



Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ nanobelts exhibiting remarkable photocatalytic properties under visible-light illumination

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ABSTRACT

We demonstrated for the first time that Na-intercalated $\text{H}_2\text{Ti}_3\text{O}_7$ ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$) NBs, prepared in the typical alkaline hydrothermal process, can effectively absorb visible light to carry out photocatalytic reactions. With the capability of effective light absorption in visible range, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs performed much better in the photodegradation of thionine than the other three counterpart products including $\text{H}_2\text{Ti}_3\text{O}_7$, mixed $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ and anatase TiO_2 under visible-light irradiations. As compared to the relevant commercial products like P-25 TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ powders, the as-synthesized $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs exhibited superior photocatalytic efficiency under UV illumination, demonstrating their potential as an efficient photocatalyst in relevant redox reactions. A further enhancement in the photocatalytic activity can be achieved for $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs when Au nanoparticles of suitable amount were deposited on their surfaces. This improvement is due to the band offsets between $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ and Au, which may promote charge carrier separation to favor the photocatalysis. The recycling test reveals that Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs could be promisingly utilized in the long-term course of photocatalysis. Furthermore, the result of performance evaluation under natural sunlight shows that the current Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs can be used as highly efficient photocatalysts which may practically harvest energy from sunlight.

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1. Introduction

With the concern about the environmental and energy issues, there has been a growing interest in developing semiconductor photocatalysts that can produce chemical energy from light [1,2]. The basic concept of photocatalysis using semiconductors involves the generation of charge carriers within semiconductors upon light irradiation, followed by the utilization of these carriers to carry out chemical reactions. In general, the fast recombination of photoexcited charge carriers in semiconductors would diminish the resulting photocatalytic efficiency. To boost photocatalytic performance, the photoexcited electrons and holes must be separated to suppress the direct recombination of them. Through the combination with metals, semiconductors may exhibit superior photocatalytic activities. This is due to the presence of semiconductor/metal interface that can promote charge carrier separation [3,4]. In semiconductor/metal heterostructures, metal can serve as an efficient electron scavenger for semiconductor. The photoexcited free electrons of semiconductor would thus preferentially transfer to the metal domain, leading to the effective separation of charge carriers to favor the subsequent photocatalysis. Till now,

many hybrid systems composed of semiconductors and metals, such as core-shell metal-semiconductor nanocrystals [5,6], metal-decorated semiconductor nanorods [7,8], and metal-deposited semiconductor nanoparticles [9,10], have been proposed and characterized to demonstrate their remarkable performance in relevant photocatalytic processes.

The most widely used semiconductor photocatalysts have been metal oxides like TiO_2 , which possesses ultraviolet (UV) absorption ability only because of its large bandgap energy. In order to practically harvest energy from sunlight, a lot of research attention is paid to manufacture photocatalysts that can respond to visible light. It has been extensively demonstrated that II-VI group semiconductors such as CdS [11,12] and CdSe [13,14] exhibit fascinating photocatalytic activities upon visible-light irradiation. The potential danger of cadmium to the organisms however limits the practical development for these cadmium derivative photocatalysts. On the other hand, through the doping of suitable elements to create an additional electronic level in the energy gap, TiO_2 can absorb visible light to carry out photocatalytic reactions [15–17]. The introduction of foreign elements into TiO_2 crystals was usually accomplished under elaborate reaction conditions, for example, high reaction temperatures [18,19] and long period of treatment in harsh atmospheres [20,21]. Such requirement complicates the configuration of manufacture process and considerably raises the cost for scale-up production. Moreover, a depressed carrier mobil-

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ity as well as the low quantum yield were observed for the doped TiO_2 under visible-light illumination [22,23], which may further hinder its performance in photocatalysis. Therefore, creation of a more facile, mild synthetic approach from which one could obtain highly efficient visible-light-responsive photocatalysts is crucial to the development of photocatalysis technology.

Nanostructures of sodium titanate ($\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$, $3 \leq n \leq 6$) and hydrogen titanate ($\text{H}_2\text{Ti}_n\text{O}_{2n+1}$) have drawn much research attention in recent years due to their unique physicochemical and chemical properties [24], which open up potential applications in photocatalysis [25,26], chemical adsorption [27,28], hydrogen storage [29,30], lithium batteries [31,32], and biomedics [33,34]. Since the pioneering work by Kasuga et al. [35,36], alkaline hydrothermal approach has been widely employed to produce these Ti–O based nanostructures. Through carefully controlling the hydrothermal conditions, various nanostructures of titanates including nanoparticles, nanotubes, and nanobelts can be readily obtained in high yield [37]. As one of the Ti–O series products derived from the alkaline hydrothermal process, Na-intercalated $\text{H}_2\text{Ti}_3\text{O}_7$ ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$) [38–41] does not draw too much research attention, especially in the field of photocatalysis. This is probably due to the ion-exchangeability of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$, which enables feasible compositional transformation into its protonated form of $\text{H}_2\text{Ti}_3\text{O}_7$.

