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Single-Atom Sn-Loaded Exfoliated Layered Titanate Shows Photocatalytic Activity in Hydrogen Generation

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As the world's population grows and improves its standard of life, the demand for energy rises steadily to previously unheard-of heights, and to address this need, solar energy emerges as the leading clean, plentiful, and secure energy source [1]. One of the most promising solutions to reduce the burden on the environment and the supply of energy is solar energy since it is cheap, plentiful, and renewable. As a result, it is very desirable to capture solar energy and transform it into usable energy via photocatalytic processes [2]. Hydrogen has been highlighted as a viable energy carrier in various low greenhouse gas energy scenarios due to its high energy capacity and environmental friendliness [3]. Layered inorganic semiconductors, such as layered titanates (LT), have been used as scaffolds for designing highly efficient photocatalysts for hydrogen generation [4]. Intrinsic ionic conductivity increases when the layers of titanate is exfoliated during the dilute acid treatment, and K^+ ions are exchanged with protons in the interlayers [5], and this explains that exf-HTO also shows better results for hydrogen generation than pristine layered titanate. Here, we demonstrate that the single-atom-loaded layered titanates indicate better photocatalytic activity in terms of hydrogen production from water.

Layered potassium lithium titanate (KTLO) was prepared by solid-state reaction method using TiO_2, K_2CO_3, and Li_2CO_3 with a molar ratio of (4.1:6.0:0.7) [6]. The starting chemicals and three drops of C_2H_5OH were ground in an agate mortar with a pestle for 2 h, and the powder mixture was calcined in a muffle furnace at 600 °C for 20 h. After that, the mixture was cooled to room temperature. The sample was mixed for another 2 h and placed in the muffle furnace for the second calcination at 600 °C for 20 h. The obtained KTLO (0.5 g) was dispersed in 0.1 M HCl solution (100 mL) and stirred at room temperature. For the protonated layered titanate (HTO), the solution was stirred for one day at 600 rpm and separated by centrifuge, washed three times with C_2H_5OH (30 mL), and dried at room temperature. For exfoliation, the dispersion was stirred at 400 rpm for three days, and then, it was centrifuged, and a fresh solution of 0.1 M HCl (100 mL) was added to the precipitate and re-stirred under the same conditions at room temperature for 11 days. After the treatment, the dispersion was centrifuged and dried in a freeze-dryer for 24 h (exf-HTO). Adsorption of Sn on exf-HTO was done by adding 10 mg of exf-HTO to the 20 ppm of 20 mL $SnCl_2.2H_2O$ solution in a test tube and mixing the solution in the dark for three hours and then under the illumination of a solar simulator for one hour. As the exfoliated layers have a negative charge, cationic species can bind the layers via the electrostatic self-assembly process. The mixture was centrifuged and dried in a vacuum oven for 24 hours.

We present a new cost-efficient method to exfoliate layered titanates that includes a long treatment of layered titanate in dilute hydrochloric acid solution at room temperature, resulting in few-layered titanate. This method allows to exfoliate layered materials without using any organic species or harmful chemicals. Similarly, by using a facile method, single atom Sn has loaded on exfoliated layered titanate. The morphology and crystal structure of both exfoliated and pristine layered titanate is indicated by SEM, TEM, and AFM techniques, including aberration-corrected transmission electron microscopy. Thickness and number of layers can also be observed with these microscopic techniques. The HR-TEM and HAADF-STEM images of the exf-HTO indicate a single crystal structure from the lateral and edge views of the layer (Figure 1a,b). Although the lateral and edge views can be assigned to the XRD peaks with the obtained d values, the crystalline structure of the titanate layers can be observed from the HR-HAADF-STEM and HR-TEM images due to the low long-range order of the exfoliated layers. Since the XRD pattern demonstrates the crystallinity rarely because of the limited long-range order of the layers, the HR-TEM image was also processed from the edge view of the exf-HTO showing the number of stacking layers without any K^+ cation compared to the pristine KTLO (Figure 1c,d). Although the Sn loading amount is increased, Sn atoms stay in single atoms instead of nanoparticles, as can be seen from HAADF-STEM images (Figure 1e,f). The photocatalytic activity of these materials was investigated. The exfoliation process of pristine layered titanate makes an important difference in hydrogen evolution when it is compared with HTO and KTLO (Figure 2). The lowest activity result belongs to KTLO since it can still be in bulk form resulting in lower hydrogen evolution. Moreover, while hydrogen production is improving with the exfoliation process of the layered titanate, Sn atom loading also has a remarkable effect on photocatalytic activity.

