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Self-organized vanadium and nitrogen co-doped titania nanotube arrays with enhanced photocatalytic reduction of CO₂ into CH₄

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Abstract

Self-organized V-N co-doped TiO₂ nanotube arrays (TNAs) with various doping amount were synthesized by anodizing in association with hydrothermal treatment. Impacts of V-N co-doping on the morphologies, phase structures, and photoelectrochemical properties of the TNAs films were thoroughly investigated. The co-doped TiO₂ photocatalysts show remarkably enhanced photocatalytic activity for the CO₂ photoreduction to methane under ultraviolet illumination. The mechanism of the enhanced photocatalytic activity is discussed in detail.

Keywords: TiO₂; Photocatalytic; CO₂; Nanotube; CH₄

Background

Greenhouse gases such as CO₂ and chlorofluorocarbon (CFCs) are the primary causes of global warming. The atmospheric concentration of CO₂ has steadily increased owing to human activity, and this accelerates the greenhouse effect. The photocatalytic reduction of CO₂ is a promising technical solution since it uses readily available sunlight to convert CO₂ into valuable chemicals, such as methanol or methane, in a carbon friendly manner [1].

TiO₂ is a popular catalyst for photoreduction of CO₂ owing to the advantages of earth abundance, low toxicity, and chemical stability. Yet it has so far yielded only low carbon dioxide conversion rates despite using ultraviolet illumination for band gap excitations [2]. While the intrinsic idea of photocatalytic conversion of carbon dioxide and water (vapor) into hydrocarbon fuels is appealing, the process has historically suffered from low conversion rates. Numerous studies have been reported on how to increase the photoreduction activity of TiO₂ using transition metal-doped and/or modified TiO₂. Transition metal doping has been applied not only to modify the photoactivity of TiO₂ but also to influence the product selectivity. For example, mesoporous silica-supported Cu/TiO₂ nanocomposites showed significantly enhanced CO₂ photoreduction rates due to the synergistic combination

of Cu deposition and high surface area SiO₂ support [3]. Dispersing Ce-TiO₂ nanoparticles on mesoporous SBA-15 support was reported to further enhance both CO and CH₄ production due to the modification of TiO₂ with Ce significantly stabilized the TiO₂ anatase phase and increased the specific surface area [4]. However, increasing the content of metal dopant does not always lead to better photocatalytic activity. The promotion of the recombination efficiency of the electron-hole pairs may be due to excessively doped transition metal.

Besides, nonmetal-doped TiO₂ have been used as visible light-responsive photocatalysts for CO₂ photoreduction. Significant enhancement of CO₂ photoreduction to CO had been reported for I-doped TiO₂ due to the extension of TiO₂ absorption spectra to the visible light region by I doping [5]. Enhanced visible light-responsive activity for CO₂ photoreduction was obtained over mesoporous N-doped TiO₂ with noble metal loading [6]. Nitrogen doping into TiO₂ matrix is more beneficial from the viewpoint of its comparable atomic size with oxygen, small ionization energy, metastable center formation and stability. However, a main drawback of N doping is that only relatively low concentrations of N dopants can be implanted in TiO₂.

In order to overcome the abovementioned limitations, modified TiO₂ by means of nonmetal and metal co-

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doping was investigated as an effective method to improve the photocatalytic activity. Among the current research of single ion doping into anatase TiO₂, N-doping and V-doping are noteworthy. Firstly, both elements are close neighbors of the elements they replace in the periodic table. They also share certain similar physical and chemical characteristics with the replaced elements. Secondly, impurity states of N dopants act as shallow acceptor levels, while those of V dopants act as shallow donor levels. This results in less recombination centers in the forbidden band of TiO₂ and thus prolongs the lifetime of photoexcited carriers [7]. So the co-doping of V and N into the TiO₂ lattice is of particular significance. Recently, V and N co-doped TiO₂ nanocatalysts showed enhanced photocatalytic activities for the degradation of methylene blue compared with mono-doped TiO₂ [8]. Wang et al. synthesized V-N co-doped TiO₂ nanocatalysts using a novel two-phase hydrothermal method applied in hazardous PCP-Na decomposition [9]. Theoretical and simulation work also found that N-V co-doping could broaden the absorption spectrum of anatase TiO₂ to the visible light region and increase its quantum efficiency [10]. However, the effect of V, N co-dopant in TiO₂ on the efficiency of CO₂ photocatalytic reduction has not been studied yet. In the present work, we made efforts to improve photocatalytic carbon dioxide conversion rates by the following strategies: (1) employ high surface area titania nanotube arrays, with vectorial charge transfer, and long-term stability to photo and chemical corrosion; and (2) modify the titania to enhance the separation of electron-hole pairs by incorporating nitrogen and vanadium. This article reports the synthesis, morphologies, phase structures, and photoelectrochemical of self-organized V, N co-doped TiO₂ nanotube arrays as well as the effect of V and N co-doping on photocatalytic reduction performance of CO₂ into CH₄.

