

# Nitrogen and vanadium Co-doped TiO<sub>2</sub> mesosponge layers for enhancement in visible photocatalytic activity



JiasongZhong<sup>a</sup>, Jinrong Xu<sup>b</sup>, Qingyao Wang<sup>c,\*</sup>

<sup>a</sup> College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, P.R. China

<sup>b</sup> Department of Mathematics and Physics, Anhui University of Architecture, Hefei, 230022, P.R. China

<sup>c</sup> School of Chemistry and Materials Science, Ludong University, Yantai, 264025, P.R. China

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## ABSTRACT

Novel N and V co-doped TiO<sub>2</sub> mesosponge (N-V-TMSW) layers were successfully prepared by one-step hydrothermal treatment of TiO<sub>2</sub> nanotube arrays, and the phase composition, morphology and optical property were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and UV–vis diffusion reflectance spectroscopy (DRS). The crystal structure and density of states were studied by means of the first-principle pseudo-potential plane wave. The results indicated that titanium ions and oxygen atoms in TiO<sub>2</sub> were successfully substituted by vanadium ions and nitrogen atoms, respectively. The sample N-V0.1-TMSW showed a remarkable absorption in the visible light range of 400–600 nm and high visible photocatalytic activity

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## 1. Introduction

Since the discovery of water photolysis on TiO<sub>2</sub> electrode by Fujishima [1] in 1972, TiO<sub>2</sub> became one of the most widely researched materials for use in solar cells, pollutant degradation, photolysis of water and gas sensor due to its unique and favorable physiochemical properties [2–6]. However, the photoelectrochemical property of TiO<sub>2</sub> is limited by its UV-responsive band gap of approximately 3.2 eV. Therefore, much effort has been made in the attempt to improve its visible light absorption [7–9], and the most popular approach for tailoring absorption edges is to dope TiO<sub>2</sub> with foreign species.

In order to resolve above obstacle and modify electronic structure of TiO<sub>2</sub> to narrow its band gap, nonmetal atoms have been doped into TiO<sub>2</sub> frequently and in particular with nitrogen [10]. However, only a limited enhancement in visible light absorption has thus far been obtained. For N-doping, the light-absorption edge remains almost the same with bare TiO<sub>2</sub>. Thus, the significant extension of visible light absorption only via anion doping remains a big challenge.

Moreover, a number of research groups [11,12] have approached this problem by doping TiO<sub>2</sub> with different transition metal ions to improve the visible light absorption. Vanadium doping has been found to be one of the most effective methods of enhancing TiO<sub>2</sub> absorption in the visible light region. More recently, The TiO<sub>2</sub> co-doped by both nonmetal elements and V ions has received much attention, which shows high photoactive due to the synergistic effect. The result reported by Zhang and coworkers [13] suggested that TiO<sub>2</sub> nanoparticles co-doped by C and V ions highly enhanced the visible-light photocatalytic performance. Liu et al. [14] prepared N and V co-doped TiO<sub>2</sub> nanocatalysts by two-step hydrothermal method, and the V-N-TiO<sub>2</sub> improved the photocatalytic efficiency under visible light irradiation. Nevertheless, the sizes of V-N-TiO<sub>2</sub> nanocrystals were too big, and the visible light absorption was still weak. Very recently, titania mesosponge, a novel structure with considerably higher photocatalytic activity and specific surface area than TiO<sub>2</sub> nanoparticles and nanotubes, was prepared on Ti by anodization [15]. Therefore, the combination of mesosponge nanostructure and N and V co-dopants provides a better system to overcome the above problems. In this paper, we reported a successful attempt to fabricate N and V co-doped anatase TiO<sub>2</sub> mesosponge layers by one-step hydrothermal method. The N-V-TMSW showed enhanced photocatalytic activity for methylene orange degradation under visible light.

\* Corresponding author.

E-mail address: [wangqingyao0532@163.com](mailto:wangqingyao0532@163.com) (Q. Wang).

