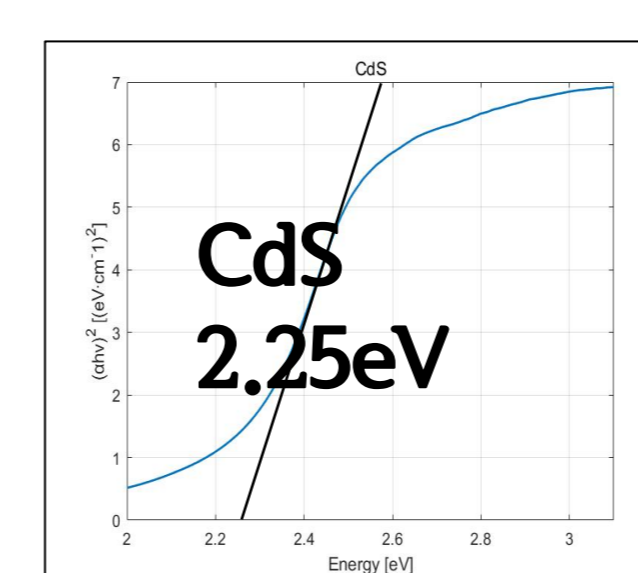
1. Absorbance



Light Harvesting ability

: The Absorbance increases in the order of g-C₃N₄ < CdS/g-C₃N₄ < CdS/g-C₃N₄/CoNiP

