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Physical properties of V-doped TiO_2 nanoparticles synthesized by sonochemical-assisted process

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Abstract

V-doped TiO_2 nanoparticles were synthesized by sonochemical process using titanium isopropoxide as a titanium source, vanadyl acetylacetonate as a dopant source. Sonication was conducted using sonic horn operated at 20 kHz for 20 min until the completely precipitated product was reached. The as-synthesized precipitates with various vanadium dopant (1–5 mol %) were calcined at 500–1000 °C for 4 h. The relevant physical properties of the nanoparticles were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and transmission electron microscope (TEM). The anatase phase TiO_2 nanoparticles can be synthesized by sonochemical process. Post calcinations process results in the anatase-to-rutile phase transformation and the enhancement in crystallinity with increasing temperature. The results also indicate good incorporation of V ions in TiO_2 lattices and significant effect of V dopant on alternation of interplanar spacing of TiO_2.

Keywords: A. Powders: Chemical preparation; B. Microstructure-final; D. TiO_2

1. Introduction

In recent years, titanium dioxide (TiO_2) has attracted considerable interest due to their promising applications in many areas such as smart window, buffer layer in dye-sensitized solar cell, self-cleaning materials, UV-detector, photodegradation and gas sensor. Due to the limitation of its properties such as rather high recombination of photo-generated electron-hole pairs, weak absorption in the visible region and weak magnetic property, the findings of a study examining doping with various elements such as Fe, N, Cu, Ag and Pd could indicate a promising method to resolve these problems [1]. Among transition metal ions, vanadium (V) is an attractive potential candidate as an effective additive into TiO_2 due to the close ionic radius between these two elements. Recently, there have been a number of research works focusing on effective techniques for synthysizing TiO_2 such as hydrothermal process [2], flame spray pyrolysis [3], co-precipitation process [4] and sonochemical process [5]. Among these techniques, the sonochemical process is well suited for the synthesis of these materials because of its simplicity, low equipment cost, ease of synthesis and doping. To our best knowledge, the synthesis of V-doped TiO_2 via sonochemical process in combination with post thermal calcinations has is not available in the literatures.

In this work, we report on the simple synthesis of V-doped TiO_2 nanoparticles by sonochemical precipitation process. The effect of vanadium content and the calcinations temperature on crucial physical properties of as-prepared products were thoroughly scrutinized.

2. Experimental and method

V-doped TiO_2 with various vanadium contents were synthesized by sonochemical-assisted process. Titanium isopropoxide [$Ti(C_6H_{14}O_2)_2$] and vanadylacetylacetonate [$VO(C_5H_8O_2)]_2$ were used as starting source materials for Ti and V, respectively. All chemicals were purchased form

