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Two-dimensional defective tungsten oxide nanosheets as high performance photo-absorbers for efficient solar steam generation

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ABSTRACT

Efficient solar-driven evaporation has engendered great interests as a sustainable and environmental approach for solar energy utilization. The development of high-performance photo-absorbers is of paramount importance for realizing efficient solar evaporation. Among the light-harvesting materials, transition metal oxide (TMO) is regarded as one of the most promising substitutes for photothermal conversion. Here, two-dimensional (2D) defective tungsten oxide (WOx) nanosheets are prepared via introducing oxygen vacancies in WO_3. It demonstrates that the novel 2D plasmonic WOx nanosheets can be used as high performance photo-absorbers for efficient solar steam generation, displaying broadband and intense light absorption in the full solar spectrum due to the tunable localized surface plasmon resonances. Its evaporation efficiency reaches ~ 78.6% under 1 kW/m^2 (one sun) irradiation. The result reveals that adjusting the surface nanostructures and morphologies of TMO can be thought to be a potential strategy to promote the light-harvesting performance for solar steam generation. This study is significant for further exploring potential applications of plasmonic semiconductors in sterilization, desalination, and photothermal power through solar steam generation.

1. Introduction

Water scarcity, environmental pollution and climatic anomaly are serious global challenges in contemporary society [1,2]. The obtained energy derived from the combustion of fossil fuels such as coals, oils and gases, inevitably leads to large carbon footprints, which contribute to the aggravation of atmospheric pollution and global warming [2]. To alleviate the severe global energy crisis and environmental problem, the development of renewable energy sources, especially solar energy, which exists as an inexhaustible, sustainable and green energy, has triggered the extraordinary progress in enabling low-carbon economy and renewable energy utilization [3–6]. In recent years, solar-induced steam evaporation as a promising technology has attracted significant attention, due to its minimum carbon footprint, low cost and high efficiency, and has many applications in various fields from water purification, power generation to sterilization [7,8].

Gold nanoparticles were firstly reported to convert light to heat under specific laser illumination for solar steam generation [9]. Therewith, tremendous efforts have been implemented to enhance the solar-evaporation efficiency and promote their practical applications [10–12]. With the development of photothermal conversion materials for solar steam generation, the trend of photo-absorbers can be summarized into three main branches, including noble metals (Au, Ag, Cu, etc) [13–17], metals oxides/sulfides (TiO_2, Fe_3O_4, CuS_x, etc) [18–24] and carbon-based materials (carbon black, graphene, carbon nanotube, etc) [16,25–38]. The nanomaterials for photothermal conversion are dispersed uniformly in the liquid mediums as nanofluids or assembled into the macro hierarchical structures floating on the water surface, such as plasmonic films [20,38], foams and aerogels [28,37]. Through the surface plasmon resonance effect or energy level transition mechanisms, the sunlight absorbers can convert light to heat for low-temperature solar vapor generation. However, these designs and structures possess a relatively poor mechanical stability and complicating fabrication processes. Besides, the inevitably high price and low abundance of novel metal-based materials are non-negligible factors for large-scale applications. Recently, among all nanostructured materials, two-dimensional (2D) materials, i.e. graphene and its derivatives materials [39], transition metal carbide (MXenes) [40], transition metal dichalcogenides (TMDs) [41], exfoliated metal-organic frameworks (MOFs) and zeolite nanosheets [42,43], have attracted increasing attention due to their superior mechanical properties, excellent thermal stability and remarkable photothermal conversion efficiency.

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Especially, to realize the portable and economical utilization of solar energy, the non-noble-metal oxides materials could be taken into consideration as an ideal material, because of their natural abundance and comparable performances. [44,45].

TMO is a promising light-absorbing material for photothermal conversion. For instance, the non-stoichiometric MoOx quantum dots [22], mesoporous black TiO_2 thin films and hierarchical carbon coated Fe_3O_4 nanospheres [18,23] have been reported for boosting their photothermal conversion property, due to their larger surface area and stronger light absorption compared with the bulk materials. Another important reason for efficient photothermal conversion is the localized surface plasmon resonance (LSPR) of TMO [46–48]. Although WOx nanoparticles with tunable LSPR effect have also been successfully synthesized [49]. However, the WOx-based photothermal conversion materials for direct solar steam generation has not been investigated yet.

In our previous study, we developed a series of solar steam generation systems, including noble metals nanoparticles [16,17], graphene-related materials and scalable solar steam generation devices [20,25,27,31–33]. Here, the 2D defective WOx nanosheets are prepared through a facile bottom-up approach, and the resulted WOx nanosheets exhibit different colors (from light-green to black) and superior light absorption of the solar spectrum. it is demonstrated that the solar steam generation efficiency of the 2D defective WOx nanofluids reaches ~ 78.6%. Introduction of oxygen vacancies to the 2D Wox, as a promising strategy, is beneficial to promote their LSPR effect. This work exhibits the potential of the WOx-based material as an excellent light absorber in the utilization of solar energy.