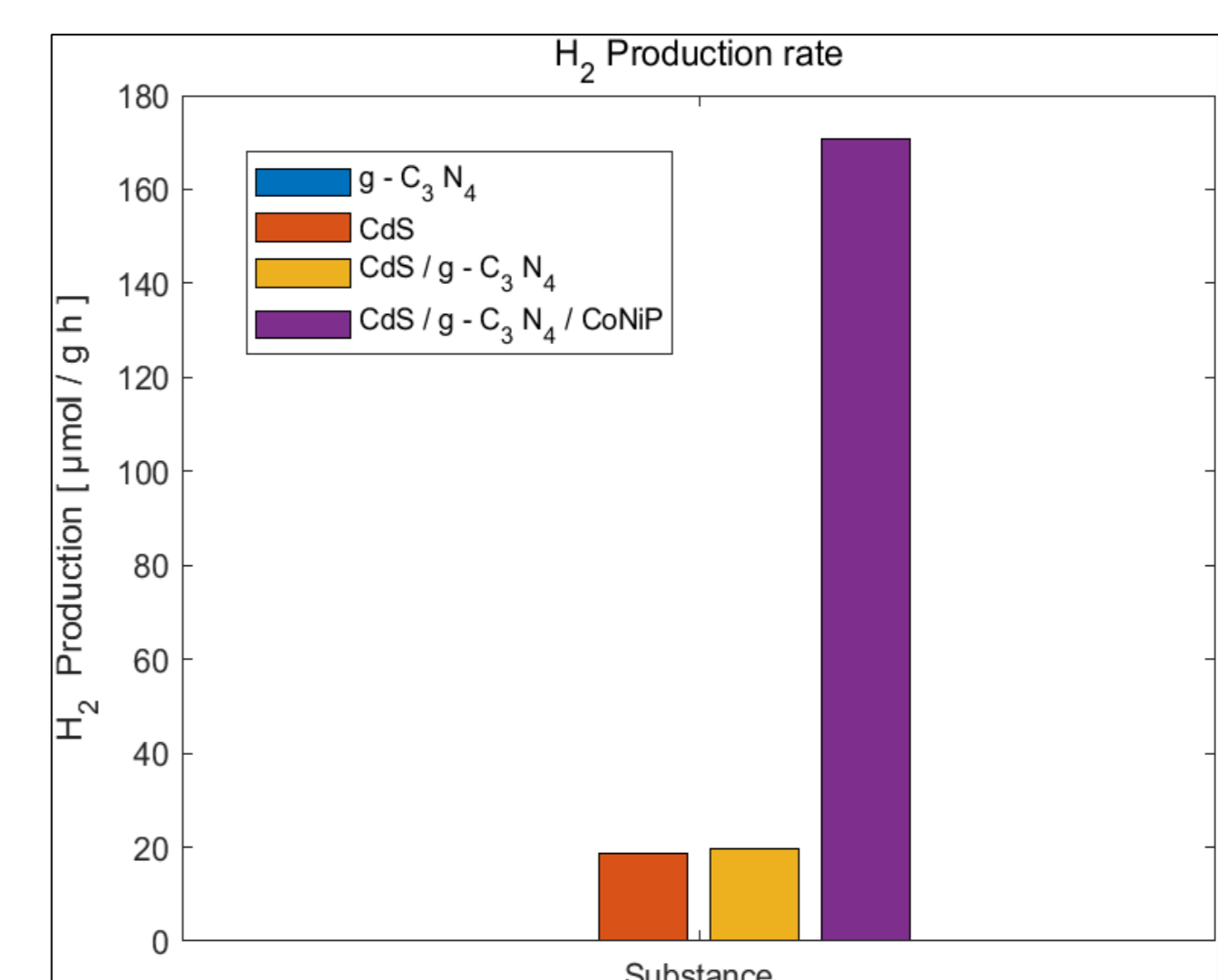
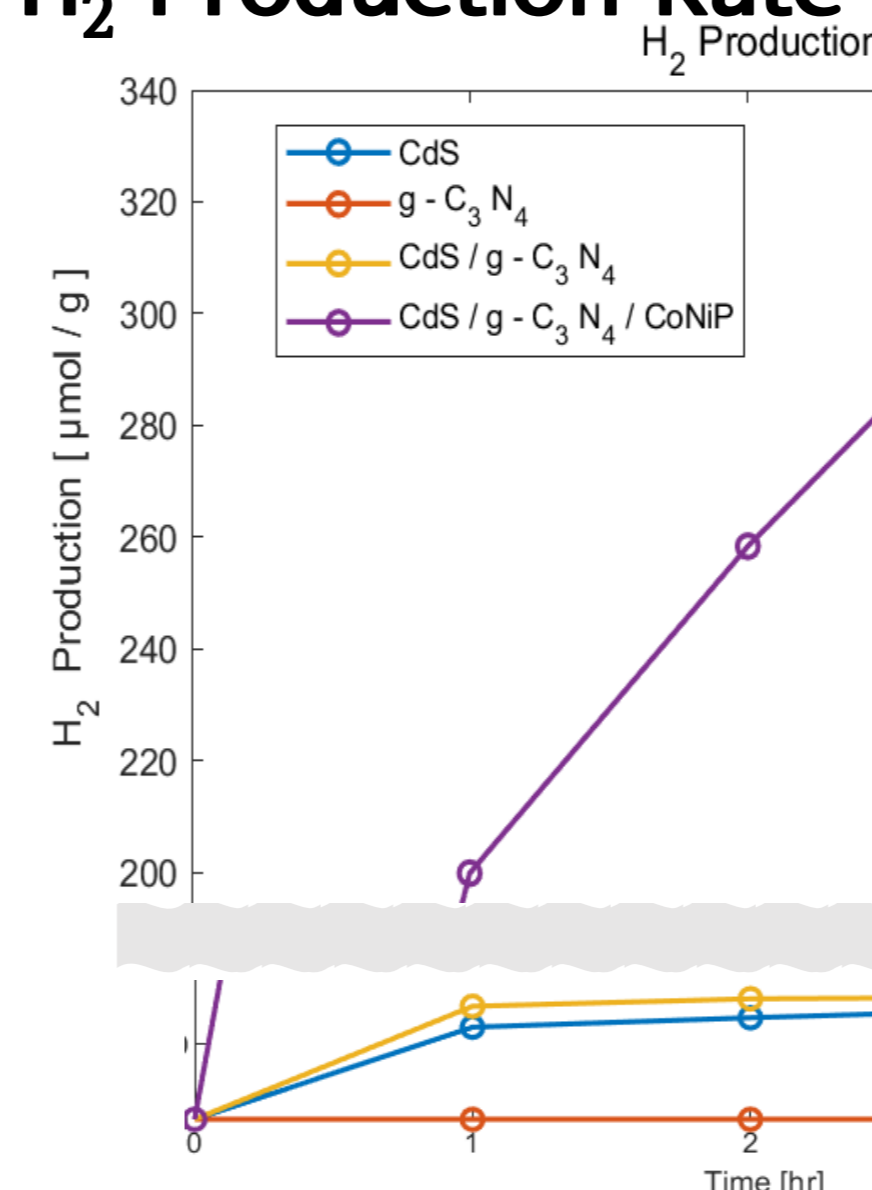
2. Band gap