Methods

Fabrication of V, N co-doped TiO₂ nanotube arrays

V, N co-doped TiO₂ nanotube arrays (TNAs) were fabricated by a combination of electrochemical anodization and hydrothermal reaction. Firstly, highly ordered TNAs were fabricated on a Ti substrate in a mixed electrolyte solution of ethylene glycol containing NH₄F and deionized water by a two-step electrochemical anodic oxidation process according to our previous reports [11]. Interstitial nitrogen species were formed in the TNAs due to the electrolyte containing NH₄F [12]. Then, the amorphous TNAs were annealed at 500°C for 3 h with a heating rate of 10°C/min in air ambience to obtain crystalline phase. We denoted these single N-doped TNAs samples as N-TiO₂.

V, N co-doped TNAs were prepared by a hydrothermal process. As-prepared N-TiO₂ samples were immersed in

Teflon-lined autoclaves (120 mL, Parr Instrument, Moline, IL, USA) containing approximately 60 mL of NH₄VO₃ aqueous solution (with different concentration 0.5, 1, 3, and 5 wt.%) as the source of both V and N. All samples were hydrothermally treated at 180°C for 5 h and then naturally cooled down to room temperature. Finally, all samples were rinsed with deionized water and dried under high purity N₂ stream. The corresponding samples (0.5%, 1%, 3%, and 5%) were labeled as VN0.5, VN1, VN3, and VN5. For control experiment, sample denoted as VN0 was prepared by the previously mentioned hydrothermal process in 60 mL pure water without NH₄VO₃ addition.

Characterization

Surface morphologies of all samples were observed with field emission scanning electron microscope (FESEM, JEOL JSM-7001 F, Akishima-shi, Japan) at an accelerating voltage of 15 kV. Phase structures of the photocatalysts were analyzed by X-ray diffraction (XRD) analysis on an X'Pert Philips (Amsterdam, The Netherlands) diffractometer (Cu K α radiation, 2 θ range, 10° to 90°; step size, 0.08°). Chemical state and surface composition of the samples were obtained with an Axis Ultra X-ray photoelectron spectroscope (XPS, Kratos, Manchester, UK; a monochromatic Al source operating at 210 W with a pass energy of 20 eV and a step of 0.1 eV was used). All binding energies (BE) were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. UV-vis diffused reflectance spectra of N-TiO₂ and V, N-co-doped TiO₂ nanotube arrays were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan).

Photoelectrochemical measurements

Photoelectrochemical experiments were monitored by an electrochemical workstation (IM6ex, Zahner, Germany). V, N co-doped TNAs (an active area of 4 cm²) and platinum foil electrode were used as working electrode and counter electrode, and saturated calomel electrode (SCE) acted as reference electrode, respectively. 1 M KOH aqueous solution was used as the supporting electrolyte and purged with N₂ for 20 min before measurement to remove the dissolved oxygen. A 300-W Hg lamp was used as the light source. Photocurrent measurements were carried out under UV-vis irradiation at an applied bias voltage of 0.4 V (vs. SCE) in ambient conditions at room temperature.

Photocatalytic reduction of CO₂

Photocatalytic reduction of CO₂ was performed in a 358-mL cylindrical glass vessel containing 20 mL 0.1 mol/L KHCO₃ solution with a 300-W Hg lamp fixed parallel to the glass reactor as light source. TNAs films were placed in the center of the reactor before sealing the reactor. Prior to reduction experiment under irradiation, ultra-

pure gaseous CO₂ and water vapor were flowed through the reactor for 2 h to reach adsorption equilibrium within the reactor. Each experiment was followed for 6 h. The analysis of CH₄ was online conducted with a gas chromatography (GC).

Results and discussion

Morphology

Figure 1 shows FESEM images of N-TiO₂ and V, N co-doped TNAs with various doping amounts. N-TiO₂ nanotube arrays before hydrothermal treatment are uniformly stacked with tubular structures with an average diameter of 130 nm and an average wall thickness of 20 nm (Figure 1a). The side view image in Figure 1b also reveals that the vertically orientated nanotubes have an average length of 11 μm. According to SEM observations

in Figure 1c,d, the VN0 sample after hydrothermal treatment in pure water presents no apparent structural transformation. The side view image in Figure 1d also shows the highly ordered nanotube arrays with similar diameter and wall thickness of N-TiO₂ sample before hydrothermal reaction. Yu et al. had reported that the nanotube array structures were completely destroyed after 180°C hydrothermal treatments with TNAs samples due to the enhanced anatase crystallinity and phase transformation from amorphous to anatase [13]. In our experiments, oxidized TNAs samples were calcinated at 500°C to realize phase transformation from amorphous to anatase before hydrothermal process. By this way, the reported hydrothermally induced collapse was prevented with a simple calcination step. All hydrothermal-treated TNAs samples including the V, N co-doped TNAs show no apparent

