Enhanced Ofloxacin Degradation Efficiency on Porous CeTi$_2$O$_6$ Photocatalyst - CTAB Induced Porosity

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Abstract: Background: Photocatalytic oxidation of organic pollutants in the environment is being studied for more than half a century. Titanate has the activity on the degradation of organic pollutants under UV light illumination. Template directed sol-gel method is capable of producing porous structure in titanate during high temperature thermal treatment. Methods: The materials were characterized using X-ray powder diffraction, transmission electron microscopy, scanning electron microscopy, surface area and pore size analyses, UV-Visible spectrometry, and X-ray photoelectron spectroscopy. Photocatalytic activity of the CeTi$_2$O$_6$ material was evaluated through ofloxacin degradation. Results: Brannerite structured CeTi$_2$O$_6$ was the major component in the samples, and the addition of CTAB caused a slight growth of CeTi$_2$O$_6$ crystals. Porous structure formed in the porous sample after the removal of CTAB template, and the surface area and pore volume were greatly enlarged. The first order reaction rate constant for photocatalytic degradation of ofloxacin was $9.60 \times 10^{-3}$ min$^{-1}$ on the nonporous CeTi$_2$O$_6$ sample, and it was as large as $2.44 \times 10^{-2}$ min$^{-1}$ on the porous CeTi$_2$O$_6$ sample. The addition of CTAB can influence the physico-chemical properties of the porous CeTi$_2$O$_6$, such as the improved activity on photocatalytic degradation of ofloxacin. Conclusion: The CeTi$_2$O$_6$ samples composed of majority brannerite CeTi$_2$O$_6$, and CeTi$_2$O$_6$ crystal sizes for the nonporous and porous samples were 38.1 and 43.2 nm. The burning up of CTAB during calcination produced abundant pores in the porous material. After 50 min of reaction, photocatalytic degradation efficiencies on the nonporous and porous CeTi$_2$O$_6$ samples were 38.1% and 70.5%. Keywords: CeTi$_2$O$_6$, photocatalysis, Cetyltrimethyl Ammonium Bromide, Ofloxacin, degradation, organic pollutants.

1. INTRODUCTION

Photocatalytic oxidation of organic pollutants in the environment has been studied for more than half a century [1-3]. Antibiotics are a major type of organic pollutants that have been discharged into the aquatic system [4, 5]. Photocatalytic mineralization of such harmful substances has aroused great attention, such as MoS$_x$, Ag–CuO and CrTiO$_3$ nanotube [18-17]. Many other types of materials have also aroused great attention, such as MoS$_x$, Ag–CuO and CrTiO$_3$ nanotube [18-22].

Titanate has the activity on photogeneration of electrons and holes under UV light illumination [23-27]. Recently, lanthanide titanates were used for water splitting and organic pollutants decomposition. Abe et al. reported the enhanced hydrogen evolution from water on gadolinium titanate Gd$_2$Ti$_2$O$_7$ and yttrium titanate Y$_2$Ti$_2$O$_7$ [28]. Methyl orange was decomposed on neodymium titanate Nd$_2$Ti$_2$O$_7$, gadolinium titanate Gd$_2$Ti$_2$O$_7$ and erbium titanate Er$_2$Ti$_2$O$_7$ [29], and methylene blue was degraded on cerium titanates CeTiO$_4$ and CeTi$_2$O$_6$ [30]. Cationic elements in titanates can be alkaline earth metals, transition metal and lanthanide elements. These materials usually have a small pore volume and surface area due to high temperature thermal treatment during the preparation process. Although calcination at high temperature is essential for the crystallization of lanthanide titanates, the lack of porosity is not beneficial for the photocatalytic oxidation process.

Template directed sol-gel method is capable of producing porous structure in titanate during high temperature thermal treatment [31-34]. In this work, CTAB was applied in a sol-gel process to act as pore-forming template. It is a novel attempt to show the effects of CTAB on physico-chemical properties of the porous CeTi$_2$O$_6$ material. The materials were characterized using X-ray powder diffraction, transmission electron microscopy, scanning electron microscopy, surface area and pore size analyses, UV-Visible spectrometry, and X-ray photoelectron spectroscopy. The photocatalyst...
lytic activity of the CeTi$_2$O$_6$ material was evaluated through ofloxacin degradation.

2. EXPERIMENT

2.1. Preparation of Porous CeTi$_2$O$_6$ Material

Cetyltrimethyl ammonium bromide was added in the precursor to prepare porous CeTi$_2$O$_6$ material. A transparent solution was composed using 8 mL deionized water, 8 mL acetic acid, 2 g CTAB and 0.4652 g Ce(NO$_3$)$_3$·6H$_2$O, and another solution was made from 8 mL ethanol, 2 mL glycol and 0.85 mL tetrabutyl titanate. After mixing the two solutions to form the final precursor, the sol-gel transforming process was conducted at 70°C. The gel was dehydrated at 110°C, and then it was calcined in air at 800°C for 3 h. The nonporous CeTi$_2$O$_6$ sample was prepared in a similar process without adding CTAB in the precursor.