Calculate the Band gap using Tauc Plot

: The Band gap of CdS & g-C₃N₄ coincide with the literature value, and slightly decreases in band gap of CdS/g-C₃N₄

3. H₂ Production Rate



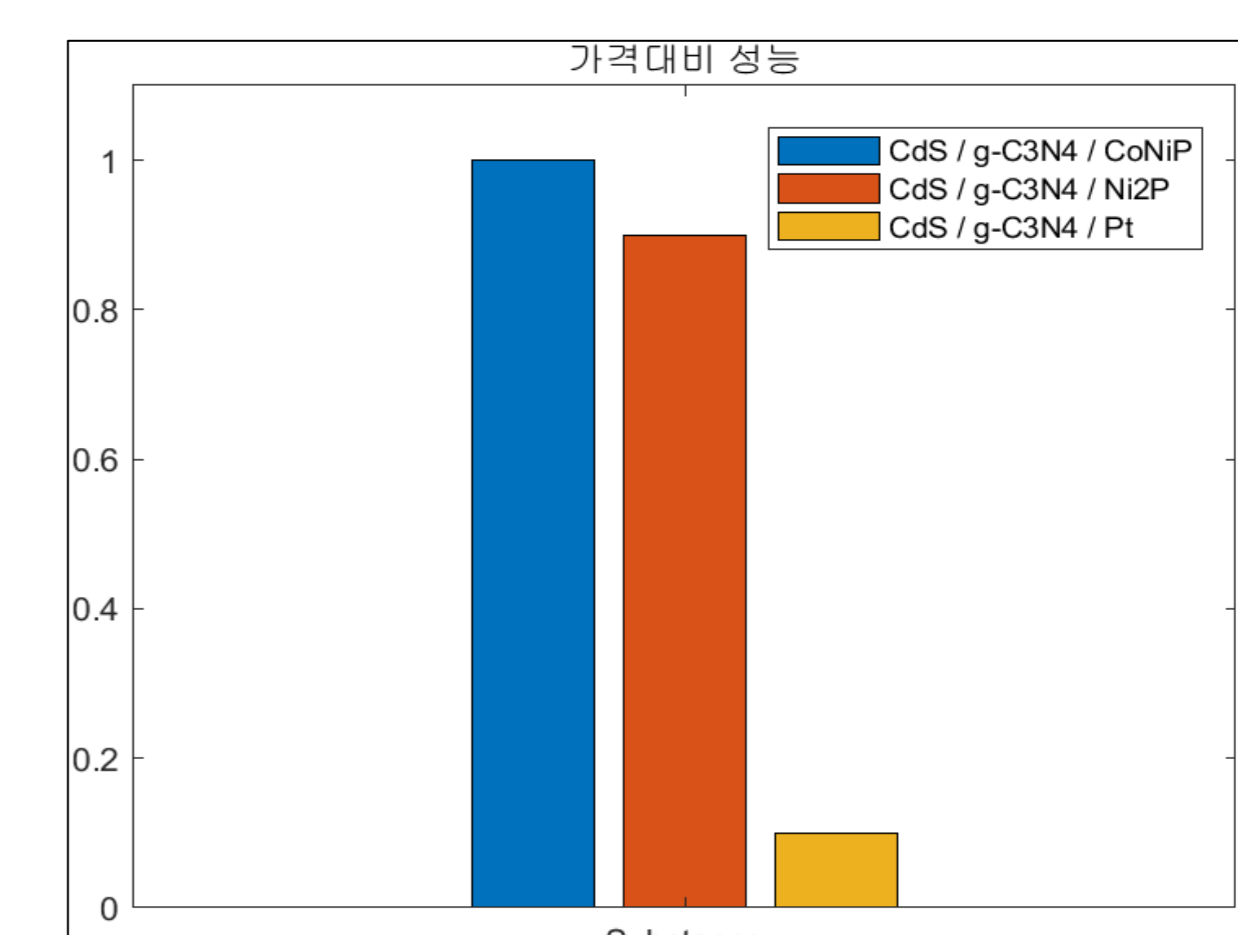
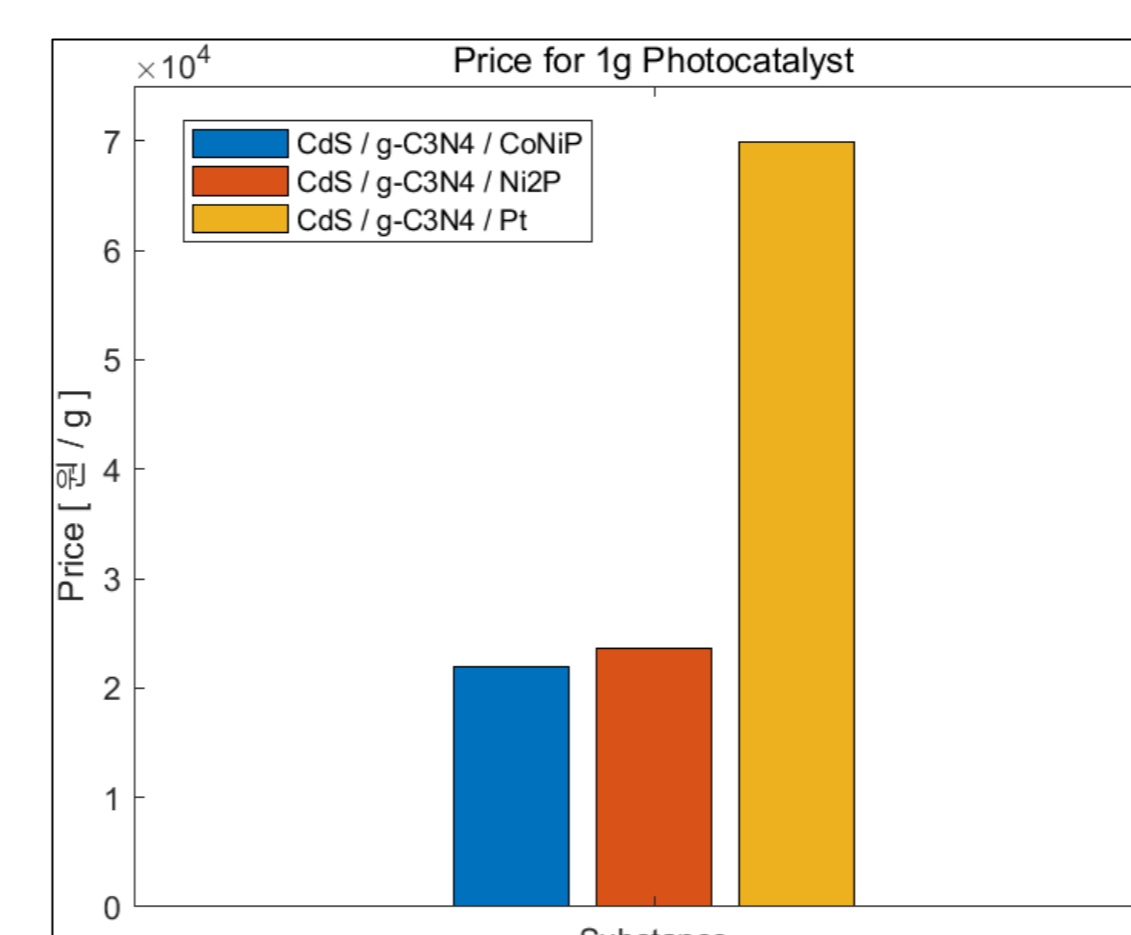
A graph showing the rate of hydrogen production

: The H₂ production rate increases in the order of CdS, CdS/g-C₃N₄, CdS/g-C₃N₄/CoNiP

Principle

- Because of Type2 Heterojunction Bandgap structure, holes move to g-C₃N₄ and electrons move to CdS. So, electron-hole recombination can be prevented & Catalytic activity increases.
- Negative charge on P can act as proton trap & weaken the bond strength of to absorbed hydrogen(easy dissociation of H₂)

4. Evaluation of commercialization potential



Comparison when using Pt, Ni₂P, and CoNiP as Cocatalyst

: CoNiP has the highest performance improvement compared to the price per gram (8.86times better than Pt and 1.11 times better than Ni₂P)

Conclusion

CdS/g-C₃N₄/CoNiP as water-splitting HER catalyst

1. By using Type2 Heterojunction, Higher catalytic activity is obtained
2. By using TMP, Higher catalytic activity is obtained (Noble metal free cocatalyst)
3. By using Co-Ni bi-metallic phosphide, Higher catalytic activity is obtained
4. CoNiP has the highest catalytic performance improvement compared to the price per gram

→Achieved the initial goals of

“Fabricating the economical photocatalyst by replacing noble metals with Transition metal phosphides (TMPs)”