



Short communication

Photocatalytic overall water splitting over an open-framework gallium borate loaded with various cocatalysts



Biao Ma, Rihong Cong, Wenliang Gao, Tao Yang*

College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, People's Republic of China

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ABSTRACT

We present a systematic investigation on the photocatalytic ability of an open-framework gallium borate, Ga-PKU-1. It was reported to be intrinsically active for water reduction or oxidation, however, acquiring sacrificial reagents. Here the loading of CoO_x , RuO_x , Pt, Au, NiO_x and Ag as cocatalysts greatly enhanced the catalytic activity, which eventually lead to overall water splitting into stoichiometric H_2 (28.4 $\mu\text{mol/h/g}$) and O_2 (14.5 $\mu\text{mol/h/g}$) for 1 wt.% RuO_x –1 wt.% Pt loaded Ga-PKU-1. After three cycles of photocatalytic water splitting experiments, it gave the constant H_2 evolution rate with no degradation of the catalyst.

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1. Introduction

The major characteristics of the structural chemistry of metal borates are the abundant and diverse connectivity of borate ionic framework, where metal cations are imbedded. Most borates are insulators or semiconductors because the borate ionic framework cannot conduct electrons or holes efficiently, therefore optical properties, i.e. second harmonic-generation and photoluminescent properties, are well-explored for metal borates [1–3]. In literature, there are only a few particular metal borates showing substantial photocatalytic properties. For example, InBO_3 can photocatalyze the degradation of 4-chlorophenol [4]; CuB_2O_4 and $\text{Cu}_3\text{B}_2\text{O}_6$ (by loading Pt as cocatalyst) can catalyze water reduction or oxidation under visible light irradiation [5]; $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_2\text{O}_2[\text{BO}_2(\text{OH})]$ show observable visible light activities for methylene blue degradation [6]; and the nonlinear optical material $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$ shows a good catalytic activity in UV-induced de-chlorination of chlorophenols [7].

It is commonly agreed that photocatalytic water splitting is a green process to convert the solar energy into chemical energy. The ongoing research in this field is very active. People are seeking for materials capable of catalyzing the overall water splitting without sacrificial reagents, which, however, is particularly difficult because of the high recombination rate of the photogenerated e^- and h^+ before they could react with substrates [8,9]. There are of course several strategies to at least partially restrain the charge recombination. One is to shorten the pathway for the electrons moving to the surface by making catalysts in nanosize or mesoporous form. For example, a gallium borate

($\text{Ga}_4\text{B}_2\text{O}_9$) cannot photocatalyze the water reduction in its bulk form even with the assistance of CH_3OH in aqueous solution, while it became highly efficient to photocatalyze overall water splitting without cocatalysts, when it was prepared by sol–gel method and crystallized in nano-stripes [10].

On the other hand, it is usually helpful to suppress the charge recombination by loading cocatalysts, such as Pt, Pd, RuO_x , Ag, and Au [11,12]. Extensive efforts have been applied on this aspect to improve the catalytic activities of well-known photocatalysts like TiO_2 and $g\text{-C}_3\text{N}_4$ [13–20]. Very recently, an open-framework gallium borate $\text{Ga}_9\text{B}_{18}\text{O}_{33}(\text{OH})_{15}\cdot\text{H}_3\text{B}_3\text{O}_6\cdot\text{H}_3\text{BO}_3$ (Ga-PKU-1) has been reported as a UV-light photocatalyst for water splitting, however, requiring the assistance of sacrificial reagents [21]. This boron-rich compound possesses a GaO_6 -based three-dimensional (3D) framework (see Fig. S1 in Supplementary information, SI), and the unoccupied 4s orbitals of Ga contribute to the bottom of the conducting band. Ga-PKU-1 can be prepared by hydrothermal method and were single crystals in micrometer (see Fig. S2 in SI). It is a natural idea to apply the cocatalyst loading to enhance its photocatalytic activity. Here we performed a systematic investigation on this aspect, where it indeed exhibits a greatly improved activity and is even capable of overall water splitting under UV-light irradiation.

2. Experimental sections

The preparation of Ga-PKU-1 was performed according to the therapy in literature [21]. First, $\beta\text{-Ga}_2\text{O}_3$ was dissolved in concentrated HNO_3 at 180 °C for 10 h in a closed system. The resultant solution evaporates to nearly dry by just opening to air. Thereafter, H_3BO_3 (3.0 g) was charged and the system was sealed again and maintained at 220 °C for

* Corresponding author.

