



# Nickel sulfide modified TiO<sub>2</sub> nanotubes with highly efficient photocatalytic H<sub>2</sub> evolution activity<sup>☆</sup>

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## ABSTRACT

TiO<sub>2</sub> nanotubes (TNTs) with nickel sulfide (NiS) co-catalyst were prepared by a simple solvothermal method and characterized by X-ray diffraction, transmission electron microscope, N<sub>2</sub>-physisorption, UV–vis diffuse reflectance spectroscopy and photoluminescence spectroscopy. Loading NiS nano-clusters can significantly enhance the photocatalytic H<sub>2</sub> evolution performance of TNTs. The optimum NiS loading content was found to be 8 wt% and the corresponding hydrogen production rate is ca. 7486 μmol/h/g, being about 79 times higher than that of pure TNTs. This enhancement of photocatalytic H<sub>2</sub> evolution was attributed to the synergistic effect between NiS and TNTs.

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## 1. Introduction

Hydrogen is widely considered as an ideal energy source for solving energy crisis and environmental contamination issues. Photocatalytic H<sub>2</sub> production from water splitting using semiconductor is considered as a green way to convert solar energy into H<sub>2</sub> [1–4]. In order to satisfy industrial application, the semiconductor photocatalysts should be good stability, high efficiency, low price and low toxicity [5,6]. Recently, TiO<sub>2</sub> nanotubes (TNTs) have drawn extensive attention due to its wide range of electrical and optical properties [7,8]. Nevertheless, the photocatalytic H<sub>2</sub> production activity of pure TNTs is still limited by the light absorption properties, recombination rate of photogenerated electrons and holes, reduction and oxidation reaction rates on the surface [9]. Some modifications have been used to improve the efficiency of H<sub>2</sub> evolution, such as metal and nonmetal ion doping [10,11], semiconductors coupling [8,12] and co-catalysts loading [13–15]. Transition metals, especially the noble metals, are widely used as effective co-catalysts for photocatalytic water splitting [13,15,16]. Zhao et al. [13] used Au (or Pt) as co-catalyst to modify TNTs, and found that the photocatalytic activities of TNTs enhanced significantly. Wu et al. [16] reported that the surface plasmon resonance effect of Ag/TNTs contribute to extending the visible light response and enhance the absorption capacity of TNTs. Nevertheless, scarcity and expensiveness of noble metals

restrict their practical applications [17]. Therefore, it is vital to design economical and efficient co-catalysts as alternatives to noble metal co-catalysts for improving the H<sub>2</sub> evolution performance of TNTs.

Nickel compounds (e.g., NiS, NiO and Ni(OH)<sub>2</sub>) have been demonstrated to be cost-effective and good co-catalysts for H<sub>2</sub> production via water splitting. Dang et al. [18] used Ni(OH)<sub>2</sub> as co-catalyst to modify red phosphorus (P) and higher photocatalytic performance of H<sub>2</sub> evolution than Pt/P was achieved. Chen et al. [19] investigated hydrogen generation over Ni(OH)<sub>2</sub>/TaON, and found that Ni(OH)<sub>2</sub> improved the separation of electrons and holes generated by TaON. Furthermore, NiS has been proved to be a good co-catalyst, which can promote the reduction reaction on photocatalysts [20,21]. However, to the best of our knowledge, there are few reports on the photocatalytic H<sub>2</sub> generation over NiS modified TNTs till now.

In the current study, a highly active photocatalyst of the TNTs loaded with NiS nano-cluster was prepared by a simple solvothermal method. The photocatalytic H<sub>2</sub> evolution from water splitting was investigated under UV irradiation to evaluate the catalytic behavior of composite samples. The NiS nano-clusters were found to be highly efficient co-catalysts for significantly enhancing the photocatalytic H<sub>2</sub> evolution activity of TNTs. The detailed structural characterization and possible reaction mechanism of the photocatalytic process with NiS/TNTs photocatalyst were also proposed.