2.2. Characterization of the Materials

X-ray powder diffraction patterns were taken on a D8 X-ray diffractometer using Cu Ka radiation (Tube voltage 40 kV, tube current 40 mA, scanning step 0.05°/min, scanning speed 4°/min). TEM images of the materials were taken on FEI Tecnai G2 20 transmission electron microscope (Tube voltage 200 kV). Pore size distribution and specific surface area were examined on ASAP 2460 surface area and pore size analyzer. The specific surface area of the material was determined by the multipoint Brunauer-Emmett-Teller (BET) method. Mesopore volume distribution was determined using the Barrett-Joyner-Halenda (BJH) method. UV-Vis diffuse reflectance spectra were recorded by LAMBDA 35 UV-Vis spectrometer. An integrating sphere was equipped to determine the reflectance intensity. The scanning speed was 480 nm/min in the wavelength range between 200 and 600 nm. The binding energy of the element was measured on ESCALAB 250Xi X-ray photoelectron spectroscopy with a monochromatic Al Kα source. The binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. (Al Ka, pass energy 100.0 eV, energy step 1.000 eV). The steady-state PL spectra of the powders were obtained by the Perkin Elmer LS55 fluorescence spectrophotometer with an excitation wavelength at 253.7 nm.

2.3. Photocatalytic Activity Evaluation

Photocatalytic degradation of ofloxacin was conducted in a lab-scale reactor to compare the activities of CeTi$_2$O$_6$ material. The reactor was composed of a 100 mL quartz beaker and a UV source. The light source was a 20 W ultraviolet lamp, which can irradiate 253.7 nm with an intensity of 2300 μW/cm$^2$. 50 mL 20 mg/L ofloxacin solution was used as the wastewater that was mixed with 20 mg photocatalyst. Firstly, the adsorption of ofloxacin on the material was measured in the dark after adsorption-desorption equilibrium. Subsequently, the lamp was turned on to initiate the photocatalytic degradation of ofloxacin. The water samples were taken out of the ofloxacin solution and were filtrated to remove the particulate matter. Ofloxacin concentration was measured by the UV detector on Agilent 1260 high performance liquid chromatography. The column was Zorbax Eclipse XDB-C18 (150×4.6 mm, 5 μm), and the mobile phase was the mixture of 1% phosphoric acid aqueous solution and acetonitrile.

3. RESULTS AND DISCUSSION

Fig. (1) shows XRD patterns of the nonporous and porous CeTi$_2$O$_6$ samples. Most of the diffraction peaks in the XRD pattern of the nonporous CeTi$_2$O$_6$ sample are in accordance with brannerite structured CeTi$_2$O$_6$ of the monoclinic system [30, 35]. A weak diffraction peak at 2θ=56.3° can be attributed to fluorite type CeO$_2$ (JCPDS file No.34-0394). The nonporous CeTi$_2$O$_6$ sample is composed of 79.7% brannerite CeTi$_2$O$_6$ and 20.3% fluorite CeO$_2$. The diffraction pattern of the porous sample is different from the nonporous one. The diffraction intensity of brannerite CeTi$_2$O$_6$ decreases, whereas the diffraction intensity of fluorite CeO$_2$ becomes stronger, especially for the (111) and (311) planes in a face-centered cubic lattice. The porous CeTi$_2$O$_6$ sample is composed of 67.8% brannerite CeTi$_2$O$_6$ and 32.2% fluorite CeO$_2$.

The phase transformation from CeTi$_2$O$_6$ to CeO$_2$ is not possible in the existence of CTAB since both the nonporous and porous CeTi$_2$O$_6$ samples are prepared at the same calcination temperature. The formation of Ce-O-Ti bonding in the gel is essential for the production of CeTi$_2$O$_6$. However, the addition of CTAB in the precursor inhibits the formation of Ce-O-Ti bonding. Alternatively, the free cerium ion in the gel tends to be oxidized during the calcination process. Scherrer formula, L=Kλ/(β·cosθ), is used to calculate the crystallite size on the preferred (110) plane (2θ=26.1°) of brannerite CeTi$_2$O$_6$. The crystallite sizes for the nonporous and porous CeTi$_2$O$_6$ are 38.1 and 43.2 nm, so that the addition of CTAB causes a slight growth of CeTi$_2$O$_6$ crystals.

![Fig. (1). XRD patterns of the nonporous and porous CeTi$_2$O$_6$ samples.](image)

TEM and SEM images of the nonporous and porous CeTi$_2$O$_6$ samples are presented in Fig. (2). Particles in the nonporous sample can be as large as several micrometers. The surface of the large particle is quite rough due to the aggregation of small particles. CeTi$_2$O$_6$ crystals fuse into each other without apparent interface. As a result, holes or
cavities cannot be found in the large particles. On the other hand, small CeTi$_2$O$_6$ crystals can be clearly observed in the image of the porous sample, and the crystal size is comparable to the calculated size, i.e., 43.2 nm. The small crystals do not aggregate into large particles or fuse into others so that the crystal boundary can be clearly distinguished. Meanwhile, the porous structure can be found in the porous sample due to the removal of CTAB template during calcination.