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Sigma Aldrich. In the synthesis process, certain doping amount of vanadylacetylacetonate was dissolved into designated amount of titanium isopropoxide and stirred at room temperature for 24 h until a transparent pale yellow solution was obtained. The V doping concentration was varied from 1–5 mol %. 10 mL of the stocked solution and 150 mL of deionized water was filled into the chamber and then the mixed liquid was irradiated with high intensity ultrasound (650 W 20 kHz) by a Sonics Model VCX 750 at room temperature in ambient air for 20 min until the completely precipitated product was reached. After cooling down to room temperature, the resulting precipitates were washed with deionized water and ethanol and centrifuged at 5000 rpm for 5 min. After that the cleaned precipitates were calcined at different temperatures from 500–1000 °C for 4 h. The crystal structure and phase identification of the samples were investigated by X-ray diffraction with a monochromatic source of Cu Kα ($\lambda = 0.15405$ nm). Raman spectroscopy (Thermo Scientific DXR Raman Microscope with 532 nm DPSS laser) was employed to verify the substitution of the Ti sites with V in the TiO_2 lattice. X-ray photoelectron spectroscopy (AXIS Ultra ^{DLD} with dual anode Mg and Al K_α X-ray source) was applied to verify the chemical states of Ti and V. Their morphologies were monitored with JEOL JSM-6340 F field emission scanning electron microscope with an accelerating voltage of 5.0 kV. Transmission electron microscopy images and selected area electron diffraction (SAED) patterns were taken with TECNAI G2 20 transmission electron microscope, using an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the 5 mol% V-doped TiO_2 powders calcined at different temperatures from 500–1000 °C in air for 4 h. Noticeable diffraction peaks positioned at $2\theta = 25.29°$, 37.82°, 48.07°, 53.99° and 55.12° which are observed on the spectra of as-sonochemically-synthesized product and doped sample calcined at 500 °C was attributed to (101), (004), (200), (105) and (211) orientation plane of anatase-TiO_2 [JCPDS89-4921]. This result indicates that as-sonochemically-synthesized powder in anatase phase of TiO_2 can be obtained by single-step sonochemical process without the calcination [6]. Plausible formation mechanism of TiO_2 particles initiated by the sonochemical process is suggested. During sonication, dissolved titanium isopropoxide in deionized water can undergo hydrolysis and condensation process to create hydrolyzed alcoxides, which have numerous amount of functional hydroxyl groups. Simultaneously, rapid collision driven by intense ultrasound energy can sufficiently generate localized high temperature region, which is able to expedite the condensation reactions of hydroxyl groups to produce the nucleation of fine TiO_2 nanoparticles. When the calcinations temperature elevated to 600 °C, the mixture peaks of the anatase and rutile phase were observed with rutile phase being predominant and completely transformed to rutile phase as the temperature was over 600 °C. These results indicate that the phase transformation between anatase and rutile phase is activated at calcinations temperature-higher than 500 °C. Fig. 1(b) exhibits the XRD patterns of the V-doped TiO_2 with different V doping contents. As observed in all doped samples, the intense and sharp diffraction peaks situated at $2\theta = 27.49°$, 36.12°, 39.26°, 41.29°, 44.12°, 54.40° and 56.73° are assigned to (110), (101), (200), (111), (210), (211) and (220) plane of rutile phase [JCPDS89-4920]. No characteristic peaks ascribed to vanadium oxides (such as V_2O_5 or VO_2) were detected, indicating that the V ions can suitably be doped into TiO_2 lattice [7]. In addition, the significant shifts of peak positions to higher angle are observed (an inset of Fig.1(b)) as V doping content increases up to 3 mol% thereafter shifts back to lower angle, indicating the alternation of *d*-spacing of TiO_2 with specific V doping content. The inteplanar spacing (*d*-spacing) and crystallite size of the V-doped TiO_2 could be determined by Bragg's law and

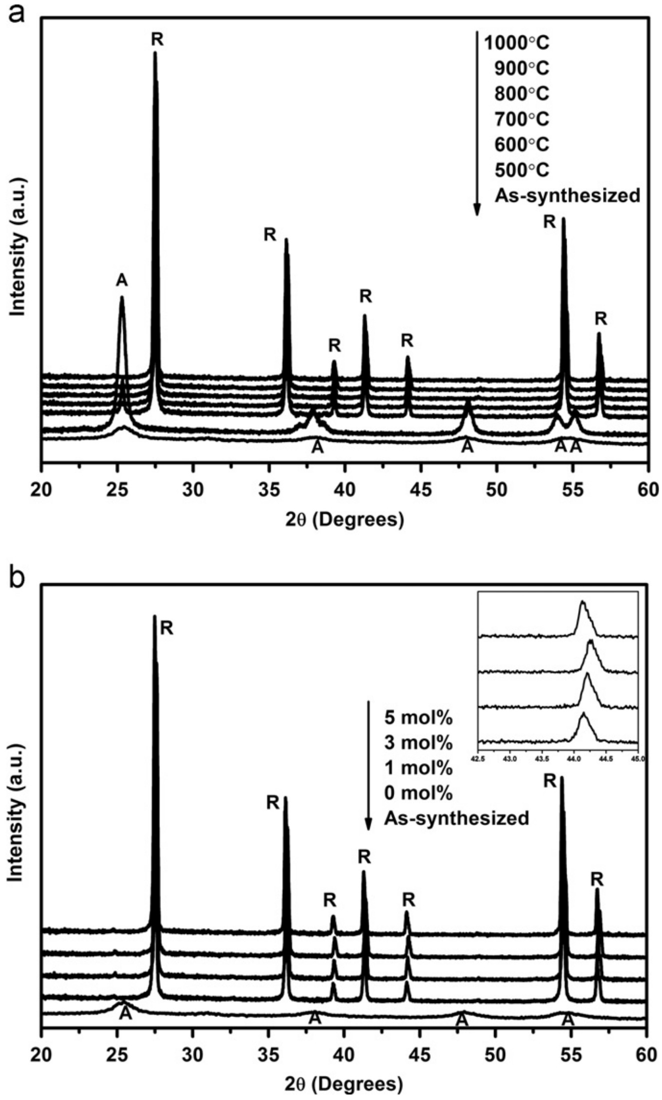

Fig. 1. XRD patterns of the V-doped TiO_2 nanoparticles synthesized by sonochemical process with different (a) calcination temperatures and (b) vanadium doping contents.

the Scherrer equation as shown in Table 1. This alternation in *d*-spacing may be attributed to the proper replacement of smaller ionic radius of V^{4+} (0.72 Å) at specific content on some of Ti^{4+} (0.75 Å) sites leading to the noticeable spacing shrinkage in TiO_2 [8].

