

Sunlight- driven photocatalytic hydrogen production from water using metal-doped Strontium Titanate perovskite

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Abstract:

The effects of various metal dopants on the photocatalytic water splitting activity of SrTiO₃-based photocatalysts were investigated using experimental studies. The SrTiO₃: Rh (1%) has been found to give the best efficiency in water splitting out of the various metal-doped samples studied. However, the same host doped with other metal dopants such as Fe, V, Ga, and Sb leads to negligible H₂ evolution even when at least Fe has a better visible light response. Our results accompanied by previously conducted theoretical studies by our group explain the high photocatalytic water splitting activity of Rh doped SrTiO₃. Furthermore, the effects of the amount of catalyst, the proportion of sacrificial agent and pH were studied for the SrTiO₃: Rh (1 mol%) along with studying its activity with seawater.

Introduction:

The efficient use of solar energy to synthesize fuels is believed to be an efficient solution to energy and environmental issues we are currently facing. Interest in renewable fuels for energy production is growing rapidly and H₂ is identified as a source of ultimate clean energy. It is used in chemical industries, for example, in industrial ammonia synthesis. Current production relies on steam reforming of hydrocarbons, which are mainly obtained from fossil fuels. Such reactions are not only energy-intensive but also release greenhouse gases. Thus, driven by the current growing concern about global climate change, efforts have been made to develop new alternative and environmentally friendly energy sources, such as the photocatalytic production of hydrogen from natural resources such as water and solar energy because they are abundant, renewable and have a better impact on the environment compared to fossil fuels. Fujishima and

Honda¹ discovered that water could be decomposed under UV light using a TiO₂ electrode by the generation of electrons and holes where the water is oxidized by the holes to generate O₂ and H⁺, while the free electrons reduce H⁺ to produce H₂ on the cathode. To initiate such a reaction, the highest level of the valence band should be more positive than the water oxidation level (1.23 V vs NHE), while the lowest level of the conduction band should be more negative than hydrogen evolution potential (0 V vs NHE). However, TiO₂ does not absorb visible light and now a lot of research focuses on developing new materials having visible light absorption ability. The ABO₃ type perovskite strontium titanate (SrTiO₃) is one of the promising photocatalyst, which matches this requirement. The wide bandgap (3.3 eV) of this photocatalyst results in a less than 5% sunlight absorption and low evolution efficiency². Substituting some metal ions with dopants introduces extra band positions forming new energy levels near CB and VB resulting in the reduced minimum light absorption energy gap. Attempts have been made to dope particulate SrTiO₃ with noble metals such as Rh, Pd, Ir, Ru, Mn and Pt for enhancing the photocatalytic activity^{3,4}. However, many correlated factors⁵ such as the recombination of active electrons, structural defects of the crystal and energy barrier at surface reaction site make the designing of high-performance photocatalyst, a confounding task.

Experiments:

A closed batch photoreactor was used to perform the hydrogen evolution reaction, which was used offline with a gas chromatograph (GC). A 300 W Xe lamp with AM 1.5 filter was used as a light source to mimic visible light. A certain amount of photocatalyst was dispersed in water (with methanol as a sacrificial agent) using magnetic stirrer in the Pyrex glass photoreactor. During all the experiments, helium was used to purge the reactor to expel any remaining gases inside before initiating the reaction. The gas samples were taken periodically and analyzed with a Younglin Instruments GC (molecular sieve 5 A column, PDHID detector with He carrier). Doped SrTiO₃ was prepared by mixing SrCO₃ (Aldrich, 99%), TiO₂ (Aldrich, 99.5%) and respective metal oxides: Rh₂O₃, Sb₂O₃, Ga₂O₃, V₂O₅ and Fe₂O₃ according to the composition of SrTiO₃: M (1 mol %) and then calcining the mixture in air at 1273 K for 10 h. The photocatalysts synthesized were confirmed from XRD and were further characterized by UV visible spectroscopy. For the seawater splitting experiments, the seawater was obtained from the Tamsui River in Taiwan and the anion concentration in seawater as measured by Ion Chromatography (IC) machine equipped with a conductivity detector and IonPac AS4A-SC (4 X 250 mm) column. Standard IC solutions of Cl⁻, Br⁻, and SO₄²⁻ ions were prepared to make the anion calibration lines.

Results and Discussion:

XRD showing no extra diffraction lines from other crystal phases confirmed the successful introduction of dopants to SrTiO_3 perovskites slab. UV visible spectrum confirms the better visible light response of SrTiO_3 : Fe than SrTiO_3 : Rh.

