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Enhanced visible light photocatalytic water reduction from a g-C_3N_4/$SrTa_2O_6$ heterojunction

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ABSTRACT

A new g-C_3N_4/$SrTa_2O_6$ heterojunction photocatalyst was designed and prepared by *chimie douce* (soft chemistry) method where carbon nitride (g-C_3N_4) was deposited over the metastable perovskite phase of $SrTa_2O_6$. The morphological study of the heterojunction using SEM and STEM revealed that g-C_3N_4 nanofibers are dispersed uniformly on the surface of $SrTa_2O_6$ plates leading to the intimate contact between them. The heterojunction could achieve a high and stable visible light photocatalytic H_2 generation of 137 mmol/h/mole of g-C_3N_4, which is much larger than the amount of hydrogen generated by one mole of pristine g-C_3N_4. A plausible mechanism for the observed enhanced photocatalytic activity for the heterojunction is proposed on the basis of effective charge separation of photogenerated electron-hole pairs, supported by band position calculations and photo-physical properties of g-C_3N_4 and $SrTa_2O_6$.

1. Introduction

Semiconductor-based heterogeneous photocatalysis is considered as one of the most important green technologies capable of converting solar energy into chemically stored energy. The discovery of photoelectrochemical splitting of water by *n*-TiO_2 electrodes in the 1970s led to the study and development of numerous semiconductor-based photocatalysts including oxides, sulfides, and oxynitrides for solar fuels generation and environmental remediation [1–4]. However, most of these photocatalysts require ultraviolet (UV) light to generate electron-hole pairs, necessary for electrochemical processes at the surface of the semiconductors. An optimal photocatalyst should be: (i) active under visible light to maximize the use of solar spectrum, which consists of ~4% UV, ~45% visible, and ~50% infrared light, (ii) chemically and photo stable, and (iii) readily available and inexpensive [5,6]. In addition, for a photocatalyst to be active efficiently towards specific electrochemical processes, the position of its valence band (VB) and conduction band (CB) should be appropriately located [7,8]. For instance, for the photo-reduction of water to produce hydrogen, the bottom of the CB must be located at energy levels lower than 0 eV (*i.e.* H^+/H_2 energy level in NHE scale).

Band gap engineering is a common approach to extend the absorption range of UV active materials towards visible light region [9,10]. Besides doping with an anion, and/or a cation, great efforts have been made to design semiconductor heterojunctions by coupling a UV-active semiconductor with a second material (either a dye or another semiconductor) [11–13]. In addition to the extension of light absorption range towards the visible light region, properly designed heterojunctions can also lead to separation of photogenerated charge carriers, thus increasing their lifetime and allow them to participate in surface electrochemical processes [14–16].

Layered perovskites possess a wide variety of properties, such as chemical intercalation, ionic exchange, electron transport and excellent catalytic activities [17,18]. They consist of two-dimensional perovskite slabs interleaved with cations or cationic structural units[19]. A number of layered perovskites were investigated for their photocatalytic properties due to the possibility of modulating their physical properties by modifying their chemical composition and their structure by means of

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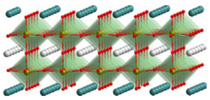
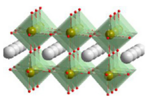
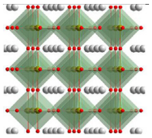
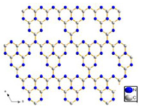
Table 1
Crystal structure representations and parameters of photocatalysts in this study.

Compounds	KSTO	HSTO	STO	CN
Crystal structure representation				
Crystal structure parameters	*I4/mmm* $a = 3.976(2)$ Å, $c = 21.711(5)$Å	*P4/mmm* $a = 3.869(9)$ Å, $c = 9.652(4)$ Å	$Pm\bar{3}m$ $a = 3.943(2)$ Å	$P\bar{6}$ $a = 6.508(7)$ Å, $c = 6.695(2)$ Å

ion-exchange, intercalation, or pillaring. Among different types of layered perovskite, Ruddlesden-Popper (RP) phases consist of two-dimensional anionic perovskite slabs held together by cations [20]. $A_2SrTa_2O_7$ (A = H, Li, K, and Rb)-type tantalates are new members of the RP-type layered perovskite composed of $\{SrTa_2O_7\}^{2-}{}_{\infty}$ perovskite sheets held together by Li^+, K^+, Rb^+, or H_3O^+ [21–23]. The layered acid phase converts to metastable three-dimensional cubic perovskite $SrTa_2O_6$ that can be isolated only through *chimie douce* synthesis method.

The recent discovery of graphitic carbon nitride (g-C_3N_4) as visible-light active photocatalyst has attracted tremendous attention in the last few years due to its layered structure, and its high chemical stability in aqueous solutions over a broad pH range [24]. Its relatively small band gap (~2.7 eV) makes it promising for large-scale photocatalytic applications [25]. Nevertheless, g-C_3N_4 suffers from shortcomings such as rapid recombination of photo-generated electron–hole pairs and relatively small surface area [26,27]. To overcome these drawbacks, several strategies, including elemental dopings with sulfur or phosphorus [28,29], engineering mesoporous structure [30–33], and coupling with other semiconductors to form heterojunctions, were used. In the context of heterojunction formation, the two-dimensional layered structure of g-C_3N_4 similar to graphene is amenable to hybridization with other components to form different heterojunctions. Several g-C_3N_4-based heterojunctions have been synthesized and displayed significantly higher photocatalytic activity under visible light irradiation [34,35].