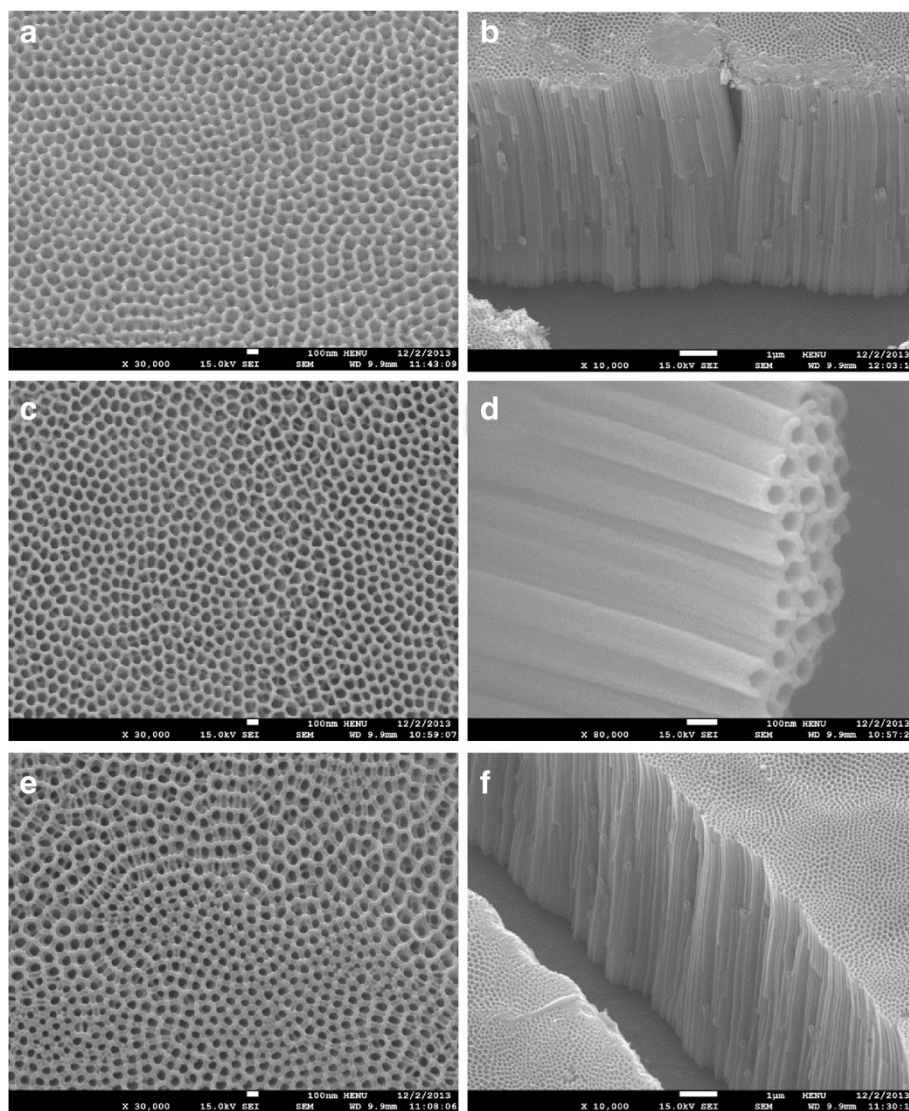


Figure 1 FESEM top views and side views for N-TiO₂ (a, b), VN0 (c, d), and VN5 (e, f).

morphology change after hydrothermal co-doping process. Figure 1e,f presents the top and side view images of the V, N co-doped TNAs with maximal doping amounts of 5% in our experiments. Nanotube arrays structure is kept unchanged in VN5 sample after hydrothermal co-doping process as shown in Figure 1f. We found that appropriate doping amount of V and N does not change the diameter of nanotubes. However, excessive dopants may lead to some particles or aggregates on the surface of nanotube arrays and some even block the pores and channels.

Crystal structure

The structural analysis of doped TiO₂ nanotube arrays was usually carried out by using X-ray diffraction (XRD) and Raman spectroscopy [14]. Here, XRD measurements were performed to investigate the changes of phase structures of N-TiO₂ sample and V, N co-doped TNAs with various doping amounts. As shown in Figure 2, diffraction peaks of all samples were ascribed to pure anatase TiO₂ diffraction pattern consistent with the values in the standard card (JCPDS card no. 21-1272) [15]. No significant characteristic peak of vanadium species is found in corresponding XRD patterns. Numerous reports showed that the incorporation of transition metal ions into other compounds as dopant could distort the original crystal lattice of the doped materials [16]. A detail analysis of XRD patterns was performed by enlarging the anatase (101) plane of the samples as shown in the inset of Figure 2. Compared with N-TiO₂, the peak position of the V, N co-doped TNA samples gradually shifted toward a higher diffraction angle. It suggests that the V ions might be successfully incorporated into the crystal lattice of anatase TiO₂ as vanadyl groups (V⁴⁺) or