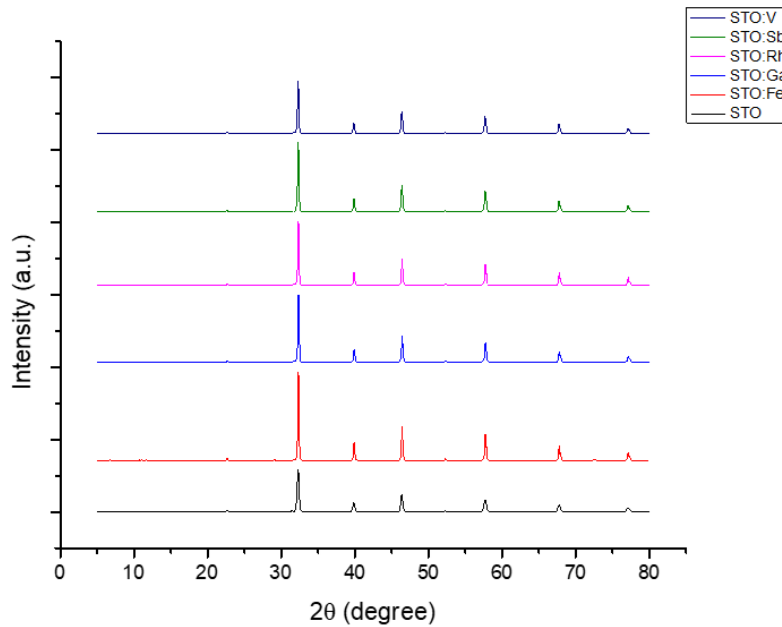


Figure 1: XRD patterns of SrTiO_3 : M (1%), M= V, Sb, Rh, Ga, Fe, and pristine SrTiO_3

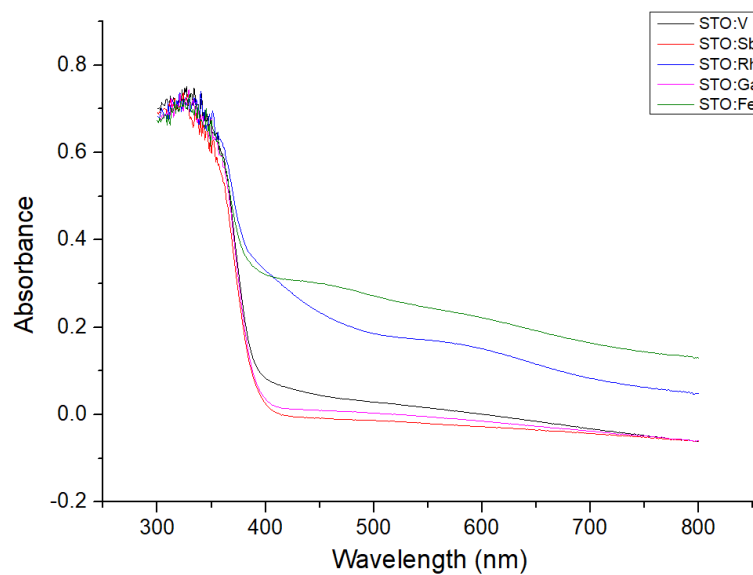


Figure 2: UV visible spectrum of SrTiO_3 : M (1%), M= V, Sb, Rh, Ga, and Fe from 300 nm to 800 nm

The hydrogen evolution of SrTiO₃: M (1 mol %) was confirmed by gas chromatography as described before for the batch photoreactor with 0.1 g catalyst dispersed in 100 mL water with 10 mL MeOH (i.e. 9% by volume methanol solution). In addition to the aforementioned dopants, Li and Gd were also included. The outstanding photocatalytic activity of Rh doped SrTiO₃ may be explained by the suitable position of the dopant energy levels as shown by first principle DFT calculations by our group⁶. In Rh doped SrTiO₃, the dopant energy level is slightly above VB and therefore the excitation energy threshold is a bit lower. After the excitation, the vacant dopant states can become a recombination center for electrons in CB. The nearness of the Rh dopant states to VB allows a fast replenishment of electron by absorbing either thermal vibration of lattice or low energy photons. For Fe, perhaps the new dopant states are near the middle of the bandgap, away from the VB edge that prevents the replenishment of electrons via lattice thermal vibration. Thus, it needs to be refilled by absorbing new photons and thus giving a longer lifespan to Fe recombination centers. Another possibility might be that the higher Fe states compared to Rh states make them much closer to O₂/H₂O oxidation potential and thus implying a smaller driving force for oxidation.

