

Hydrothermal synthesis and visible-light-driven oxygen production from water splitting of InVO₄ micron-rods

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A new type of InVO₄ micron-rods photocatalyst was successfully synthesised by a facile additive-assisted hydrothermal method as a novel O₂ evolution photocatalyst. The as-obtained micro-rods are well-crystallised with about 2 µm lengths and 500 nm widths. In the authors system, the sodium dodecyl sulfate amount, as well as the reaction time and temperature, plays an important role in the formation of the InVO₄ microrods. From the UV-vis absorption spectrum, the bandgap energy of as-obtained InVO₄ microrods is 2.3 eV. Under visible-light irradiation, InVO₄ microrods show excellent photocatalytic O₂ production activity (2.663 mmol h⁻¹ g⁻¹) with AgNO₃ as sacrifice reagents.

1. Introduction: Recently, photocatalytic water splitting has received much attention because of the potential to convert solar energy into chemical energy [1]. Comparing the two half-reactions of overall water splitting, the oxygen evolution reaction (OER) is considered to be kinetically more challenging than hydrogen generation [2, 3], because oxygen generation requires the abstraction of four electrons [4, 5].

Much effort has been done to explore new type photocatalysts for OER. For example, Kudo and Hiji [6] reported Bi₄Ti₃O₁₂, BaBi₄Ti₄O₁₅ and Bi₃TiNbO₉ photocatalysts to produce O₂ under UV-irradiation. Zou *et al.* [7] prepared Bi₂GaNbO₇, Bi₂AlNbO₇ and CaBi₂Nb₂O₉ photocatalysts which also show OER activity under UV-irradiation. These titanate and niobate photocatalysts show high photocatalytic activity for OER in an AgNO₃ solution under UV irradiation. However, the UV energy only accounts for about 4% of the solar energy, which effectively makes the practical application of OER under visible-light impossible. Therefore developing novel visible-light-driven O₂ evolution photocatalysts is regarded as one of the key issues in achieving efficient photocatalytic water splitting [8]. Unfortunately, the number of visible-light-driven photocatalysts for O₂ evolution is still limited, even if the photocatalytic reaction is assisted with an electron scavenger (such as Fe³⁺).

As a ternary oxide semiconductor with narrow bandgap energy (2.0 eV), InVO₄ has been reported to be an effective photocatalyst for the application of environmental remediation [9, 10] as well as for energy conversion by water splitting [11]. To improve the photocatalytic activity of InVO₄, the nanostructuring strategy is often employed by constructing InVO₄ nanostructures or microstructures with different morphology, such as nanoparticles, nanotubes and microspheres [12–15]. However, most of research ignores the capacity for oxygen production of InVO₄. As an excellent photocatalyst, it is necessary to study the InVO₄ OER capacity.

In this reported work, InVO₄ micron-rods were successfully synthesised by a hydrothermal method, in which sodium dodecyl sulfate (SDS) was the surfactant. The key to the controllable synthesis was the amount of SDS added, reaction temperature and reaction time. The visible-light-driven photocatalytic activity of the micron-rods was evaluated by the oxygen production from water splitting.

2. Experimental

2.1. Synthesis of sample: The InVO₄ micron-rods were prepared through hydrothermal process. All chemicals used were analytic

grade reagents without further purification. Deionised water was used in all experiments. In a typical preparation progress, 2 mmol of NaVO₃ and moderate SDS were dissolved into 50 ml deionised water. Then the above solution was vigorously stirred. 10 min later, 2 mmol of In(NO₃)₃·4.5H₂O was added into the above solution. After stirring for another 30 min, the as-obtained mixture was transferred into a Teflon-lined stainless steel autoclave of 100 ml capacity. The hydrothermal route was carried out at 160°C for 7 h. After the autoclave cooled to room temperature, the final yellowish products were collected by centrifugation, washed with the deionised water and ethanol several times, and dried in air at 60°C for 24 h.

2.2. Characterisation: The products were characterised by X-ray diffraction measurements carried out on X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu-Kα radiation in the range of 10–80° at a scanning rate of 7° min⁻¹. The accelerating voltage and the applied current were 50 kV and 300 mA, respectively. Scanning electron microscopy (SEM) images were collected on an S-4800 field-emission SEM (FESEM, Hitachi, Japan). Transmission electron microscopy (TEM) images were collected on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.), using a 200 kV accelerating voltage. UV-vis diffused reflectance spectra of the products were obtained from a UV-vis spectrophotometer (UV2450, Shimadzu, Japan). BaSO₄ was used as a reflectance standard.