## 2. Experimental

### 2.1. Catalyst preparation

All analytical grade reagents, including P25 nanoparticles (TiO<sub>2</sub>), sodium hydroxide (NaOH), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), thiourea

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(CN<sub>2</sub>H<sub>4</sub>S) and glycol ((CH<sub>2</sub>OH)<sub>2</sub>), were used without any purification. Titanate nanotubes (TNTs) were synthesized via an alkali hydrothermal method with P25 as starting material [22].

NiS/TNTs composites with different NiS contents (2, 5, 8, 10, 15 wt%) were synthesized via a solvothermal treatment route. The obtained samples were denoted as 0.02-NiS/TNTs, 0.05-NiS/TNTs, 0.08-NiS/TNTs, 0.10-NiS/TNTs and 0.15-NiS/TNTs, respectively. In a typical synthesis of 0.08-NiS/TNTs, 1.00 g TNTs, 0.279 g nickel nitrate and excessive thiourea were dispersed in 80 mL of a glycol solution. The resultant mixture was transferred into a Teflon-lined autoclave (100 mL) and maintained at 180 °C for 12 h for crystallization. The gained precipitate was washed by distilled water and dried at 60 °C for 12 h.

## 2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were collected by a rotating-anode diffractometer with Cu K $\alpha$  radiation (D8 Advance, Germany). UV–vis diffuse reflectance spectra (DRS) were obtained using a UV–vis spectrophotometer (U-3010, Hitachi, Japan). Photoluminescence (PL) spectra were measured at room temperature on a fluorescence spectrophotometer (F-4500, Hitachi, Japan). Specific surface areas were determined by BET measurement (Micromeritics ASAP 2020M, USA). Transmission electron microscopy (TEM) observations were conducted with a JEM-2010F electron microscope (JEOL, Japan).

## 2.3. Photocatalytic activity

Water splitting reactions were carried out in a top-irradiation quartz reactor connected to a gas-closed circulation system in vacuum. The light source in the experiments was a 300 W Xe lamp (PLS-SXE-300UV, Beijing Trusttech Co. Ltd., China) and the integrated light intensity on the reaction reactor was ca. 60 mW/cm<sup>2</sup>. In a typical experiment, 50 mg of the photocatalyst was dispersed in a 100 mL of aqueous solution containing 25 mL of methanol as the sacrificial reagent. Prior to irradiation, the air and the dissolved oxygen inside the system were removed by employing a vacuum pump. The temperature of the reactant solution was maintained at 15  $\pm$  5 °C using a low-temperature thermostat bath. Subsequently, the photocatalytic activity measurement system was exposed to UV light. The evolved H<sub>2</sub> was analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC9800, N<sub>2</sub> carrier, TDX-01 column).

## 3. Results and discussion

### 3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of TNTs with different amounts of NiS. As shown in Fig. 1, the peaks at  $2\theta = 25.3^\circ, 37.8^\circ, 48.1^\circ$  and  $54.0^\circ$  were assigned to the TiO<sub>2</sub> anatase phase (JCPD card no. 21-1272), indicating that there is no obviously phase change in TNTs during glycol solvothermal process. Meanwhile, no peaks of NiS were observed in the XRD patterns of sample 0.02-NiS/TNTs, 0.05-NiS/TNTs, 0.08-NiS/TNTs, 0.10-NiS/TNTs, which indicates that NiS were highly dispersed on the surface of the TNTs at a low loading level [21]. However, when NiS contents increased to 15 wt% in addition to anatase, some new characteristic diffraction peaks at  $2\theta = 29.9^\circ, 34.4^\circ$  and  $45.5^\circ$ , ascribed to the (100), (101) and (102) crystalline planes of hexagonal NiS (JCPD card no. 02-1280), can be clearly found in the XRD patterns of sample 0.15-NiS/TNTs. This phenomenon illustrates that NiS would aggregate with increasing loading contents, which interferes TNTs absorbing the UV radiation.