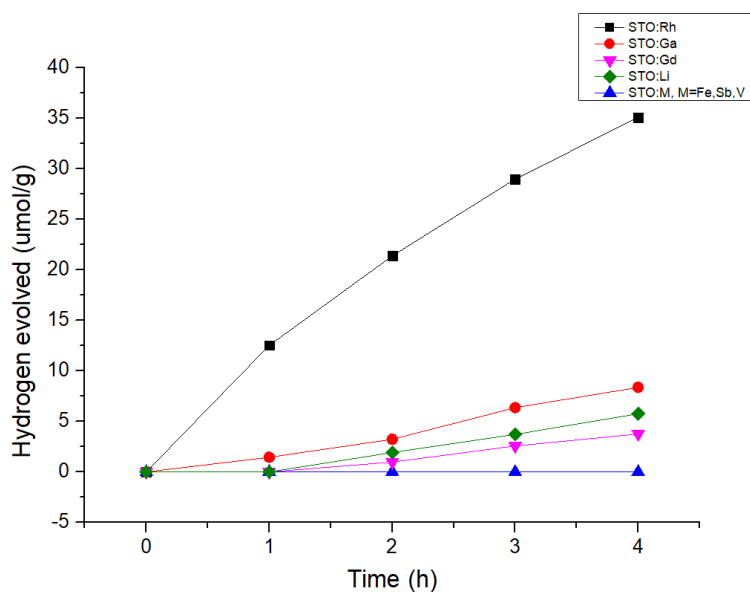


Figure 3: Photocatalytic water splitting activity of SrTiO₃: M (1 mol %), 0.1 g catalyst dispersed in 100 mL water and 10 mL methanol under 300 W Xe lamp light source

Influence of reaction parameters:

Since SrTiO_3 doped with Rh showed more promising results, we studied the influence of various reaction parameters for the photocatalytic water splitting activity for the same photocatalyst. Increasing the amount of catalyst will increase the amount of light absorbed by the semiconductor particles and thus the hydrogen production; however, eventually, a point will be reached where the entire incident visible light will be absorbed and rate cannot be increased further. Increasing the amount of catalyst further will reduce the penetration depth of the light irradiation due to loss of scattered light to the exterior, and thus reducing the hydrogen evolution. The next parameter to be tested was the volume of the sacrificial agent methanol. As the concentration of the methanol increases, the number of recombination is reduced, but at the same time the water molecules, which give hydrogen after going reduction decreases and thus these two opposing mechanisms, lead to an optimum volume. The third parameter to be examined was the pH of the reactant solution whose influence on the rate of H_2 evolution was investigated by the addition of HCl and NaOH. The pH of the solution can directly affect the stability of the photocatalyst as well as the redox processes of water reduction and oxidation. It was observed that at acidic pH, the hydrogen evolution substantially increased which is due to increased adsorption of H^+ on the semiconductor surface, and thus increasing the possibility of reduction of H^+ to H_2 by free electrons.

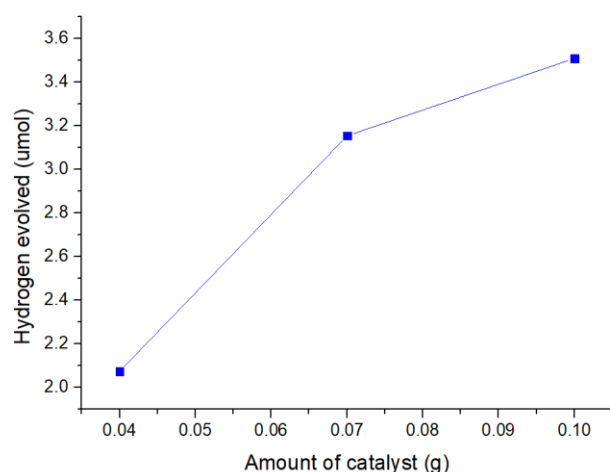


Figure 4: Photocatalytic water splitting activity of SrTiO_3 : Rh (1 mol%) with varying amount of catalyst in 100 mL water and 10 mL MeOH under 300 W Xe lamp light source after 4 hours