2.3. Photocatalytic oxygen production: The photocatalytic oxygen production experiments were carried out in a 250 ml Pyrex round-bottom flask. Before the photocatalytic reaction began, the openings of the round-bottom flask was sealed with a silicone rubber septum. A 500 W Xenon arc lamp with a UV-cutoff filter (420 nm) was used as a visible light source and was positioned 20 cm away from the reactor. In a typical photocatalytic experiment, 100 mg of the InVO₄ micron-rods was added to 0.04 M AgNO₃ solution (200 ml). Prior to the light irradiation, the above suspension was thoroughly degassed to remove air completely and the reaction temperature was below 5°C. During the whole reaction process, vigorous agitation was performed to ensure the uniform irradiation of the InVO₄ photocatalysts suspension. The amount of evolved O₂ was determined with a gas chromatograph (GC, SP-7800A, thermal conductivity detector, 5 Å molecular sieve columns and Ar carrier). All

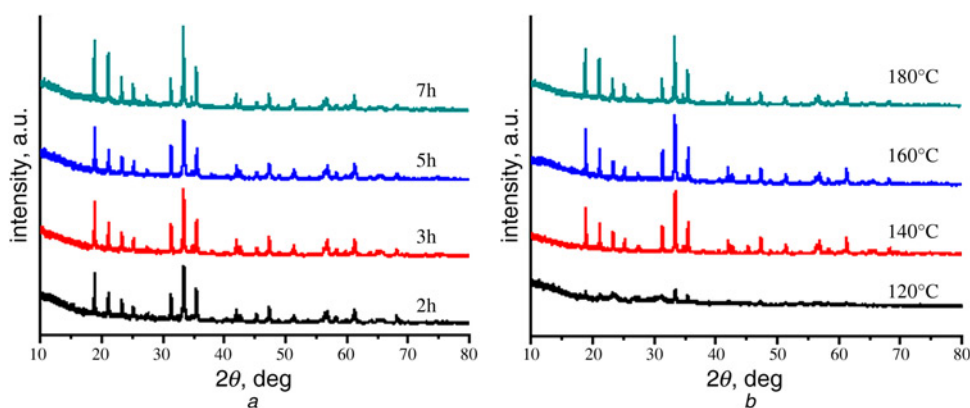


Fig. 1 XRD patterns for InVO_4 products prepared by hydrothermal treatment
a 160°C
b 7 h

glassware was rigorously cleaned and carefully rinsed with distilled water prior to use.

3. Results and discussion

3.1. Formation of the InVO_4 crystalline: The time-dependent and temperature-dependent XRD patterns of the as-obtained InVO_4 samples are shown in Fig. 1. All peaks in Fig. 1a in the XRD pattern can be readily indexed to the orthorhombic phase of InVO_4 , which is in good agreement with the standard card (JCPDS No. 48-0898). From Fig. 1b, the XRD pattern of the sample synthesised at 120°C is different from other samples which were synthesised at 140, 160 and 180°C, respectively. The diffraction peaks obtained at 120°C are very weak, indicating the sample obtained at 120°C is amorphous. Once the hydrothermal temperature rose to 140°C, the diffraction peaks for InVO_4 could be clearly seen, suggesting that this temperature is sufficient for the preparation of InVO_4 micron-rods. Other peaks in Fig. 1b are also in good agreement with the standard card (JCPDS No. 48-0898).

3.2. Morphologies of the InVO_4 samples: The morphology and size of the InVO_4 micron-rods were studied through SEM, which is shown in Figs. 2 and 3. This product is obtained by hydrothermal treatment at 160°C, 7 h with the addition of 240 mg SDS. Fig. 2a shows the low magnification SEM images of InVO_4 micron-rods. The products consisted of relatively uniform rod-like structures of about 2 μm length and 500 nm width. High magnification SEM shows that the micron-rods were composed of micronsheets in Fig. 2b.

Further insight into the morphology and microstructure of the InVO_4 micron-rods were obtained by using a TEM and a

high-resolution TEM. Fig. 3b displays the area marked by a rectangle in Fig. 3a, with the FFT patterns (inset). The clear lattice fringe which is shown in Fig. 3b confirms the high crystallinity of the micron-rods. The measured d spacing is 0.386 nm, which corresponds to the (111) planes of orthorhombic InVO_4 .

