A Novel Single-Mode Microwave Assisted Synthesis of Metal Oxide as Visible-light Photocatalyst

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Abstract

Visible-light photocatalyst titanium dioxide (TiO\textsubscript{2}) was successfully prepared via a novel and facile single-mode microwave assisted synthesis process. In this one-step synthesis, Ti as target material selectively oxides in magnetic field throughout rapid heating, whose process requires less energy consumption and short time. In obtained TiO\textsubscript{2}, self-doping of Ti\textsuperscript{3+} was confirmed, which makes TiO\textsubscript{2} performed sufficient light absorption in visible region with wavelength above 400 nm. Such Ti\textsuperscript{3+} self-doped TiO\textsubscript{2} exhibits much narrower optical bandgap (2.14 eV) to compare with stoichiometric TiO\textsubscript{2} (3.0-3.2 eV). The synthesized TiO\textsubscript{2} also shows superior photocatalytic activity to commercially available TiO\textsubscript{2} towards the degradation of Rhodamine B under visible light irradiation.

Keywords: Single-mode microwave, TiO\textsubscript{2}, Ti\textsuperscript{3+}, visible light photocatalyst
1. Introduction

Titanium dioxide (TiO$_2$) is one of the most widely utilized photocatalysts with respect to its physical and chemical stability, high photocatalytic activity, and nontoxicity [1,2]. However, the wide bandgap (3.0 - 3.2 eV) of TiO$_2$ seriously limits its photocatalytic performance only in UV light region, which is about only 5% of incoming solar spectrum. The development of TiO$_2$ with activated photocatalysis under visible light irradiation is important for practical application. In order to improve the limited optical absorption of TiO$_2$, many efforts have been made to optimize the band structure of TiO$_2$ by inducing donor or acceptor states via doping of metals [3,4] or nonmetals impurities [5-8]. It has been also reported that inducing of oxygen vacancies and self-doping of Ti$^{3+}$ into stoichiometric TiO$_2$ effectively enhanced the light absorption in visible region and photocatalytic activities. Several approaches have been reported for the preparation of oxygen-deficient and Ti$^{3+}$ doped TiO$_2$, such as sol-gel processing, hydrothermal/solvothermal synthesis and magnetron sputtering method and so on. However, these processes require harsh experimental conditions, such as inert atmosphere, high temperature heating and high-pressure operation [9-11].

Microwave (MW) has been widely utilized as rapid heating process for past several decades, according to the direct interaction between target material and electro (E)- / magnetic (H)- field involved in MW and higher efficiency compared to conventional heating process. The absorbing properties of material in electromagnetic filed depend on its physical and chemical properties. Namely, metals perform good absorbing properties in H-filed while oxides perform absorbing properties in E-field[12-15]. Therefore, single-mode microwave applicator which can separate E- and H- filed components effectively has attracted much attention for selectively heating of different target materials [12-15].
In this work, we report a novel and facile single-mode MW assisted synthesis process of Ti$^{3+}$ doped TiO$_2$. Upon the one-step irradiation of single-mode MW on titanium (Ti) target in oxygen, Ti$^{3+}$ doped TiO$_2$ was successfully prepared in tens of second reaction via rapid temperature change and short heat history, which can be attributed to the drastic change of MW absorbing properties accompanied with change of chemical state in target material. To the best of our knowledge, the present work should be the first report on preparation of functional metal oxide from metal target via single-mode MW assisted synthesis. In addition, the obtained Ti$^{3+}$ doped TiO$_2$ performs sufficient light absorption in visible region and exhibits narrow band gap of 2.14 eV as well as superior photocatalytic activity in degradation of Rhodamine B under visible light irradiation. The innovative synthesis process of present work provides a brand-new direction of synthesis routine for metal oxides with specific chemical and physical properties.