We recently reported the synthesis, characterization, and photocatalytic activity of g-C_3N_4/$Sr_2Nb_2O_7$ heterojunction [36]. The incorporation of g-C_3N_4 in $Sr_2Nb_2O_7$ not only extends light absorption range of $Sr_2Nb_2O_7$ but more importantly, dramatically enhances the photocatalytic activity of g-C_3N_4. We showed how proper selection of materials and proper synthetic techniques to chemically form genuine and stable heterojunctions can lead to remarkably enhanced photocatalytic activity. Here, we report results of a study in which we extended our scope to *in situ* synthesis of a heterojunction in which one component is a metastable oxide. Thermal condensation of melamine in the presence of $H_2SrTa_2O_7$ led to the formation of g-C_3N_4/$SrTa_2O_6$ (CN/STO) heterojunction. Metastable oxide ($SrTa_2O_6$) was formed during dehydration/condensation of $H_2SrTa_2O_7$. Thus, CN/STO heterojunction was synthesized *in situ* at relatively low temperatures using so-called "***chimie douce***" method, previously applied to the synthesis of metastable oxides as reported by Oliver and Mallouk [37]. In addition to the photocatalytic study of CN/STO heterojunction, we also performed a comprehensive study of $K_2SrTa_2O_7$ (KSTO), its proton exchanged form, $H_2SrTa_2O_7$ (HSTO), and the metastable perovskite, $SrTa_2O_6$ (STO). The crystal structure representation along with refined unit cell parameters of KSTO, HSTO, STO, and CN are presented in Table 1. The photocatalysts studied were characterized by a variety of techniques, and their photocatalytic performances in the reduction of water under visible and UV light irradiation were evaluated. The CN/STO heterojunction was found to exhibit remarkably enhanced the photocatalytic generation of H_2 under visible light irradiation.

2. Experimental section

2.1. Synthesis

2.1.1. Preparation of $K_2SrTa_2O_7$ (KSTO) and hydrated KSTO

The compound $K_2SrTa_2O_7$ was synthesized by a high-temperature solid-state reaction using potassium citrate ($K_3C_6H_5O_7 \cdot H_2O$, Fisher Scientific, 99.0%), strontium nitrate ($Sr(NO_3)_2$, Alfa Aesar, 99%) and tantalum oxide (Ta_2O_5, Alfa Aesar, 99.95%) as precursors. In a typical synthesis, 5 mmol of each precursor (33% molar excess $K_3C_6H_5O_7 \cdot H_2O$) were ground together in an agate mortar to form a homogeneous powder, then transferred to an alumina crucible, and heated to 500 °C at the rate of 2 °C/min. The temperature was maintained at 500 °C for 4 h to decompose the citrate precursors, then cooled to room temperature. The product was ground again to obtain a fine white powder, then transferred back to an alumina crucible and heated to 1000 °C at a rate of 10 °C/minute and held at this temperature for 12 h, then cooled to room temperature to obtain a white microcrystalline powder, which was confirmed to be anhydrous $K_2SrTa_2O_7$ by PXRD. The anhydrous phase is spontaneously hydrated to form $K_2SrTa_2O_7 \cdot 0.92H_2O$ upon exposure to air for 48 h or washing with water, as previously reported in the literature [21,22,37]. The number of water molecules per formula unit was determined by TGA.

2.1.2. Preparation of $H_2SrTa_2O_7$ (HSTO)

The acid form $H_2SrTa_2O_7$ was obtained by ion exchange of $K_2SrTa_2O_7$ using 4 M HNO_3 aqueous solution. In a typical experiment, 2.00 g of $K_2SrTa_2O_7$ was added to 250 mL 4 M HNO_3 at room temperature and stirred for 4 days. The acid solution was refreshed twice during this period. The white solid, $H_2SrTa_2O_7$ was isolated by filtration, and washed with deionized water, then dried under vacuum at 25 °C for 6 h. Complete exchange of K^+ ions with protons was confirmed by induced coupled plasma optical emission spectroscopy (ICP-OES) analysis.

2.1.3. Preparation of g-C_3N_4/$SrTa_2O_6$ (CN/STO) heterojunction, pristine g-C_3N_4 (CN), and $SrTa_2O_6$ (STO)

The heterojunction, g-C_3N_4/$SrTa_2O_6$ (CN/STO), was synthesized by thermal decomposition of melamine ($C_3H_6N_6$, Sigma-Aldrich, 99.0%) in the presence of $H_2SrTa_2O_7$. In a typical reaction, 1.000 g of HSTO was added to 50 mL of water containing 5.000 g of melamine (the 1:5 HSTO: Melamine mass ratio was determined from optimization experiments done to determine the best performing heterojunction, Fig. S12, ESI). The mixture was sonicated for 15 min, stirred for 30 min, then transferred to a Teflon-lined stainless steel autoclave, sealed, and heated at 200 °C for 24 h under autogenous pressure. The product was filtered and washed twice with water to obtain a white microcrystalline powder. The white powder was