E-mail address: taoyang@cqu.edu.cn (T. Yang).

another 5 days. Finally, the white powder product was washed by deionized water for several times. Powder X-ray diffraction (XRD) was performed to confirm the phase purity. As a representative, the powder XRD pattern of as-prepared Ga-PKU-1 was refined using the cell lattice reported in literature (see Fig. S3 in SI) [21], no impurity reflection could be found. In addition, all samples used in current study, including monometallic and bimetallic modified catalysts, were characterized by powder XRD after catalytic reactions and none of them show any degeneration, indicating the high stability of Ga-PKU-1 (see Figs. S4–S6 in SI).

Powder XRD data were collected on a PANalytical X'pert diffractometer equipped with a PIXcel 1D detector (Cu K α radiation). The operation voltage and current are 40 kV and 40 mA, respectively. Photocatalytic activities were tested on a gas-closed circulation system equipped with a vacuum line (CEL-SPH2N system), a reaction vessel and a gas sampling port that is directly connected to a gas chromatograph (Shanghai Techcomp-GC7900, TCD detector, molecular sieve 5A). In a typical run, 50 mg of a catalyst was dispersed by a magnetic stirrer in 50 mL pure water or 20 vol.% methanol aqueous solution in a 150 mL Pyrex glass reactor with a quartz cover. The solution has been kept stirred, and a 5 °C recycling water bath was applied to keep the reaction vessel cool. The light irradiation source was generated by a 500 W high-pressure mercury lamp (CEL-M500, Beijing AuLight). The spectrum of the lamp was provided in Supplementary information. The H₂ and O₂ evolution was analyzed by an online gas chromatograph, separately. For detecting so-generated H₂ and O₂, the gas carrier was selected to be N₂ and He, respectively, due to the sensitivity of the TCD detector. The detailed gas production curves against time are presented in Figs. S7–S10 in SI.

The noble metal or metal oxide co-catalyst loading was performed in a photo-deposition method using the above setup. For example, 0.1 g of catalyst together with 1 wt.% Ru aqueous solution (RuCl₃) was charged into 50 mL 40 vol.% methanol aqueous solution under magnetic stirring. Then a UV incident beam was irradiated to this mixture for 3 h. Then, the powder sample was collected and washed by deionized water. For other metal loading, the used sources are Ni(NO₃)₂·6H₂O, AgNO₃, H₂PtCl₆·6H₂O, HAuCl₄·4H₂O and CoCl₂·6H₂O, respectively. It is assumed that most cocatalyst ions in aqueous solution were successfully loaded. The accurate amount of the loading cocatalyst is in fact difficult to determine. For example, we performed semi-quantitative elemental analyses on NiO_x and CoO_x-loaded samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Leeman Profile-spec. The results show that the content of NiO_x and CoO_x was roughly 0.2 wt.% and 0.1 wt.%, respectively. Nevertheless, the photo-deposition method was commonly used by most researchers and it is proved to be effective, though the accurate quantitative of cocatalyst cannot be easily determined.

3. Results and discussion

In literature, the structure of Ga-PKU-1 was described as an open-framework metal borate, where the GaO₆ octahedra share the common edges to form a 3D continuous backbone and the triangular BO₃ species are grafted on the surface [21]. The theoretical calculations suggest that the top of the valence band (VB) is composed of O 2p orbitals and the bottom of the conduction band (CB) is contributed by both the Ga 4s and B 2p orbitals. The band structure is as-expected and suggests a wide gap characteristic. Accordingly, when irradiated by UV-light photons, the VB electrons, which are located at the O 2p orbitals, can be promoted to excited states, either Ga 4s or B 2p unoccupied orbitals. Benefiting from the uninterrupted 3D Ga-O ionic framework, the photon-excited electrons and holes can itinerate to the surface of the particle and catalyze the water reduction.

The preliminary results in literature proved the above scheme by carrying out both two half reactions, i.e. the water reduction and oxidation, with the assistance of CH₃OH and AgNO₃, respectively [21].