2. Materials and methods

As for the synthesis of TiO$_2$, TE$_{111}$ mode 2.45 GHz cylindrical MW cavity was used in MW heating. 1.0 g of Ti powder (3N, powder under 45 μm mesh, Kojundo Chemical Laboratory, Japan), as target material, was loaded into a quartz tube and heated up in oxygen atmosphere under H-Field at fixed output of 20 W. During MW heating, the resonance frequency and temperature of the sample were measured by Vector Network Analyzer (VNA) and radiation pyrometer, respectively. The temperature and resonance frequency during MW heating are shown in Fig. S1.

The crystal structure of synthesized TiO$_2$ (hereinafter named as “MWS”), raw Ti powder and two kinds of commercial TiO$_2$ powders (rutile (Kojundo, Japan) and P-25 (Degussa), respectively) as references were analyzed by X-ray diffraction (XRD: Ultima IV, Rigaku,
Japan) with Cu-Kα line. The chemical structure of synthesized sample was also investigated by Raman spectra (NRS-3100, Jasco, Japan). The morphology and crystallinity of TiO$_2$-x on Ti particle were investigated by transmission electron microscopy (TEM: JEM-ARM200F, JEOL, Japan) and electron diffraction pattern. Surface chemical state of Ti in sample was analyzed by X-ray photoelectron spectroscopy with Al Kα X-rays radiation ($\nu = 1486.6$ eV) (XPS: M-prove, SSI, USA). UV and visible light absorption spectra were characterized by a commercial UV-Vis spectrophotometer (V-7100, Jasco, Japan).

As for photocatalytic degradation of Rhodamin B, a 500 W xenon lamp was used as the visible light source. Rhodamine B solution (20 ml) and the catalysis (MWS and S2) were taken in a beaker and exposed to visible light for up to 180 min. The solution samples of about 2-3 ml were taken out at a regular interval from the test solution, centrifuged for 5 min at 10000 rpm and their absorbance were recorded at 555 nm using a spectrometer (V-7100, Jasco, Japan). The decomposition amount of Rhodamine B was calculated as following formula.

$$\Delta C = c_i - c_0 \quad (1)$$

Here, $\Delta C$ is the decomposition amount of Rhodamine B (ppm), $c_i$ and $c_0$ are the concentration of Rhodamine B in the solution after being exposed and being reached equilibrium in dark. The concentration was estimated from the calibration curve using absorbance of Rhodamine B by Beer-Lambert law.
3. Results and Discussion

The XRD patterns of synthesized TiO$_2$, raw Ti, rutile and P-25 TiO$_2$ are shown in Fig.1. It can be confirmed that rutile TiO$_2$ phase (JCPDS-ICDD card No. 01-084-1283) was observed in synthesized sample while unreacted Ti was also remained. As Raman spectra shown in Fig. S2, the characteristic Raman-active modes of the rutile TiO$_2$ phase was also observed with bands appear at 143 cm$^{-1}$ ($B_{1g}$), 250 cm$^{-1}$ (multi-phonon process), 420 cm$^{-1}$ ($E_g$) and 612 cm$^{-1}$ ($A_{1g}$) [16]. No signals corresponding to any other crystallized TiO$_2$ was detected.

![XRD pattern of raw and obtained material](image)

**Fig. 1.** The XRD pattern of raw and obtained material.

Fig.2 displays the TEM images, selected area electron diffraction pattern and EDS mapping results of synthesized TiO$_2$. The EDS mapping (Fig.2 (c-e)) results of the elemental distribution of Ti and O indicates that part of O was only distributed in surface
area. It illustrates that the synthesized sample exhibits core/shell structure of Ti/ TiO$_2$ with 2.8 μm thickness of shell. In Fig.2 (b), rutile phase with a tetragonal crystal system and a space group P4$_2$/mnm was confirmed in the surface part of TiO$_2$ shell.