## 2. Experiments

### 2.1. Preparation of N and V co-doped TiO<sub>2</sub> mesosponge layers

NH<sub>4</sub>F, NH<sub>4</sub>VO<sub>3</sub>, ammonia and ethylene glycol were purchased from Shanghai Chemical Reagent Co. Ltd. Ti foil (0.25 mm, 99.8% purity, Advent Materials) was ultrasonically degreased in acetone, isopropanol and methanol for 15 min in turn, and then chemically etched in a mixture of HF and HNO<sub>3</sub> (HF:HNO<sub>3</sub>:H<sub>2</sub>O = 1:4:5 in volume, total 20 mL) for 20 s, afterwards rinsed with deionized water, and finally dried in air prior to anodization. All reagents are of analytical grade and used without further purification.

TiO<sub>2</sub> nanotubes were prepared according to a two-step anodization as reported previously [16]. The first-step anodization was performed under 60 V for 1 h in ethylene glycol solution containing 0.5 wt.% NH<sub>4</sub>F and 3 vol.% H<sub>2</sub>O. After the first step, the as-formed TiO<sub>2</sub> layer was peeled off by intense ultrasonication in deionized water to expose the Ti substrate. The second-step anodization was carried out in the same electrolyte for 4 h.

N and V co-doped TiO<sub>2</sub> mesosponge layers were synthesized using the as-prepared TiO<sub>2</sub> nanotubes as precursors. In a typical experiment, an amount of NH<sub>4</sub>VO<sub>3</sub> was dissolved into 1 M ammonia solution with ultrasonication for 1 h to form a transparent solution. The as-prepared TiO<sub>2</sub> nanotubes were immersed into the mixed solution held in a Teflon autoclave, which was subsequently transferred to a baking oven for hydrothermal treatment at 180 °C for 12 h. After the autoclave cooled down naturally, the sample was taken out and ultrasonically cleaned with acetone and deionized water.

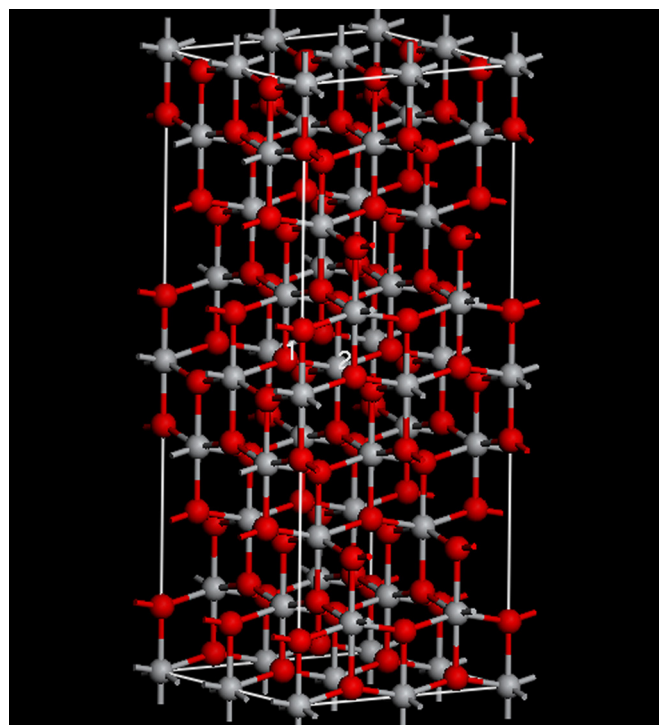
A series of N and V co-doped TiO<sub>2</sub> mesosponge layers were prepared by changing the concentration of NH<sub>4</sub>VO<sub>3</sub>, and denoted as N-V0.05-TMSW, N-V0.1-TMSW, and N-V0.2-TMSW for TiO<sub>2</sub> nanotubes in 0.05 M, 0.1 M and 0.2 M NH<sub>4</sub>VO<sub>3</sub> solution, respectively. In addition, only N doped TiO<sub>2</sub> mesosponge layer was prepared in 1 M ammonia solution for comparison, and it was denoted as N-TMSW.