2. Materials and methods

2.1. Materials

Sodium tungstate dehydrate ($Na_2WO_4·2H_2O$, 99.5%) and commercial WO_3 (99.9% metal basis) were purchased from Aladdin's official site. Citric acid (CA, > 99.5%) was purchased from Sigma-Aldrich. D (+)-Glucose (AR), hydrochloric acid (36–38%, AR) and anhydrous ethanol (AR) were supplied by Sinopharm Chemical Reagent Co. Ltd. Ultra-deionized water was used in the processes of synthesis and dissolution. All chemical reagents with analytical grade were used as received without further purification. All glasswares in the experiments were soaked and cleaned with aqua regia and DI water for several times.

2.2. Synthesis of 2D defective WOx nanosheets

The 2D defective WOx nanosheets were synthesized by a multistep process, which contains the exfoliation of layered tungstic acid to 2D WOx nanosheets and then the creation of oxygen vacancies in the 2D WOx nanosheets. Briefly, $WO_3·H_2O$ nanosheets were firstly synthesized as a precursor in an autoclave using a mild hydrothermal method. Then, the defective WOx nanosheets with controlled concentrations of oxygen vacancies were obtained through a calcination method in Ar/air atmosphere with different calcination times, as shown in Fig. S1. Operational details are provided in Section S1. The obtained samples were collected for further using and characterization.

2.3. Synthesis of 2D defective WOx nanofluids

The defective WOx nanofluids were prepared by dispersing the same dose of the 2D WOx nanosheets into deionized water, following by mild magnetic stirring for 3 min and ultrasonicating for 30 min in ultrasonication bath to gain uniform mixtures. The concentration of the 2D WOx nanosheets in all dispersions was 2 mg/mL. All obtained nanofluids used in the experiment were out of further separation and purification. Here, as a matter of convenience, the commercial WO_3 nanosheets was named as WO nanosheets, and the others were respectively labelled from WO_{Air2} to WO_{Ar2} according with their color deepened.

2.4. Characterization

Scanning electron microscopy (SEM) images of the 2D defective WOx were observed by scanning electron microscope (JSM7100F, Japan). And the high-resolution TEM (HR-TEM) images were obtained using a TECNAI G2 20 U-Twin instrument (Netherlands), which was operated at an acceleration voltage of 200 kV to characterize the sizes and crystal structures of defective WOx nanosheets. Element distribution of 2D defective WOx was detected by the X-ray energy dispersive spectroscopy (EDS; JSM6510LV, Japan). The absorbance spectra of all samples were measured through a UV–vis–NIR spectrophotometer (Shimadu UV–vis–NIR UV-3600 double beam spectrophotometer), using fine $BaSO_4$ powder as reference baseline. The powder X-ray diffraction (XRD) analysis was evaluated by a D8-Advance diffractometer (Bruker, Germany), employing a Cu Ka radiation source (k = 0.15418 nm) at 40 kV and 40 mA. XPS spectra were obtained by using a Physical Electronics 5000 Versa Probe II Scanning ESCA (XPS) Microprobe. The temperatures of all samples before and after irradiation were measured by the IR-camera (FLIR E4) and thermocouples.

2.5. Evaluation of solar steam generation

To evaluate solar steam generation performance of the 2D defective WOx nanosheets, the mass change and temperature as a function of time were monitored by an experimental setups under solar illumination. The simulated solar light was generated by a Xenon lamp (CELHXF300, Education Au-light Co., Beijing, China) with a solar filter (AM1.5). 20 mL WOx nanosheets dispersion were poured into a Petri dish (6 cm diameter), which is embedded in the PE foam with an aperture (6 cm diameter) to limit the heat loss and the irradiation on the surface of dishes (See Fig. S2a). A high accuracy balance was used to record mass changes while the real-time data was synchronously transferred to the experimental computer. To specifically investigate the solar-thermal conversion capability, 10 mL nanofluids were dispersed in a 15 mL quartz tube half coated by a thermal insulation foam to reduce heat loss, and a thermocouples was inserted in the tube to monitor the liquid temperature change. The test devices are shown in Fig. S2b. Moreover, an infrared camera (FLIR E4 Pro, America) was applied to acquire the thermography of all samples. Different light intensities were identified by a full-spectrum optical power meter (CEL-NP2000-2, Beijing Education Au-light Co., Ltd.). In addition, the containers (Petri dishes and tubes) used in the test were all made from quartz, which had the same light transmittance and heat capacity.

3. Results and discussion

In this work, the 2D WOx nanosheets were successfully synthesized via a facile surface defect engineering (See Fig. S3). As shown in Figs. 1a and S4a, the SEM images indicate the 2D nanosheets morphologies of WOx. It could be noticed that all the as-prepared samples exhibited average sizes of ≈ 150 nm and average thickness of ≈ 5 nm, which is approximately six layers of the monoclinic WO_3 unit cells [45]. TEM images as shown in Fig. 1b and c also directly affirm the 2D sheet-like morphologies of WOx nanosheets. In addition, the morphologies and sizes of the samples didn't suffer from significant changes after introducing the oxygen vacancies (See Figs. 1a–c and S4a–c). Through the HR-TEM observing, the 2D defective WOx nanosheets exhibit clear lattice fringes, which verify their high crystallinity. According to Fig. 1d, the lattice spaces of 3.65 Å and 3.84 Å match well with the (200) and (002) atomic planes of WOx, respectively. As well as the angle is 90 °C, which is consistent with the lattice parameters of monoclinic WOx [45].