**A novel photoreactor for separating hydrogen and oxygen in photocatalytic water splitting**

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**Abstract**

H₂ and O₂ were produced in a twin reactor with two compartments divided by a Nafion membrane. Ce³⁺ and Ce⁴⁺ are adopted as redox mediator, which transferred the electron and holes between H₂-evolving catalyst (Pt/SrTiO₃:Rh) and O₂ evolving catalyst (BiVO₄). The optimal pH in the twin reactor was 1. Water splitting under Ce³⁺/Ce⁴⁺ equilibrium concentrations between two compartments gave the highest initial and average H₂ generation rates, 1.21 and 1.45 μmol/g-hr, respectively. Our results indicates that the rate limiting step falls on the catalyst itself rather than the diffusion resistance of Ce³⁺/Ce⁴⁺ by Nafion membrane. H₂ and O₂ were separated in water splitting thus preventing backward reaction.

**Introduction**

Hydrogen has been considered to be one of the potential energy sources because it is energy efficient, clean, and abundant in nature. A better way to produce cleaner hydrogen is by the so-called 'photocatalytic water splitting' which can utilize sunlight to decompose water into hydrogen and oxygen with the aid of photocatalyst. The H₂ photocatalyst and O₂ photocatalyst are separated in two vessels and are divided by a Nafion membrane. Redox mediators are used to balance the electrons and holes on two sides of the Nafion membrane in order to sustain the reaction. Therefore, the reverse reaction of H₂ and O₂ in a single reactor can be avoided and the photocatalytic efficiency is improved. The cost of separation is also saved.

**Experimental**

The H₂ catalyst, Pt/SrTiO₃:Rh, was prepared by a sol-gel method. The O₂ catalyst was BiVO₄. Figure 1 shows the schematics of twin photoreactor. First, 0.15 gram of Pt/SrTiO₃:Rh and 0.15 gram of BiVO₄ was added in 180 mL of 2mM Ce₂(SO₄)₃ and Ce(SO₄)₂ solution respectively. Two compartments was divided by a Ce⁴⁺ pretreated Nafion membrane. The reaction was under 300W Xe lamp irradiation for 6 hr and the H₂ and O₂ evolved were collected respectively and analyzed by GC. The visible light intensity at 1.76 mW/cm².

![Figure 1: Schematics of twin photoreactor](image)

**Results and Discussion**

1. Characteristics of photocatalyst

   The H₂ catalyst, Pt/SrTiO₃:Rh, the absorption band at 450~600nm proves that Rh has been doped into SrTiO₃ and therefore band position has blue shift. The band gap of the Pt/SrTiO₃:Rh calculated from UV result is 2.31eV, which is narrower than that of SrTiO₃, 3.26eV. Fig2 shows the XRD result of Pt/SrTiO₃:Rh and BiVO₄ (monoclinic). The diffraction peaks of the loaded Pt and the doped Rh are absent due to the trace amount presented in the catalysts. Fig3 shows the SEM of Pt/SrTiO₃:Rh and BiVO₄. The round and plate-like morphology is observed and the particle size ranges from 0.7μm to 2μm. Pt/SrTiO₃:Rh is observed to have round and cubic shape and its

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particle size is around 50nm to 100nm. The specific surface area of BiVO₄ is 1.24 m²/g, while that of Pt/SrTiO₃ is 6.49 m²/g.

2. Photocatalytic water splitting

As shown in Figure 4, the initial H₂ and O₂ generation rate are 1.21 and 0.67 μmol/g-hr, respectively. The average H₂ and O₂ generation rate under equilibrium concentration are 1.45 and 0.71 μmol/g-hr, respectively. The photo quantum efficiency for H₂ production under equilibrium Ce³⁺/Ce⁴⁺ concentration is calculated to be 0.445%.

Summary

The twin reactor system can produce H₂ and O₂ separately with visible light driven photocatalysts, that can eliminate the potential explosion of H₂/O₂ mixture for industrial production. Furthermore, the twin reactor gave higher H₂ generation rate than that in the single reactor, which is the result by preventing holes/electrons recombination and backward reaction.