3.3. Effects of reaction condition on the growth of InVO_4 micron-rods: To explore the InVO_4 micron-rods crystal growth condition, a series of controlled experiments were carried out to determine the parameters that may affect the formation of the InVO_4 micron-rods, shown in Fig. 4. The SEM images of the InVO_4 derived from different hydrothermal times at 160°C in the presence of 240 mg SDS, are shown in Fig. 4a. As we can see, the hydrothermal reaction time has an important influence on the morphology of the product. Fig. 4a shows the morphology of the rods begin to form after 2 h treatment. Fig. 4b clearly shows that the rod-like morphology has been completely obtained at 5 h. We can conclude from the pictures that the products begin to crystallise after 2 h. At the same time, the micron-rods grow and gradually separate from the precursor as the reaction progresses. At 5 h, the InVO_4 micron-rods have completely been produced with high crystallinity.

For the hydrothermal method, reaction temperature is an important condition in the process of crystal formation because crystal growth needs enough energy, and some special morphology can only be formed at specific temperatures. Fig. 4c shows that the product is hydrothermally prepared at 120°C. As can be seen, most of the products are micron-sheets without clear separation. The XRD shows that the product prepared at 120°C with low crystallinity is different from the other products which are prepared at a higher reaction

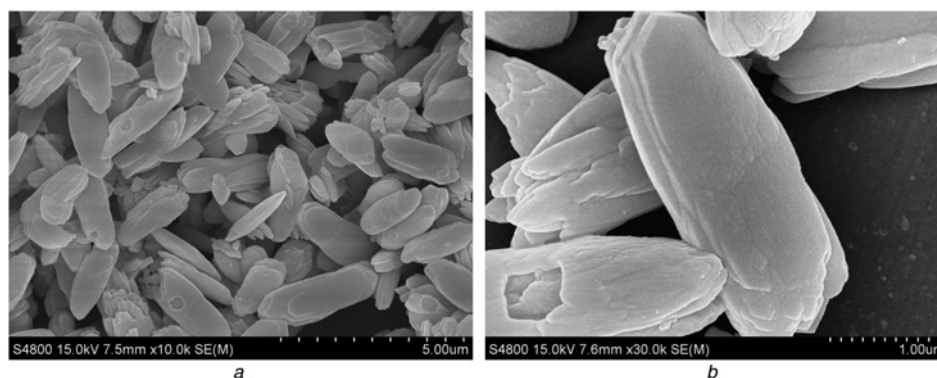


Fig. 2 FESEM
a and b Images of InVO_4 micronrods obtained by hydrothermal treatment at 160°C, 7 h with the addition of 240 mg SDS

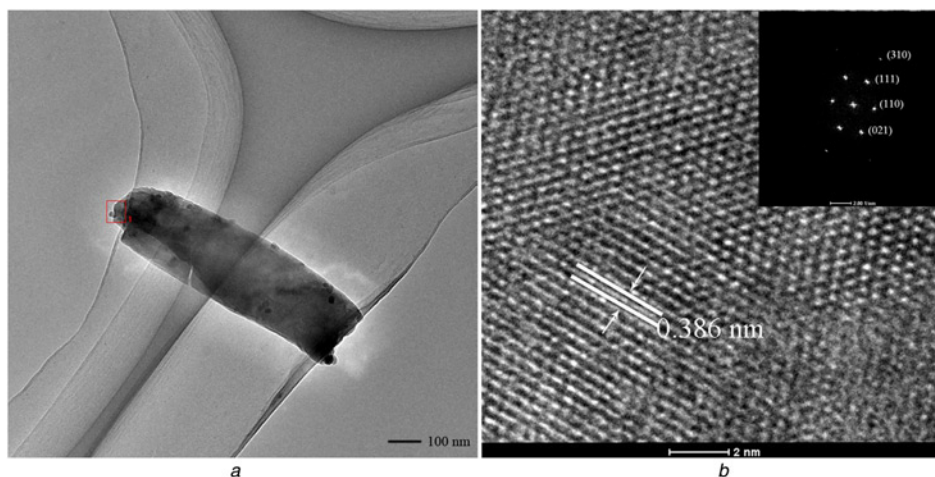


Fig. 3 TEM images

a and *b* Obtained InVO_4 micronrods by hydrothermal treatment at 160°C , 7 h with the addition of 240 mg SDS