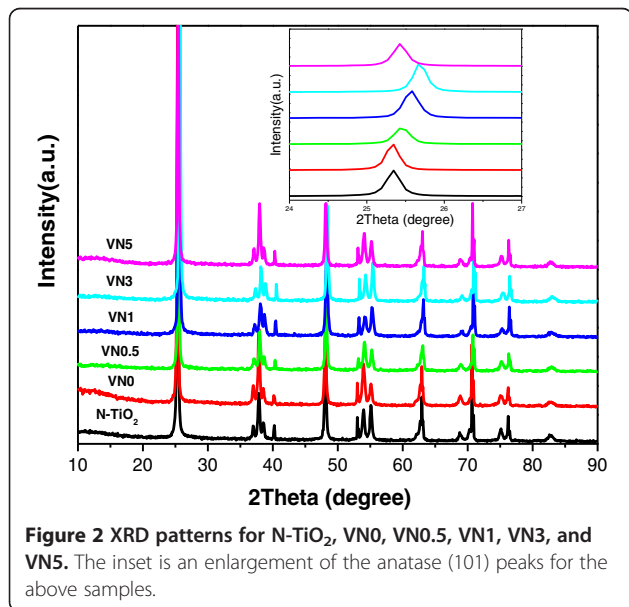


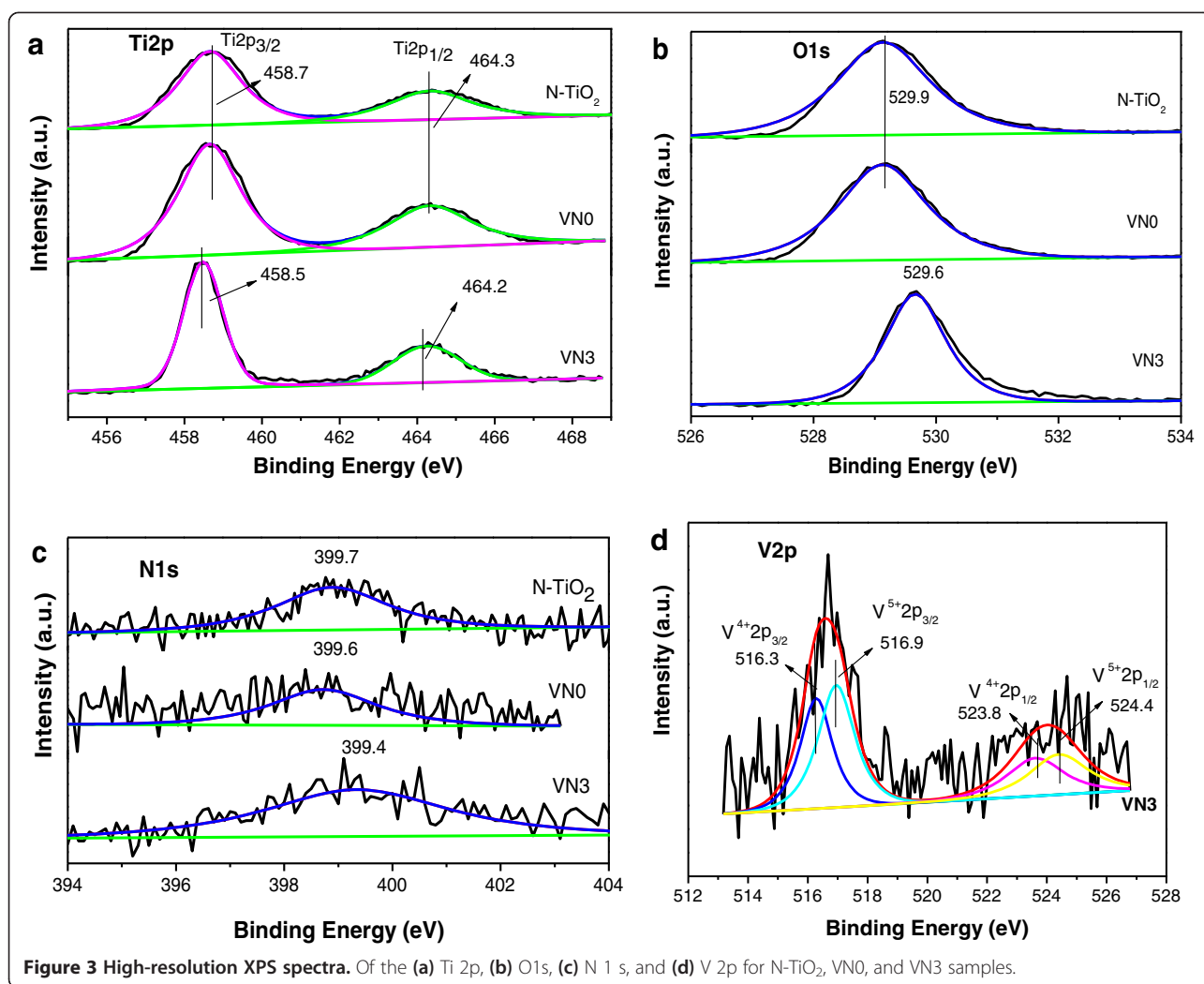
Figure 2 XRD patterns for N-TiO₂, VN0, VN0.5, VN1, VN3, and VN5. The inset is an enlargement of the anatase (101) peaks for the above samples.

