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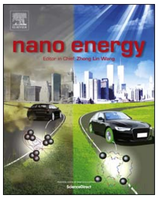

Perovskite-based nanocubes with simultaneously improved visible-light absorption and charge separation enabling efficient photocatalytic CO_2 reduction

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ABSTRACT

Finding an ideal model to disclose the role upon tuning band structure and charge separation of wide-bandgap perovskite semiconductors by introducing suitable heteroatoms remains a huge challenge in photocatalysis. Herein, we propose an efficient pathway to increase the light absorption and charge separation for nitrogen and oxygen-vacancy confined in sodium tantalate nanocubes (V_o-NaTaON) and nitrogen-doped graphene quantum dots (N-GQDs) grafted V_o-NaTaON nanocubes by solution-etching-induced phase-transition and in-situ reduction strategies. First-principles calculations demonstrate that the simultaneous incorporation of nitrogen and oxygen-vacancy in sodium tantalate can effectively regulate the electronic structure of sodium tantalate. The analysis of UV–vis spectra and electron paramagnetic resonance reveal that the synergistic contribution of nitrogen and oxygen-vacancy endows the wide-bandgap perovskites tuning the band absorption region from UV (315 nm) to visible regime beyond 600 nm. As expected, an optimized V_o-NaTaON catalyst was developed, exhibiting superior broad spectrum photochemical reduction of CO_2 to fuels. Moreover, N-GQDs/V_o-NaTaON heterojunctions further improve the broad spectrum CO_2 photoreduction due to the synergetic catalytic effect of simultaneously improved light-absorption and charge separation. This work may open up more opportunities in the design of efficient photocatalysts for applications in solar photochemical conversion.

1. Introduction

The depletion of fossil fuel and the increasing CO_2 level reserves attract extensive concerns upon the effects on the global energy supply and climate change. To overcome these problems, the utilization of abundant solar energy is one of the most promising approaches towards the effective conversion of CO_2 into valuable fuels [1]. Since the discovery of the Fujishima–Honda effect of TiO_2 photoelectrode reported in 1972, a large number of semiconductors for various photocatalytic applications have been achieved [2–6]. However, many photocatalysts meet the limited requirements such as narrow light harvesting, short lifetime of photoinduced charges, low efficiency and stability [7–9]. Thus, there is an urgent need to develop highly efficient and stable visible-light-driven photocatalysts.

To address the limitation of different UV-light-responsive oxides for solar-to-fuel conversion, different technical approaches, such as metal ions doping [10], (oxy)nitrides [11] and (oxy)sulfides [12], and reduction of oxides [7–9,13], have been conducted, extending the light absorption to the visible region. Due to a higher potential energy of the N 2p orbital than that of the O 2p orbital, the introduction of nitrogen into oxides tunes their band structures from UV to visible regime through shifting the conduction and valence band positions. Generally, various visible-light-responsive oxynitrides, such as TaON [6], GaN:ZnO [11], $LaTiO_2N$ [14], $Sr_2Ta_2O_{7-x}N_x$ [15], $Ba_5Ta_4O_{15-x}N_x$ [16], etc, were synthesized by high-temperature ammonia treatment (800–1300 °C), constrainting the component, crystal structure and relative properties under harsh environment. Moreover, the ammonothermal method and urea-assisted chemical route as alternative ways were also employed in the synthesis of (oxy)nitrides [17]. Especially, sodium tantalate as effective perovskite-type oxide photocatalyst with wide band gap around 4.0 eV, was reported for UV-light-driven water splitting [18]. However, owning to the low content of nitrogen incorporation, the traditional nitrogen-doped photocatalysts usually limit the light absorption [19]. Herein, we attempt to put

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forward the conceptually etching chemistry to novel chemical reactions of solids to access the oxynitrides under the mild condition. Thus, it would be rather imperative to build the catalyst model and gain in-depth understanding on the relationship between light absorption and solar-to-fuel conversion over the oxynitrides.

To further increase solar light harvesting, the promising way is the oxygen-vacancy engineering, also providing the active sites to inhibit the detrimental electron-hole recombination [20]. For instances, the oxygen-vacancy confined in various nanosheets show significantly promoted solar photocatalytic activity due to the enhanced carrier separation efficiency [21,22]. By introducing oxygen vacancies, the photocatalytic activities of hydrogen-treated TiO_2 and WO_3 nanostructures can be enhanced due to the increased donor density [23–25]. As a result, the manipulation of the spatial location of oxygen vacancies as the key prerequisite could extend the solar light absorption and overcome the charge carrier diffusion restrictions [20,22]. To efficiently harvest visible light, spatial location engineering of oxygen-vacancy to novel chemical reaction of extended solids is an exciting direction for developing the desired oxynitride photocatalysts covering the visible region as widely as possible.