However the activity is not high because the sample prepared by solvothermal method is in fact small single crystals in micrometer (see Fig. S2 in SI) and the recombination problem of e⁻ and h⁺ is severe. As shown in Fig. 1, the additive of 1 wt.% cocatalysts, such as CoO_x, RuO_x, Pt, Au, NiO_x and Ag, could significantly increase the H₂ evolution rate from 3.3 to 47.9 μmol/h/g (in 20 vol.% methanol aqueous solution). It is commonly agreed that a close contact can facilitate the charge (either e⁻ or h⁺) immigration from the catalyst to the corresponding cocatalyst, resulting in the extended lifetime of charge carriers [22,23]. In addition, these loaded cocatalyst nanoparticles on the surface behave as catalytic sites, and probably offer strong binding sites with substrates [11]. As shown in Fig. 1, the loading of cocatalysts in most cases leads to the enhancement of photocatalytic activity in one order. Here we need to mention that CoO_x and RuO_x are well-known cocatalyst for O₂ evolution. CoO_x and RuO_x particles can behave as collectors for h⁺ and accelerate its consumption by reacting with sacrificial reagents. As a consequence, it is beneficial to extend the lifetime of e⁻, and therefore increase the H₂ evolution rate. More importantly, the representative samples loaded with 1 wt.% RuO_x, Ag and Pt eventually endow Ga-PKU-1 crystallites observable ability of the pure water splitting (see Fig. 2). Note that the commonly used P25 (TiO₂ nanoparticles) without cocatalyst shows no activity of pure water splitting when applying the same experimental conditions.

Usually, Pt particles offer the water reduction sites and the RuO_x cocatalyst is capable of water oxidation, which means that photogenerated e⁻ and h⁺ prefers to move to Pt and RuO_x particles, respectively [24,25]. We selected Pt and RuO_x for the bimetallic loading onto Ga-PKU-1 and changed the loading content for each component. As shown in Fig. 3, it shows an optimized activity for 1 wt.% RuO_x-1 wt.% Pt loaded sample and the observed H₂ evolution rate is as high as 28.4 μmol/h/g in pure water. It is also interesting to observe that the sum of the activities for the samples with monometallic loaded (9.2 μmol/h/g for 1 wt.% RuO_x and 14.2 μmol/h/g for 1 wt.% for Pt) is smaller than 28.4 μmol/h/g. This is a hint that there exists a synergetic effect when loading an appropriate amount of RuO_x and Pt simultaneously. As is known, RuO_x and Pt cocatalysts can prompt the O₂ and H₂ generation, and their acceleration effects of consuming e⁻ and h⁺ show a good match when loading 1 wt.% RuO_x and 1 wt.% Pt in our case. Either increasing or decreasing the content of Pt or RuO_x would lead to a decrease of the activity. The combinations of RuO_x-Ag and Pt-Ag were also tested but without substantial increasing of the activity (see Fig. 3). In addition, the H₂ and O₂ production rates were determined for the optimized sample (see Fig. 4), which is very

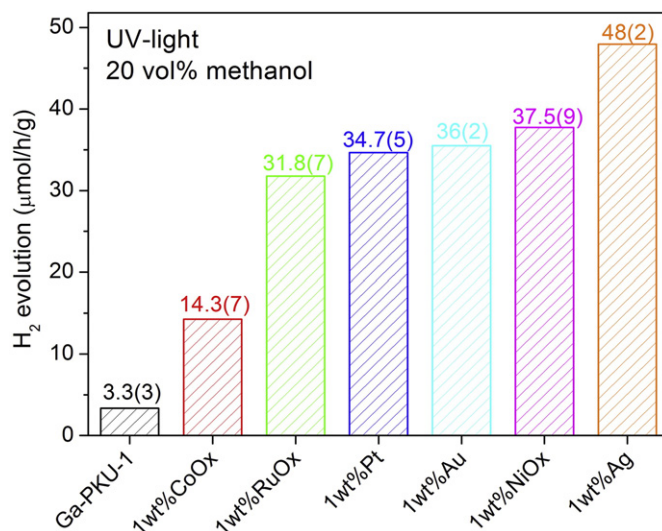


Fig. 1. H₂ evolution rates under UV-light irradiation for Ga-PKU-1, and those loaded with 1 wt.% CoO_x, RuO_x, Pt, Au, NiO_x, and Ag. Photocatalytic conditions: 50 mg of photocatalyst, 50 mL of 20 vol.% methanol aqueous solution.

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