polymeric vanadates (V⁵⁺) and substituted for Ti⁴⁺ because the ionic radii of V⁴⁺ (0.72 Å) and V⁵⁺ (0.68 Å) were both slightly smaller than that of Ti⁴⁺ (0.75 Å) [17]. However, peak position change of VN5 was not obvious, indicating that the doped V ions might be excessive and aggregate on the surface of TNAs and then inhibit the incorporation of ions into crystal lattice. For VN0 sample without co-doping, its crystal lattice did not change through the hydrothermal process and kept the similar peak position with N-TiO₂ sample.

XPS analysis

Figure 3 shows the high-resolution XPS spectra of Ti 2p, O 1 s, N 1 s, and V 2p regions for N-TiO₂, VN0, and VN3 samples. A significant negative shift is found for Ti 2p in Figure 3a and O 1 s in Figure 3b when V and N were co-doped into TiO₂ by hydrothermal process. The measured binding energies of Ti 2p_{3/2} and O 1 s for N-TiO₂ and VN0 are 458.7 and 529.9 eV, respectively. As compared to N-TiO₂ and VN0, the binding energy of Ti 2p_{3/2} for the VN3 sample is shifted to 458.5 eV. The lower binding energy of Ti 2p in co-doped TiO₂ suggests the different electronic interactions of Ti with ions and substitutes for Ti [9], which further justifies the incorporation of vanadium and nitrogen into the TiO₂ lattice. The binding energy of O 1 s of TiO₂ lattice oxygen (Ti-O-Ti) for the VN3 sample is also shifted to 529.6 eV. Oxygen molecules can be dissociatively absorbed on the oxygen vacancies induced by doping N, thereby leading to a slight shift to lower binding energy of O 1 s of TiO₂ lattice oxygen (Ti-O-Ti) [18].

Figure 3c shows the high-resolution XPS spectra and corresponding fitted XPS for the N 1 s region of N-TiO₂, VN0, and VN3. A broad peak extending from 397 to 403 eV is observed for all samples. The center of the N 1 s peak locates at ca. 399.7, 399.6, and 399.4 eV for N-TiO₂, VN0, and VN3 samples, respectively. These three peaks are higher than that of typical binding energy of N 1 s (396.9 eV) in TiN [19], indicating that the N atoms in all samples interact strongly with O atoms [20]. The binding energies of 399.7, 399.6, and 399.4 eV here are attributed to the oxidized nitrogen similar to NO_x species, which means Ti-N-O linkage possibly formed on the surface of N-TiO₂, VN0, and VN3 samples [21-23]. The concentrations of V and N in VN3 derived from XPS analysis were 3.38% and 4.21% (at.%), respectively. The molar ratios of N/Ti on the surface of N-TiO₂ and VN3 were 2.89% and 14.04%, respectively, indicating obvious increase of N doping content by hydrothermal treatment with ammonium metavanadate. As shown in Figure 3d, the peaks appearing at 516.3, 516.9, 523.8, and 524.4 eV could be attributed to 2p_{3/2} of V⁴⁺, 2p_{3/2} of V⁵⁺, 2p_{1/2} of V⁴⁺, and 2p_{1/2} of V⁵⁺ [24,25]. It was established that the V⁴⁺ and V⁵⁺ ions were successfully incorporated into



the crystal lattice of anatase TiO₂ and substituted for Ti⁴⁺ ions.