### 3.2. Transmission electronic microscopy

The morphologies of TNTs and 0.08-NiS/TNTs were investigated by TEM images. As shown in Fig. 2(a), the 1D tubular structure with

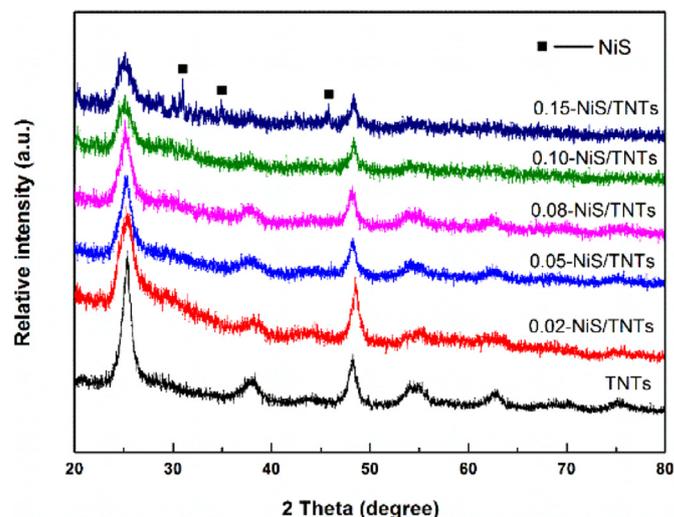


Fig. 1. XRD patterns of TNTs with different amounts of NiS.

Table 1. Specific surface area, pore volume and average pore size of the samples P25, TNTs and 0.08-NiS/TNTs.

Samples	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
P25	55.34	0.17	–
TNTs	313.79	1.25	145.72
0.08-NiS/TNTs	267.39	1.04	144.05

diameters of ca. 5–15 nm and lengths of ca. 60–100 nm can be clearly seen. All the tubes are hollow and opened at both ends, in accordance with the literature [23]. From Fig. 2(b), it can be found that NiS nanoparticles are distributed on the surface of TNTs. The HRTEM image of NiS/TNTs (Fig. 2c) clearly shows the crystal lattice fringes with 0.35 nm and 0.197 nm lattice distance, which assigned to the (101) plane of the TNTs [24] and the (102) plane of hexagonal NiS [20], respectively. The results conform the above mentioned XRD date. This composite structure reveals that the TNTs are covered by NiS, creating an intimate contact interface area, which could favor the formation of a junction between the two materials, thus improving the charge separation and increasing the photocatalytic activity [23].

### 3.3. BET analyses

Fig. 3 shows the nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves (inset) of TNTs and NiS/TNTs (0.08-NiS/TNTs). It can be seen that the pure TNTs and 0.08-NiS/TNTs had isotherms of typical BDDT type IV curves [25]. The shapes of the hysteresis loops are of type H3 at a high relative pressure range of 0.7–1.0, indicating the presence of mesopores (2–50 nm) [25]. In addition, the pore size distribution curves (inset in Fig. 3) calculated from the desorption branch of the N<sub>2</sub> isotherms by BJH method further indicate a main distribution range from 2 to 15 nm. The BET specific surface area, pore volume and average pore size are summarized in Table 1. It can be observed that introduction of NiS decreased BET surface area and pore volume, which can be attributed to the covering of NiS on the exterior surface of TNTs. However, TNTs modified with NiS still exhibit much larger BET specific surface area and higher pore volume than the precursor P25, which is expected to result in higher hydrogen generation activity [23].

### 3.4. UV–vis diffuse reflectance spectra

The UV–vis diffuse reflectance spectra of bare TNTs and different mass ratios of NiS/TNTs photocatalysts are shown in Fig. 4. An intense absorption in UV region (<400 nm) was observed for all the samples,

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