Raman spectra of the samples prepared at different calcinations temperature and with different V doping contents are illustrated in Fig. 2(a) and (b), respectively. In Fig. 2(a), for the sample calcined at 500 °C for 4 h, the characteristic peaks at around 399, 516 and 639 cm^{-1} are attributed to B_{1g}, A_{1g} and E_g mode of anatase phase, respectively [9]. The rutile phase was obtained as the calcinations temperature ascended to 600 °C or even higher, the characteristic peaks of rutile phase at 235, 447 and 612 cm^{-1} ascribed to two-phonon scattering, E_g and A_{1g} mode of rutile phase are clearly noticed [9]. These results are in harmony with the results revealed by XRD spectra. Fig. 2(b) displays the Raman scattering of the V-doped TiO_2 with different V doping contents and calcined at 1000 °C for 4 h. All results indicate the scattering peaks around 235, 447 and 612 cm^{-1} corresponded to the characteristic peaks of rutile phase and the intensities of all characteristic peaks decrease with increasing doping content. Furthermore, the scattering peaks associated to the V–O compounds were undetectable. These results also imply the suitable doping of vanadium into rutile TiO_2 [10], that is well agreeable to the presumption from XRD results.

Table 1
Characteristics of V-doped TiO_2 with different condition

V-contents (mol%)	Temperature (°C)	*d*-spacing (Å)	Crystallite size (nm)
0	1000	3.24^R	51.57^R
1	1000	3.23^R	67.31^R
3	1000	3.22^R	57.35^R
5	1000	3.24^R	67.25^R
5	500	3.51^A	15.81^A
5	600	3.24^R	46.88^R
5	700	3.24^R	57.27^R
5	800	3.24^R	61.87^R
5	900	3.23^R	61.92^R

[A] Calculated from (101) orientation plane of anatase.
[R] Calculated from (110) orientation plane of rutile.

Additionally, the chemical composition of V-doped TiO_2 nanoparticle was analyzed by XPS as shown in Fig. 3. The peaks appearing at 458.7 and 464.3 eV are associated with $Ti^{4+}2p^{3/2}$ and $Ti^{4+}2p^{1/2}$, respectively [11]. It is an indication of the existence of Ti^{4+} ions in the sample. For V-doped TiO_2, The peak positions of Ti 2*p* slightly shift to high binding energies, suggesting that V ions are incorporated into TiO_2 lattice [12]. In Fig. 3(b), the peaks appearing at binding energies of 517.2 eV could be ascribed to $V^{4+}2p^{3/2}$ [7]. It is confirmed that the V^{4+} ions exist in the V-doped TiO_2 but the vanishment of V $2p^{1/2}$ binding energy is due to the low level of V doping [7]. This result strongly confirmed that the V^{4+} were appropriately incorporated into TiO_2 lattice and substituted to Ti^{4+} site due to its close ionic radius ($Ti^{4+}=0.75$ Å and $V^{4+}=0.72$ Å) [8].

The SEM images exhibiting the morphologies of 5 mol% V-doped TiO_2 calcined at different temperatures are demonstrated in Fig. 4. The SEM images disclose that the precipitate powders from sonochemical process are