In conclusion, exf-HTO was synthesized by a facile method and resulting in higher photocatalytic activity toward hydrogen evolution reaction. Single-atom Sn is also loaded on exfoliated layered titanate, and microscopic techniques showed that Sn atoms are dispersed on the surface of layers and agglomerated with higher loading amounts instead of forming nanoclusters. As a result, single-atom Sn-loaded layered titanates can be excellent materials to increase the photocatalytic activity of pristine layered titanates.

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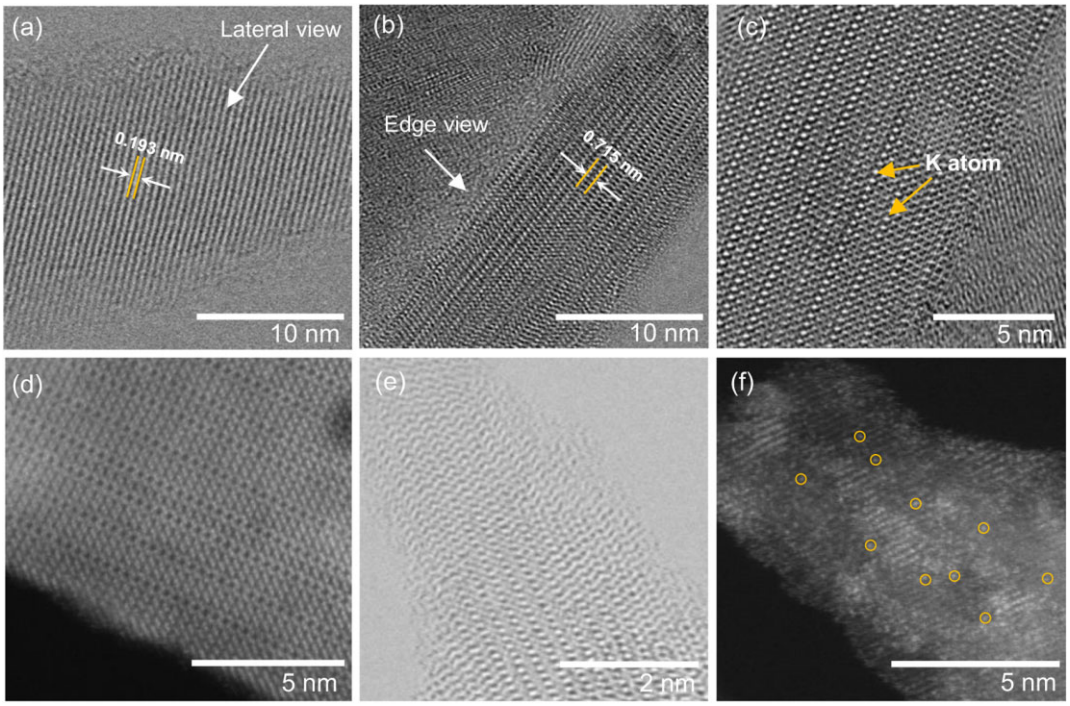


Fig. 1. HR-HAADF-STEM with a lateral view of the (200) plane according to the d value (0.193 nm) (a), and cross-sectional HRTEM of exf-HTO showing layer edges and 0.715 nm thickness (b), HRTEM image of K^+ unexchanged layered titanate (KTLO) (c), HR-HAADF-STEM image of ion-exchanged titanate, without any K^+ (d), and TEM (e), and HAADF-STEM (f) of Sn loaded exf-HTO with high loading of Sn amount [7].

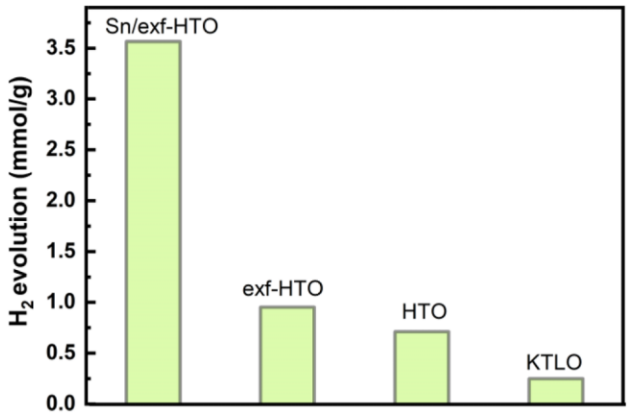


Fig. 2. Photocatalytic activity comparison of Sn/exf-HTO with pristine layered titanates and exfoliated titanates [7].

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