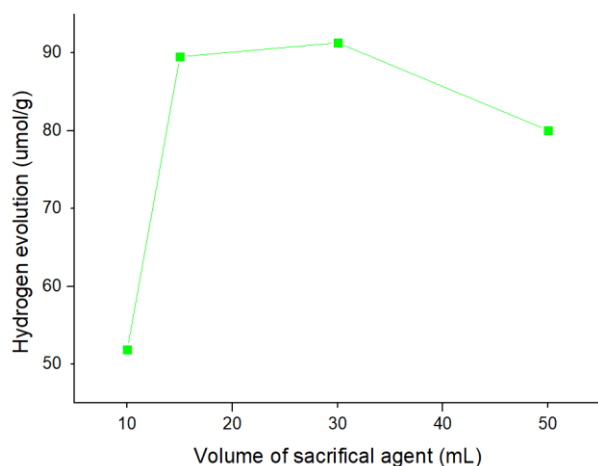


Figure 5: Photocatalytic water splitting activity of 0.04 g $\text{SrTiO}_3\text{:Rh}$ (1 mol%) with the varying volume of MeOH in 100 mL water under 300 W Xe lamp light source after 4 hours

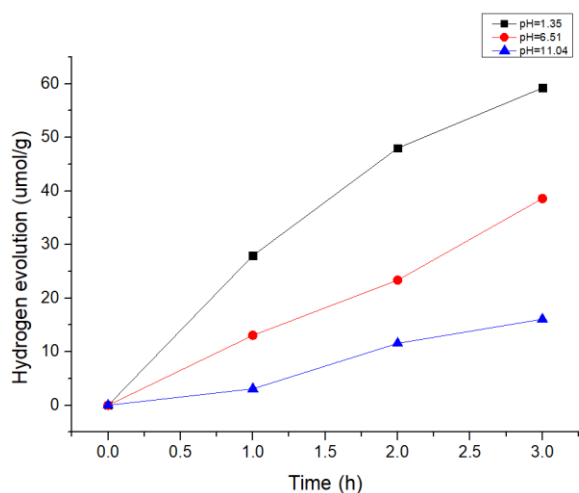


Figure 6: Photocatalytic water splitting activity of 0.04 g $\text{SrTiO}_3\text{:Rh}$ (1 mol %) with varying pH in 100 mL water and 10 mL MeOH under 300 W Xe lamp light source

Photocatalytic hydrogen evolution from seawater

Since the most promising source of water for photocatalysis in the future could be seawater; we conducted studies on the possible use of direct water from the sea for the water-splitting experiments. Another reason for using the seawater was that the abundant chlorine ions present in the seawater can act as a hole scavenger⁷. The seawater was analyzed by ion chromatography and the results are shown in Figure 8. The hydrogen evolution rates are comparatively very small as compared to distilled water used in prior experiments and thus further investigations are needed to evaluate the viability of using seawater directly.

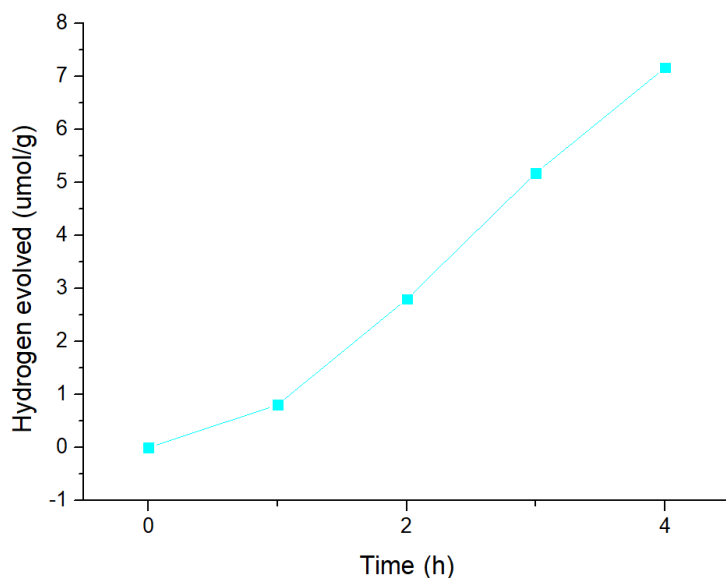


Figure 7: Photocatalytic water splitting activity of $\text{SrTiO}_3\text{: M}$ (1 mol %), 0.015 g catalyst dispersed in 100 mL water under 300 W Xe lamp light source

	Cl^-	Br^-	SO_4^{2-}
Concentration (in ppm)	2237.6	5.7674	288.32

Figure 8 Characterisation of seawater used for water splitting experiment

Conclusion:

The Rh doped SrTiO_3 exhibits the best H_2 evolution efficiency among the various doped photocatalyst studied. The proximity of the dopant Rh energy states to valence band maximum allows efficient electron replenishment and reduce the trapping of electrons from CB. Further many factors need to be considered to further optimize the hydrogen evolution from SrTiO_3 and several factors such as the intensity of light irradiation, temperature, type of sacrificial agent and pressure need to be examined. Moreover, the use of seawater directly for water splitting needs further attention.

References:

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