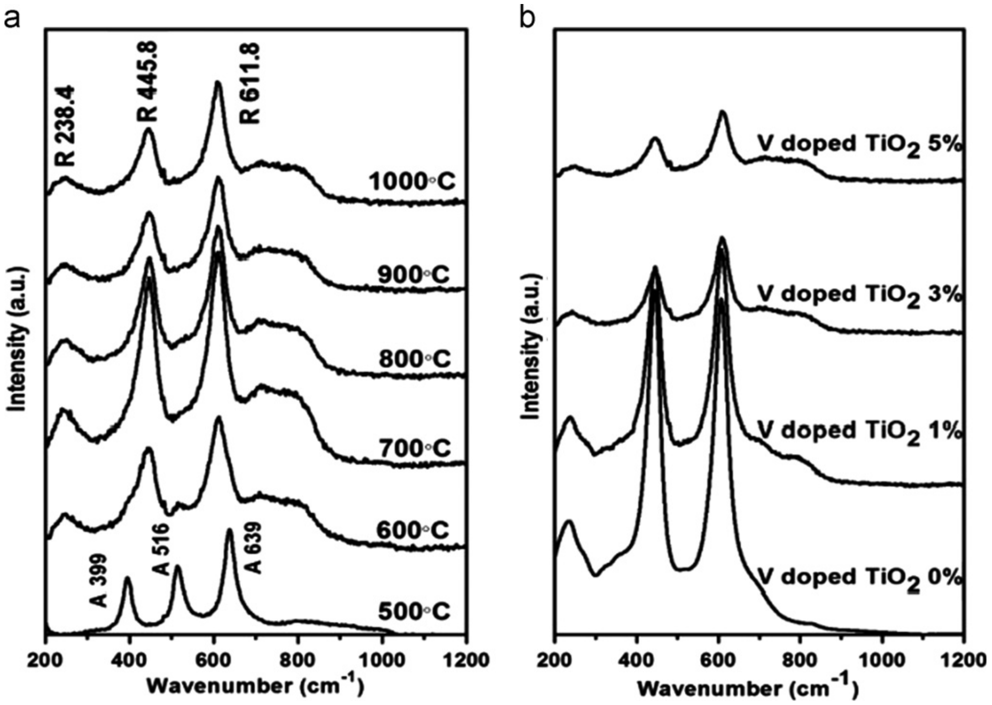

Fig. 2. Raman spectra of the V-doped TiO_2 nanoparticles synthesized by sonochemical process (a) at different calcination temperatures and (b) with vanadium contents (calcined at 1000 °C for 4 h).

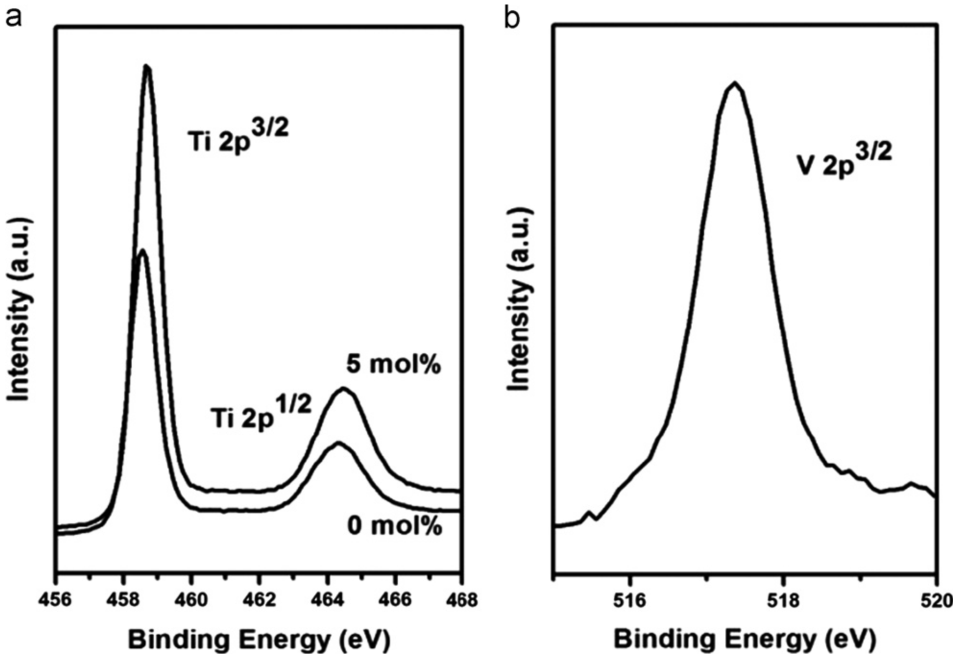

Fig. 3. XPS spectra of the V-doped TiO_2 5 mol% calcined at 1000 °C for 4 h synthesized by sonochemical process in (a) the Ti 2*p* regime and (b) the V 2*p* regime.