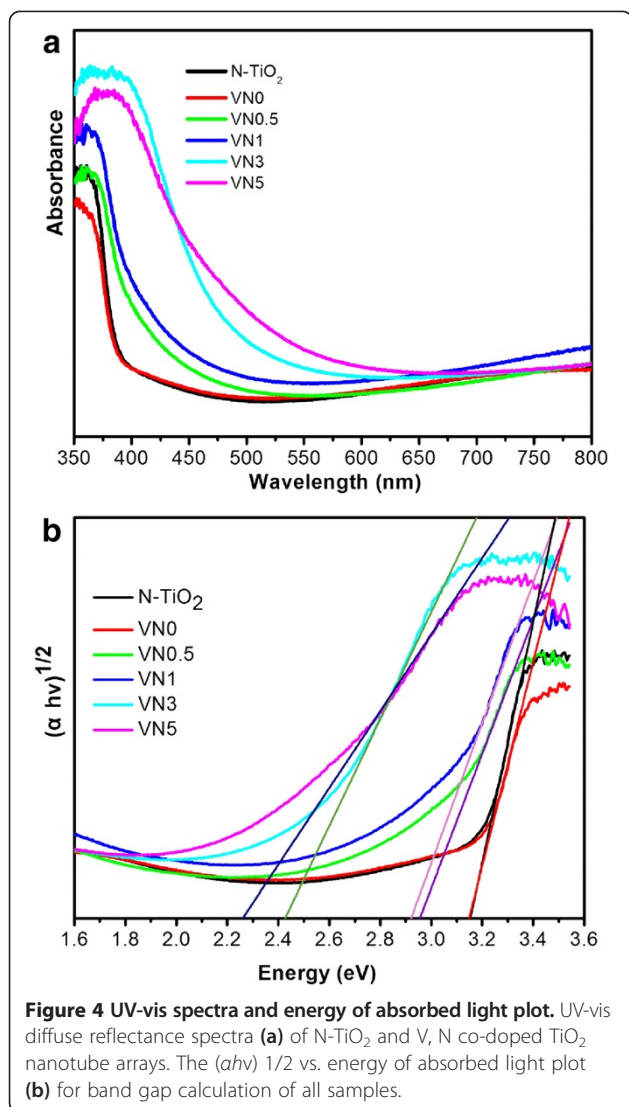
UV-vis DRS spectra analysis

UV-vis diffuse reflectance spectra of N-TiO₂ and V, N co-doped TiO₂ nanotube arrays are displayed in Figure 4. The spectrum obtained from the N-TiO₂ shows that N-TiO₂ primarily absorbs the ultraviolet light with a wavelength below 400 nm. For the V, N co-doped TNAs samples of VN0.5 and VN1, the UV-vis diffuse reflectance spectroscopy (DRS) spectra present a small red shift of adsorption edge and a higher visible light absorbance. With the increase of co-doping amount, an obvious red shift of the absorption edge and enhanced visible light absorbance were observed for the VN3 and VN5 samples. However, no obvious change of visible light absorbance was found for VN0, which indicates that the visible light absorbance of co-doped samples may be due to the contribution of both interstitially doped N and substitutionally doped V. Kubelka-Munk function was used to estimate the band

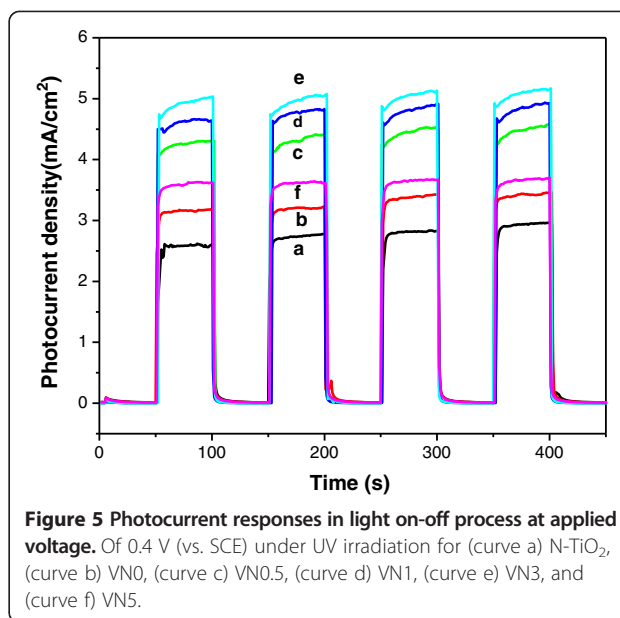
gap energy of all samples by plotting $(\alpha h\nu)^{1/2}$ vs. energy of absorbed light. The calculated results as shown in Figure 4b indicated that the band gap energies for N-TiO₂, VN0, VN0.5, VN1, VN3, and VN5 are 3.15, 3.15, 2.96, 2.92, 2.42, and 2.26 eV, respectively. It shows that the V, N co-doped TiO₂ nanotube array samples have a narrower band gap than that of N-TiO₂. When the dopant exists in an optimal doping concentration, V⁴⁺ and V⁵⁺ can easily substitute Ti⁴⁺ in the TiO₂ lattice, which might produce the new energy level and extend the light adsorption of TiO₂ due to the fact that ionic radius of V⁴⁺ and V⁵⁺ were both slightly smaller than that of Ti⁴⁺ [17]. Overall, the UV-vis DRS results indicate that N and V co-doped TiO₂ nanotube arrays are more sensitive to the visible light than N-TiO₂ samples.