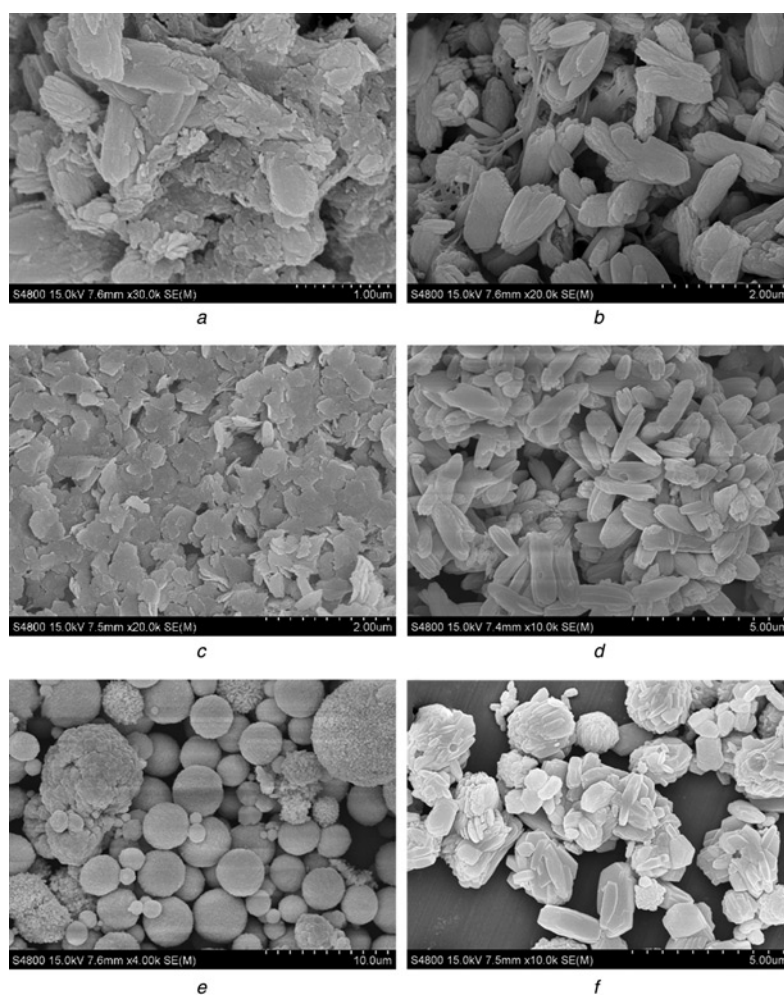


Fig. 4 FESEM images of InVO_4 micronrods obtained by hydrothermal treatment

a 2 h

b 5 h

c 120°C

d 140°C

e 0 mg SDS

f 180 mg SDS

temperature. Fig. 4*d* shows that the micron-rods can be formed at 140°C . The XRD shows that this product prepared at 140°C has good crystallinity with obvious diffraction peaks. From the XRD and SEM which are shown in Figs. 2, 4*c* and *d*, we can

conclude that the temperature is a key condition for crystal growth. The lowest reaction temperature for InVO_4 crystal growth is 140°C , and the new morphology of micron-rods can be formed at 160°C .

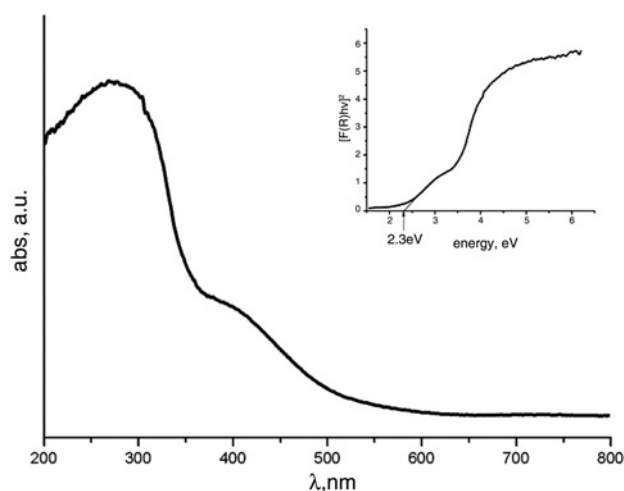


Fig. 5 UV-vis diffuse reflection patterns of as prepared InVO_4 and calculated direct bandgap energy

For the sake of studying the effect of SDS on the growth of the InVO_4 micron-rods, a controllable experiment without SDS was carried out while the other conditions were unchanged (160°C , 7 h). Fig. 4e presents the SEM images of the InVO_4 obtained by the hydrothermal treatment without SDS. As can be seen, the morphology of the product prepared without SDS is microspheres with a diameter of 1–10 μm . Fig. 4f shows the product prepared in the presence of 180 mg SDS. We can see that the morphology of the micron-rods began to form, and the micron-rods were separated from microspheres. The size of the micron-rods is smaller than the products which are shown in Fig. 4e. By comparison, the presence of SDS had a significant effect on the microstructures, which changed from microspheres to micron-rods and the existence of SDS was vital to mediate the crystal growth.