![Fig. 2.](image)

**Fig. 2.** (a) TEM image of obtained sample, (b) selected area electron diffraction pattern and EDS mapping the elemental distribution of (c) Ti, (d) O and (e) overlap

The chemical bonding state in synthesized TiO$_2$ was investigated by XPS and results are shown in Fig.S3. Fig.S3(a) displays XPS spectra of Ti$_{2p}$ orbital and peaks at 464.5, 462.8, and 461.1 eV can be assigned to Ti$^{4+}$, Ti$^{3+}$, and Ti$^{2+}$, respectively [17]. The peak area ratio of each Ti coordination number (Ti$^{4+}$, Ti$^{3+}$, and Ti$^{2+}$) were calculated by curve fitting using Gaussian function (Fig.S3 (b)). As a result, Ti$^{3+}$ was numerously existed on sample surface of synthesized TiO$_2$ which implies the formation of oxygen-deficient TiO$_2$ with
efficient self-doping of Ti$^{3+}$ during MW synthesis. Furthermore, the spectra of O1s orbital showed obvious difference between the synthesized TiO$_2$ and the conventional one. The synthesized TiO$_2$ had a shoulder peak at about 532 eV as shown in Fig. S4. The peaks at 530.1, 531.7 and 533.2 eV are assigned with O$^{2-}$ (Ti-O) and OH$^{-}$ and absorbed water [18,19]. In general, oxygen vacancy induce dissociation of H$_2$O, then taking place OH group chemisorption on the surface of TiO$_2$ [20,21]. Therefore, this result indicates that the synthesized TiO$_2$ has high concentration of oxygen vacancy.

The UV-vis spectra and calculated Tauc plot of the synthesized TiO$_2$ are given by Fig.3. As a result, MW synthesized Ti$^{3+}$ doped TiO$_2$ exhibited significantly enhanced light absorption in the visible region with wavelength above 400 nm to compare with commercial TiO$_2$. The optical band gap of synthesized TiO$_2$ estimated from Tauc plot is 2.14 eV, which is much narrower than that of stoichiometric TiO$_2$. Such narrow bandgap can be attributed to the localized states at 0.75–1.18 eV below the conduction band minimum induced by oxygen vacancy [22]. As inserted photograph shown, the MW synthesized Ti$^{3+}$ doped TiO$_2$ shows grey-black color while stoichiometric (P-25) TiO$_2$ gives white color. It has been reported that electrons trapped in oxygen vacancy of TiO$_2$ can absorb light of a specified wavelength and then color becomes grey or black [23-25]. Fig.4 shows the photocatalytic activity of MW synthesized Ti$^{3+}$ doped TiO$_2$ characterized by degradation of Rhodamine B (RhB) under visible light irradiation. The synthesized T$^{3+}$ doped TiO$_2$ performed superior photocatalytic activity to commercial P-25 under visible light.
Fig. 3. Absorption spectra of raw and obtained material: (a) Absorbance and (b) Tauc plot. Inset pictures are MWS (A) and P-25 (B).

Fig. 4. Characterization of photocatalytic activity by degradation of RhB
4. Conclusions

In summary, TiO$_2$ was successfully synthesized via a one-step single-mode MW assisted process. Ti as target material selectively oxides in H-field throughout rapid heating, whose process requires less energy consumption and short time. The synthesized TiO$_2$ exhibits rutile phase according to the results of XRD and Raman spectrum. In addition, self-doping of Ti$^{3+}$ was confirmed in obtained TiO$_2$ by XPS measurement of Ti$_{2p}$ orbitals. Such MW synthesized TiO$_2$ showed excellent absorption property in visible light region with wavelength above 400 nm and narrow optical bandgap of 2.14 eV. In photocatalysis experiment of Rhodamine B degradation, photocatalytic performance of obtained TiO$_2$ was superior to commercially available TiO$_2$ under visible light irradiation. The innovative process for preparing metal oxide with specific chemical and physical properties open a brand-new strategy for developing functional materials.

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