### 2.2. Characterization

The phase composition of the as-prepared product was determined by a Rigaku D/Max 2400 X-ray diffractometer (XRD) equipped with graphite monochromatized Cu K $\alpha$  radiation. The morphology and element composition of the as-synthesized product were directly observed by a JEOL JSM-5600LV scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurement was performed on a Kratos XSAM800 XPS system equipped with two ultrahigh vacuum (UHV) chambers. AFM experiments were performed with the equipment of Park Scientific Instruments (SFM-BD2) operating in contact mode with a scan frequency of 2 Hz. UV–vis diffuse reflectance spectra (DRS) of the samples were recorded on a UV-2550 UV–vis spectrophotometer with an integrating sphere attachment. BaSO<sub>4</sub> was used as a reflectance standard in the wavelength range of 200–800 nm.

### 2.3. Photocatalytic activity test

The photocatalytic activity of the prepared samples was evaluated by photocatalytic decomposition of 10<sup>-5</sup> M methyl orange (MO) solution under a 300 W Xe lamp (CHF-XQ-500 W, Beijing Changtuo Co., Ltd.) with a visible-light filter (>420 nm). Before photodegradation, adsorption equilibrium for the dye on catalyst surface was established by mechanical stirring in the dark for 30 min. After visible-light irradiation for 1 h, 3 mL of reaction solution was withdrawn, then, UV–vis absorption spectra were recorded on a UV1700 UV–vis spectrophotometer to monitor the concentration of MO left in the aqueous system by detecting the



**Fig. 1.** The  $2 \times 2 \times 2$  supercell of N-V-TMSW. The gray and red balls stand for Ti and O atoms. The positions of O and Ti substituted by N and V are denoted by label 1 and 2, respectively.

maximum absorption wavelength for MO at 464 nm. After measurement, the sample was put back to the reaction solution to conduct the photo-degradation experiments with the same procedure as mentioned above.

### 2.4. Theoretical calculation

For comparing to experiment results, first principle method was used to investigate the electronic structure of pure TiO<sub>2</sub> (TiO<sub>2</sub>), N-TMSW and N-V-TMSW, respectively. The computational calculations were performed using the projector augmented wave pseudopotentials [17] as implemented in the Vienna Ab initio Simulation Package code [18,19]. The energy cut of 450 eV is performed in our calculation, which ensures convergence of total energy difference of the system to 1.0 meV/cell. Because of the generalized gradient approximation (GGA) [20] leading to underestimation of band gap for strongly correlated systems, GGA + U (Hubbard coefficient) was used in this work to compensate for the limitation [21], which introduces an additional term based on a simple Hubbard model for electron on-site repulsion. After optimization, the  $U=7.0$  eV of Ti 3d electrons and  $U=4.5$  eV of V 3d electrons were adopted in density of state calculations. The  $2 \times 2 \times 2$  supercell of N-V-TMSW was built, as shown in Fig. 1, the atomic ratio of the N for N-TMSW is 1.5625%, and N and V for N-V-TMSW are 1.5625% and 3.125%, which are close to experiment results of sample N-V0.1-TMSW. The Brillouin zones were sampled by a set of k-points grid  $4 \times 4 \times 2$  for relaxation and  $9 \times 9 \times 4$  for calculation of density of states according to the Monkhorst-Pack approximation [22].

## 3. Results and discussion

Fig. 2 shows the XRD patterns of different amount of V and N co-doped TiO<sub>2</sub> mesosponge layers. All diffraction peaks from the N-TMSW and N-V-TMSW were attributable to anatase TiO<sub>2</sub>, which were consistent with the values in the standard card (JCPDS,

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