Photoelectrochemical properties

A series of the photoelectrochemical (PEC) experiments were carried out to investigate the effect of the V, N co-



doping of TNAs films on the charge carriers separation and electron transfer processes. As shown in Figure 5, prompt generation of photocurrents was observed for all TNA samples upon illumination at an applied potential of 0.4 V vs. SCE. All samples showed good photoresponses and highly reproducible for numerous on-off cycles under the light on and light off conditions. The V, N co-doped TNAs exhibited higher photocurrents than that of N-TiO₂ samples under UV irradiation. Herein, N-TiO₂ electrode shows that only a lower photocurrent density of 2.5 mA/cm² may be due to the rapid recombination of charge carriers. With the co-doping of V and N, the VN3 sample exhibited highest photocurrent (5.0 mA/cm²) with optimal concentration. These results further inferred that V, N co-doped TiO₂ nanotube arrays possess good photoresponsivity to generate and separate photo-induced electrons and holes [26]. Excessive vanadium and nitrogen content caused the detrimental



effect, which acted as recombination centers to trap the charge carriers and resulted in low quantum yields [2,27]. From the PEC experimental results, optimum content of V and N co-doped into TiO₂ play an important role in maximizing the photocurrent density mainly attributed to the effective charge carrier separation and improve the charge carrier transportation.

Photocatalytic reduction performance

Photoreduction of CO₂ to methane were performed as a probe reaction to evaluate the photocatalytic activity of the V, N co-doped TNA films. During the CO₂ photoreduction reaction, the increase of CH₄ concentration (ppm/cm², ΔCH_4 , which is the difference between CH₄ concentration at t reaction time and the initial time) was used to evaluate the photocatalytic performance. As shown in Figure 6, concentration of CH₄ increased almost linearly with the UV irradiation time for the photocatalyst. V and N co-doped TNAs possess much higher photocatalytic activity than N-TiO₂ and VN0 sample hydrothermal treated in pure water. Moreover, photoreduction activity of V, N co-doped TNAs was enhanced and then decreased with the increase of doping content of vanadium and nitrogen. VN3 sample had the highest methane yield of 64.5 ppm h⁻¹ cm⁻². For comparison, reference reactions without catalysts or light irradiation were performed with other conditions being kept unchanged. All results indicated that there was almost no methane production when the experiment was carried out in the absence of catalysts or irradiation. We also investigated the effect of hydrothermal treatment on the photocatalytic activity. VN0 sample was obtained by the hydrothermal treatment of N-TiO₂ in pure water and used as a photocatalyst. A slightly

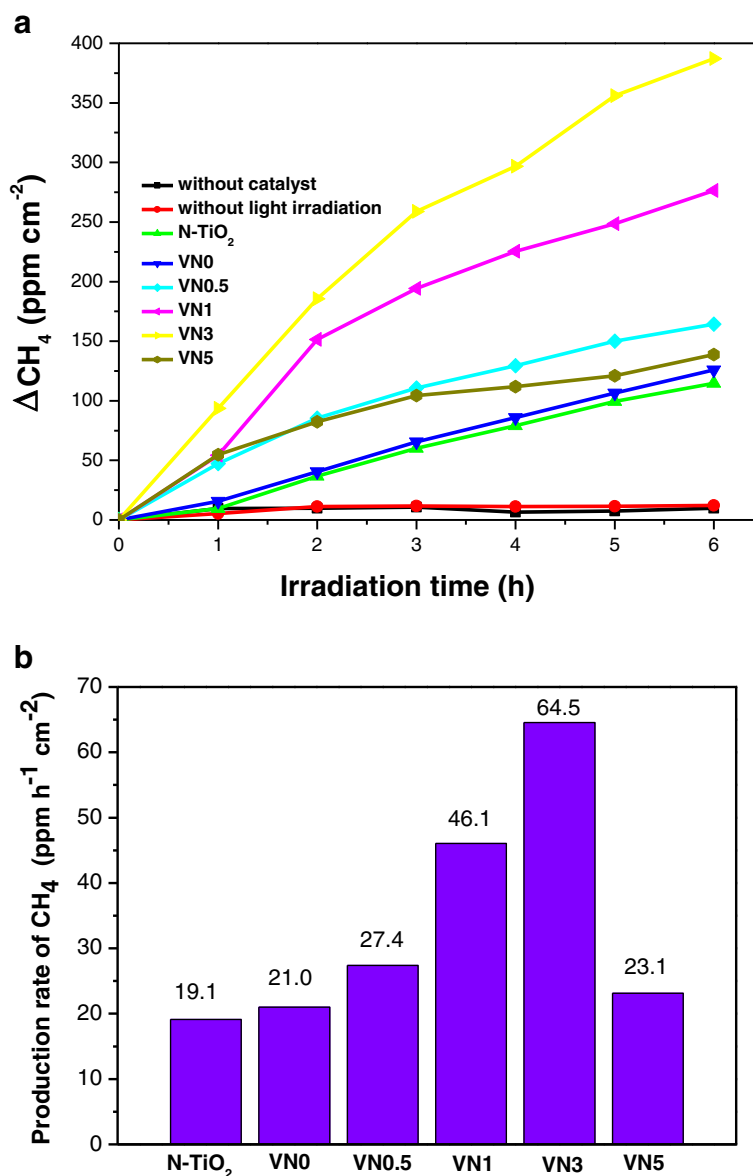


Figure 6 ΔCH_4 concentration dependence on irradiation time (a) and production rate of CH_4 (b) for all catalysts under UV irradiation.