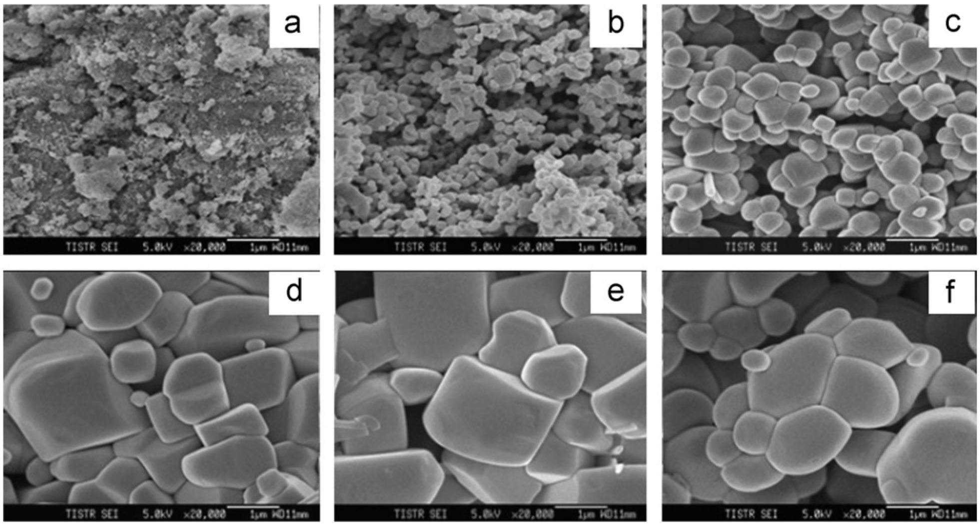

Fig. 4. SEM images of 5 mol% V-doped TiO_2 synthesized by sonochemical process and calcined at (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C and (f) 1000 °C.

aggregated from nanosize to microsize after calcinations temperature elevates from 500 °C to 1000 °C. High magnification and Selected Area Electron Diffraction (SEAD) mode of undoped and 5 mol% V-doped TiO_2 nanoparticles are shown in Fig. 5. The results reveal that the samples consist of interplanar spacing along the length direction of 3.27 Å and 3.25 Å for undoped and V-doped TiO_2, respectively. The TEM results revealing the decrease of interplanar spacing of TiO_2 due to V dopant is in good accordance with the values calculated from XRD patterns.

4. Conclusions

In summary, V-doped TiO_2 nanoparticles were successfully synthesized by sonochemical-assisted processs in combination with calcinations process in temperature range of 500–1000 °C. The XRD result disclosed that as-synthesized powder has an anatase phase of TiO_2. It was further notified that the calcinations temperature and the incorporation of V dopant have significant influence on physical properties of the powders. XRD and Raman spectra showed that the transformation of anatase to rutile

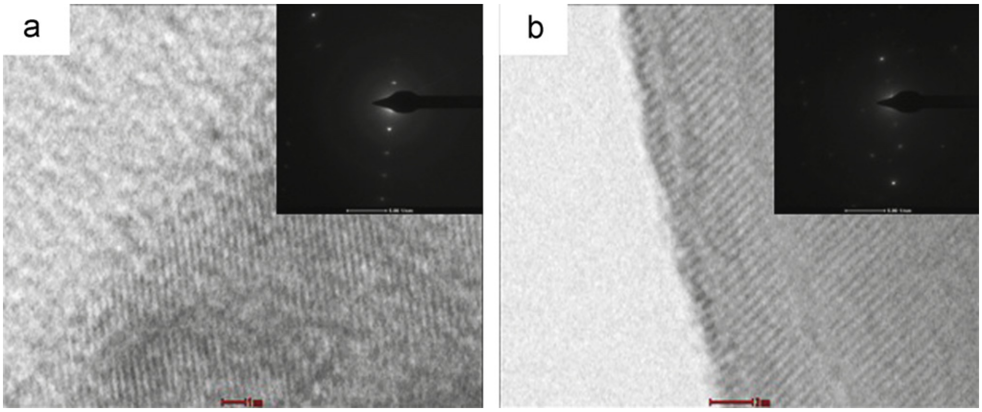

Fig. 5. TEM images of (a) undoped TiO_2 and (b) 5 mol% V-doped TiO_2 synthesized by sonochemical process and calcined at 1000 °C for 4 h (scale bar 1 and 2 nm; the inset images are SEAD mode).

phase was activated after the calcinations was over 500 °C. The amelioration in crystallinity was achieved with increasing calcinations temperature accompanying XRD and SEM results. XPS results revealed the existence of V ion incorporated into the TiO_2 lattice due to the close ionic radius between V^{4+} and Ti^{4+}. Noticeable interplanar spacing alternation was observed as the V doping content increased.

Acknowledgments

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