Although the introduction of dopant atoms into the photocatalysts has increased the visible-light absorption, the dopants in the defective photocatalysts may serve as the electron-hole recombination centers, hindering the further improvement upon the photocatalytic performance [23]. To address this problem, the heterojunction engineering is a prospective solution for the efficient separation and transfer of the photogenerated electrons and holes [26–28]. With regard to carbon-based photocatalysts, the unique features of graphene are high conductivity, excellent room-temperature mobility of charge carriers, large specific surface area and high optical transmittance [29–31]. Especially, the coupling semiconductors with graphene is extensively recognized to be an effective strategy to improve the photocatalytic performance due to the conductive platform and the intimate interfacial contact between graphene and semiconductors enabling the acceptance and shuttle of photogenerated electrons from band-gap-excitation of semiconductors [31]. Graphene oxide quantum dots (GQDs), as an important graphene derivative, are able to be photo-excited under visible light and act as a photosensitizer for semiconductors [32]. For instances, bimetal-graphene-semiconductor coaxial nanowires, graphene quantum dots-based hybrids and N-doped graphene quantum sheets/silicon nanowires exhibit enhanced photocatalytic activity and structural stability over the solar-to-fuel conversion [33–35]. To surface modification by addition of functionalities, direct substitution with heteroatoms in the graphene lattice induces the modulation of optical and electronic properties [36]. To date, it is still challenging to develop the desired heterojunction by use of nitrogen-doped graphene quantum dots decorated oxynitride hybrids towards solar-driven photocatalytic application.

In this work, taking the spatial location engineering into consideration, we theoretically and experimentally propose the nitrogen and oxygen-vacancy confined in perovskite sodium tantalum oxynitride nanocubes to be an ideal material model. This system represents an excellent platform to shed light on the correlation of the oxygen-vacancy/nitrogen-catalysis relationship through the development of the visible-light-responsive oxynitride and the suppressing of the detrimental electron-hole recombination. Especially, the novelties of this work is aim to the achievement of new photocatalysts and the application of CO_2 photoreduction owing to the following strategies: (i) developing this perovskite-type sodium tantalum oxynitride photocatalyst with solar light harvesting from UV (λ=315 nm) to visible regime above 600 nm by use of spatial location engineering of nitrogen and oxygen-vacancy as synergistic regulations for efficient band structure tuning and charge separation; and (ii) achieving nitrogen-doped graphene quantum dots grafted V_o-NaTaON as novel heterojunctions to inhibit the electron-hole recombination, thus facilitating the highly efficient photochemical reduction reaction. Moreover, mechanistic information gleaned from the time-resolved photoluminescence spectra has elucidated the relationship between the photochemical reduction performance and the electron-hole separation efficiency. As a result, this work opens new avenues towards the design and development of oxynitride-based materials for solar-driven CO_2 conversion.

2. Experimental section

2.1. Preparation of V_o-NaTaON nanocubes

Sodium tantalum oxynitrides were prepared by a facile chemical etching process. Typically, according to our previous works [37,38], the Ta_3N_5 precursors were dispersed in NaOH solution and then transferred to autoclave at 200–240 °C. After the etching chemical reaction, the nitrogen confined in sodium tantalate (NaTaON) nanocubes were obtained. In a typical procedure by in-situ reduction strategy, 100 mg NaTaON nanocubes, 200 mg $NaBH_4$, and 100 μL H_2O were filled into individual 2 mL, 6 mL and 6 mL quartz cuvette, respectively. Then the sealed quartz cuvette including NaTaON, $NaBH_4$, and H_2O was transferred to the autoclave and kept at this temperature. After cooling down, the nitrogen and oxygen-vacancy confined in sodium tantalate (V_o-NaTaON) nanocubes were achieved.

2.2. Preparation of N-GQDs/V_o-NaTaON heterojunctions

Graphene oxide (80 mg) treated in a flow of NH_3 gas at 500 °C, was dispersed into ammonium hydroxide (30 wt%), then transferred to the autoclave at 230 °C for 14 h. After centrifugation and dialysis, the as-prepared nitrogen-doped graphene quantum dots (noted as N-GQDs) were dispersed in the Ta_3N_5 and NaOH mixture solution by use of the same method of V_o-NaTaON nanocubes. Finally, N-GQDs/V_o-NaTaON heterojunctions were achieved, as shown in the schematic illustration of the synthesis of N-GQDs/V_o-NaTaON nanocubes (Scheme S1).

2.3. First-principles calculations

With regard to the first principles calculations, the plane-wave pseudopotential method based on density functional theory was used [39,40]. The geometry optimizations and the electronic structure calculations were performed by CASTEP program [41]. Under geometry optimization, the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) function was employed for the exchange correlation contribution [42]. For the calculation of band structure and density of states, the screened exchange local density approximation (sX-LDA) route was adopted [43]. A 2×1×1 supercell has been constructed to investigate the effects upon the band-gap structure of nitrogen and oxygen-vacancy confined in $NaTaO_3$ crystals. The ion–electron interactions are modelled by the norm-conserving pseudopotentials for all constituent elements, where Na $2s^22p^63s^1$, Ta $6s^25d^3$, O $2s^22p^4$ and N $2s^22p^4$electrons were conducted as the valence electrons [44]. A kinetic energy cutoff of 600 eV is chosen with Monkhorst–Pack k-point meshes spanning less than $0.04/\text{Å}^3$ in the Brillouin zone [45].

2.4. Characterization

The obtained products were examined by powder X-ray diffraction (XRD). The morphologies of the powders were performed by a field-emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The chemical states of the samples were checked by X-ray photoelectron spectroscopy (XPS) in a VG Multilab 2009 system. The optical properties were measured by UV–vis absorption spectroscopy (UV-2550, Shimadzu). Low temperature electron paramagnetic resonance (EPR) spectra were checked using a JEOL JES-FA200 EPR spectrometer at 140 K. The photoluminescence spectra were measured with a fluorescence spectrophotometer. Raman