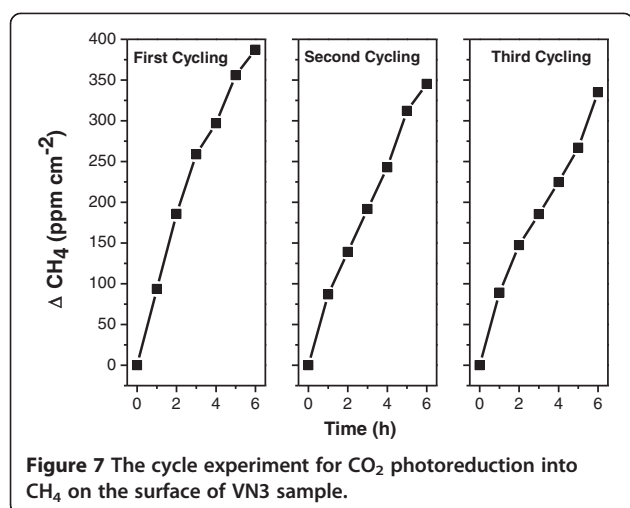
enhanced photocatalytic activity was found for VN0 sample as shown in Figure 6. This hydrothermal-assisted photocatalytic enhancement results are also confirmed by some researchers [28,29]. All results indicate that photo-excited process of V, N co-doped TNAs is essential in photoreduction process of CO_2 . However, for VN5 sample, the reduction activity is the lowest one because a further increase in the vanadium content would result in the aggregation of dopant nanoparticles, fast recombination of hole and electron pairs, and excess oxygen vacancies and Ti^{3+} defects state induced by nitrogen doping also served as recombination centers [30].

The photoreduction reaction of CO_2 over VN3 sample was also repeated to check the durability of photocatalyst.

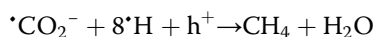
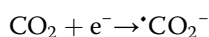
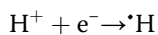
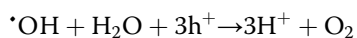
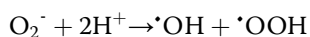
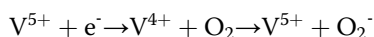
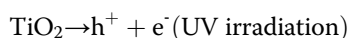
Figure 7 shows the CH_4 formation by VN3 sample for three times. After each cycle (6 h irradiation), the reaction vessel was degassed, then CO_2 and water vapor was introduced into it again. The photocatalytic activity could be restored after three cycles. In each cycle, the initial CH_4 evolution rate was recovered, and there was no CH_4 formation evolved when the light was off. The above durability results indicate that the V, N co-doped TNAs were stable under the present experimental conditions during the long irradiation time.

Photocatalytic reduction mechanism

When TNAs were radiated by the light with photon energy higher or equal to the band gaps of TiO_2 , more



electrons and holes induced by V and N co-doping lead to the reduction of CO₂ successfully. Previous studies revealed the trapping of the excited electron and hole by oxygen vacancy and doped nitrogen respectively reduced the recombination rate. The presence of nitrogen dopants was considered to reduce the formation energy of oxygen vacancies [31]. At the same time, the existence of O vacancies stabilized the N impurities [32]. When oxygen vacancies and N impurities are incorporated together, there is an electron transfer from the higher energy 3d band of Ti³⁺ to the lower energy 2p band of the nitrogen impurities [33]. The efficient separation and transfer of electron-hole pairs might also be associated with the interaction of V⁴⁺ and V⁵⁺. The V⁵⁺ species reacted with the electrons to yield V⁴⁺ species, which on surface oxygen molecules generated the oxidant superoxide radical ion O₂⁻. O₂⁻ reacted with H⁺ to produce hydroxyl radical and H⁺ and CO₂ trapped electrons to produce [•]H and [•]CO₂⁻, which further reacted with holes to yield the final product, methane [34].



Superabundant V and N could result in a decrease of photoreduction activity for increasing recombination centers of electrons and holes.

Conclusions

V-N co-doped TiO₂ nanotube arrays have been fabricated by a simple two-step method. V and N co-doped TiO₂ photocatalysts exhibit fine tubular structures after hydrothermal co-doping process. XPS data reveal that N is found in the forms of Ti-N-O and V incorporates into the TiO₂ lattice in V-N co-doped TNAs. V and N co-doping result in remarkably enhanced activity for CO₂ photoreduction to CH₄ due to the effective separation of electron-hole pairs. Meanwhile, the unique structure of co-doped TiO₂ nanotube arrays promoted the electron transfer and the substance diffusion.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

DDL carried out the synthesis, characterization, and photocatalytic reduction experiments. ZHZ participated in the synthesis and SEM characterization experiments. QYL and XDW participated in the XPS and Raman characterizations. MZ and JJY participated in the design and preparation of the manuscript. All authors read and approved the final manuscript.

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