3.4. UV-vis diffuse reflectance spectra of InVO_4 micronrods: The UV-vis diffuse reflectance spectra of the InVO_4 micron-rods products obtained by the hydrothermal process at 160°C , 7 h with the addition of 240 mg SDS is displayed in Fig. 5. As can be seen, the InVO_4 micron-rods show excellent visible-light absorption. Its absorption edge is estimated to be 550 nm, with an energy bandgap of 2.3 eV, which is completely sufficient for the visible light absorption. The InVO_4 micron-rods can absorb visible-light to excite the electrons in the valence band to the conduction band, whereas the holes are left in the valence band, which have enough energy for oxygen evolution from the water splitting. As a result, the InVO_4 micron-rods have promising visible light absorption performance.

3.5. Photocatalytic oxygen production: The photocatalytic O_2 production activity of the InVO_4 micron-rods was studied. Fig. 6 shows the time course of photocatalytic O_2 evolution from InVO_4 (100 mg) suspension systems of 0.04 M AgNO_3 aqueous solution (200 ml) under visible light ($\lambda > 420 \text{ nm}$) as a light source. The oxygen production for the InVO_4 micron-rods is 0.799 mmol after 3 h irradiation. The results show that the photocatalytic O_2 evolution rate of the InVO_4 micron-rods is $2.663 \text{ mmol h}^{-1} \text{ g}^{-1}$. It is much higher than the $\text{Zn}_3\text{V}_2\text{O}_8$ [16]. All in all, it demonstrates that the InVO_4 is a promising visible-light-driven semiconductor photocatalyst material for O_2 evolution from water splitting. A dark test with the InVO_4 micron-rods presented that no O_2 evolved when the irradiation light was turned off, indicating that O_2 production was only from water splitting rather than other effects. The crystal structure of the InVO_4 micron-rods after photocatalytic reaction was also checked using an XRD, which showed nothing changed during this reaction. As can be

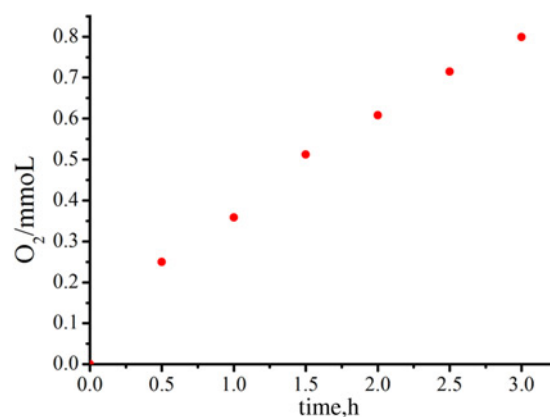


Fig. 6 O_2 production rate of InVO_4 micronrods with AgNO_3 as sacrifice reagent

seen from Fig. 6, the O_2 evolution rate of the InVO_4 micron-rods gradually decreased as the reaction progressed. This result is probably because of the shielding effect by more and more metallic silver reduced on the catalyst surface from the AgNO_3 solution as the photocatalytic reactions progressed [17]. This study indicates that the InVO_4 micron-rods have excellent photocatalytic activity for O_2 production from splitting water under visible light irradiation.

4. Conclusions: InVO_4 micron-rods were developed as a new photocatalyst for O_2 evolution from water splitting under visible light irradiation. The semiconductor photocatalyst was prepared selectively by adjusting the hydrothermal temperature, reaction time and the amount of SDS addition. The results showed that the InVO_4 micron-rods can be prepared at 160°C , 7 h and with the addition of 240 mg SDS under hydrothermal conditions. Furthermore, the process of crystal growth demonstrated that SDS is considered to be a morphology-directing reagent for the formation of micron-rods, and act as the key factor for control of crystal morphology. The final morphology of the InVO_4 micron-rods is $\sim 2 \mu\text{m}$ length and 500 nm width, which is revealed here, to the best of our knowledge, for the first time. The absorption edge of the InVO_4 micron-rods is estimated to be 550 nm with a energy bandgap of 2.3 eV, and the InVO_4 micron-rods have a high O_2 production capacity $2.663 \text{ mmol h}^{-1} \text{ g}^{-1}$ from AgNO_3 solution under visible light. This reported work highlights the potential oxygen production from water splitting of InVO_4 .

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