In this work, we demonstrated for the first time that $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ nanobelts (NBs) can effectively absorb visible light to carry out photocatalytic reactions. NBs of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ were synthesized in a typical alkaline hydrothermal reaction by using P-25 TiO_2 powder as precursor [37]. This synthetic route is simple, reliable and can be easily scaled-up to achieve mass production. In addition to $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs, three other Ti–O counterpart products including hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7$), mixed sodium titanate/titania ($\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$), and single-phase anatase titania (TiO_2) were also prepared by a proper post-treatment operation. We evaluated and compared the photocatalytic performance of the four Ti–O based samples through the photodegradation of an organic dye, thionine (TH). With the capability of effective light absorption in visible range, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs performed much better in the photodegradation of TH than the other three counterparts under visible-light irradiations. As compared to the relevant commercial products like P-25 TiO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ powders, the as-synthesized $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs exhibited superior photocatalytic performance under UV illumination, demonstrating their potential as an efficient photocatalyst in relevant redox reactions. A further enhancement in the photocatalytic activity can be achieved for $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs with the decoration of Au nanoparticles. Moreover, no appreciable decay of photocatalytic efficiency was found for Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs after repeated uses and recycled, revealing their promising potential in the long-term course of photocatalysis. The photocatalytic performance under natural sunlight was also examined, and the result shows that the current Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs can be used as highly efficient photocatalysts which may practically harvest energy from sunlight.

2. Experimental

2.1. Chemicals

All chemicals were of analytic grade and used without further purification.

2.2. Preparation of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs

$\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs were synthesized with a hydrothermal method in the concentrated NaOH solution. Typically, commercial TiO_2 powder of 1.0 g (Degussa, P-25) was dispersed in 10 mL

absolute ethanol, and then mixed with 10 mL NaOH aqueous solution (10 M) under vigorous stirring for 10 min. The mixed solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL. After being sealed, the autoclave was heated and maintained at 200 °C for 24 h, and then cooled to room temperature naturally. The resultant white slurry was collected by suction filtration and washed with deionized water until the pH value of washing solution reached 7.0. The product ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs) was then dried at 60 °C in air for later use.

2.3. Acid-washing treatment

$\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs of 0.3 g were immersed in 500 mL HCl solution (0.1 M) for 24 h, producing their protonated form of $\text{H}_2\text{Ti}_3\text{O}_7$. The product ($\text{H}_2\text{Ti}_3\text{O}_7$ NBs) was washed with copious amounts of deionized water and dried at 60 °C in air for later use.

2.4. Thermal calcination treatment

To prepare single-phase anatase TiO_2 NBs, $\text{H}_2\text{Ti}_3\text{O}_7$ NBs of a fixed amount were calcinated at 700 °C in air for 4 h. For comparison purpose, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs were also allowed for thermal calcination under the same conditions, which led to the formation of mixed $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ with irregular morphology.

2.5. Decoration of Au nanoparticles

To decorate NBs with Au nanoparticles, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs of 6.0 mg were first dispersed in the reaction solution containing 60 mL deionized water and 30 mL ethanol, followed by the addition of 600 μL NaOH solution (0.1 M). After heated to 50 °C, 60 μL of HAuCl_4 solution (5 mM) was added. Note that ethanol was used as the reducing agent [42] to facilitate the growth of Au. The mixed solution was kept at 50 °C for 3 h, resulting in the deposition of Au nanoparticles on the surfaces of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs. The product (Au-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs with the Au content of 1.0 wt%) was centrifuged, washed with deionized water and ethanol, and then dried at 60 °C in air for later use. In this work, various volumes of HAuCl_4 solution (5 mM) were employed to produce Au-decorated NBs with increasing Au contents. Besides, two other novel metals (Ag and Pt) were also deposited on NB surfaces, with which we may learn the effects of various metal decorations on the photocatalytic properties of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs. For the synthesis of Ag-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs, AgNO_3 was used as the Ag source, followed by the same procedure performed in the preparation of Au-decorated sample. As to the fabrication of Pt-decorated $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ NBs, H_2PtCl_6 was used as the Pt source, followed by the same procedure mentioned above except for the reaction temperature and reaction time set at 80 °C and 6 h, respectively.

2.6. Photocatalytic performance measurement

The photocatalytic performance of the four Ti–O based samples was evaluated by the photodegradation of thionine (denoted as TH) under both UV and visible-light irradiations. A quartz tube with a capacity of 20 mL was used as the photoreactor vessel. The optical system used for TH photodegradation consisted of a xenon lamp (500 W, 175 mW/cm^2) and a bandpass filter (bandwidth of 400–700 nm) which enabled irradiation in visible range. All the photocatalysis experiments were conducted at room temperature. In a typical experiment, 5.0 mg of photocatalyst was added into 20 mL of TH solution in the photoreactor vessel. The TH solution was prepared by dissolving thionine acetate ($\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$) in deaerated ethanol with a concentration of 1.0×10^{-5} M. Note that ethanol was used as the sacrificial hole scavenger for photocatalysts to facilitate the further utilization of photoexcited electrons.

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