Pore size distribution and specific surface area examinations are important for porous materials to ascertain the porous structure [36]. The BET specific surface areas of the nonporous and porous CeTi$_2$O$_6$ samples are 1.2 and 19.6 m$^2$/g, respectively. The total pore volume of the nonporous sample is as small as 0.0022 cm$^3$/g, and the pore volume of the porous sample is as large as 0.0459 cm$^3$/g. The burning up of CTAB during calcination leaves abundant pores in the porous material. The average pore size in the nonporous sample is 47.5 nm, which is mainly attributed to the small number of interparticle holes. The average pore size in the porous sample is 38.7 nm.

Fig. (3) shows UV-visible diffuse reflectance spectra of the nonporous and porous CeTi$_2$O$_6$ samples. The absorption edges of the materials seem to be in the visible light region and all the ultraviolet irradiation can be absorbed by the obtained CeTi$_2$O$_6$ samples. Band gap energy of the material is calculated using the Tauc plot method [37]. The band gap energies of the nonporous and porous CeTi$_2$O$_6$ samples are 2.85 and 3.06 eV, respectively. As compared to the nonporous sample, absorption edge of the porous sample has a slight blue shift. This blue shift cannot be attributed to the well-known quantum size effect since the addition of CTAB causes a slight CeTi$_2$O$_6$ crystal expansion. The change of band gap energy can be related to the constituents in the materials. As stated before, minor fluorite CeO$_2$ and anatase TiO$_2$ are produced in the porous CeTi$_2$O$_6$ sample, so that the overall band gap energy is slightly enlarged.

Fig. (4) illustrates XPS Ce$3d$, O$1s$ and Ti$2p$ spectra of the nonporous and porous CeTi$_2$O$_6$ samples. Eight electron binding energy peaks are found in the Ce$3d$ spectra. The peaks v and u belong to Ce$3d_{5/2}$ and Ce$3d_{3/2}$ electron orbitals, situating at 882.6 and 901.2 eV, respectively [38]. The other six peaks are attributed to the satellite peaks of Ce$3d_{5/2}$ and Ce$3d_{3/2}$ electron orbitals. The above-mentioned electron binding energies do not change after using CTAB to prepare porous CeTi$_2$O$_6$. Meanwhile, the existence of both Ce$^{3+}$ and Ce$^{4+}$ oxidation states of cerium can also be proven by the v’/ u’ and v”/ u” pairs [39]. According to the formula Ce$^{3+}$($\%$) =100%* (Sv+Su)/∑(Sv+Su), the ratio of Ce$^{3+}$ decreases from 18.9% in the nonporous sample to 16.7% in the porous sample. Cerium is mainly in the Ce$^{4+}$ oxidation state in both the samples, and the addition of CTAB can strengthen this tendency. This phenomenon can also be used to interpret the slightly expanded band gap energy of the porous sample, since 4/orbital electron can introduce an intermediate energy level in the cerium titanate [40].

Three electron binding energy peaks can be distinguished in the O$1s$ spectra. The peaks at 529.5, 530.0 and 531.5 eV are due to lattice oxygen in CeTi$_2$O$_6$, surface adsorbed oxygen and hydroxyl group in the adsorbed water molecule [41]. There is nearly no chemical shift of the three states of oxygen in the porous CeTi$_2$O$_6$ sample. Two symmetrical peaks
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in the Ti2$p$ spectra represent Ti2$p_{3/2}$ and Ti2$p_{1/2}$ electrons in the materials. Titanium is in the fully oxidized Ti$^{4+}$ in the obtained CeTi$_2$O$_6$ material, which can be proven by the 5.7 eV difference between the two electron binding energies \[42\].

The PL spectra of the CeTi$_2$O$_6$ samples are illustrated in Fig. (5) to show the effect of CTAB on the recombination of photogenerated electrons and holes. The excitation wavelength is 253.7 nm, which is the same as the irradiation wavelength of the UV lamp used in this work. All the samples have similar PL spectra with the maximum emission intensity around 495 nm. The emission intensity of the porous CeTi$_2$O$_6$ sample is much lower than the nonporous CeTi$_2$O$_6$, indicating the effective electron-hole separation in the porous material.

Photocatalytic activities of the two CeTi$_2$O$_6$ samples are examined through the degradation of ofloxacin under UV light irradiation, as shown in Fig. (6). Ofloxacin molecules can be adsorbed on the materials with the adsorption efficiencies of 12.5% and 22.4% on the nonporous and porous samples, respectively. However, the removal of ofloxacin from the solution mainly depends on the photocatalytic degradation process. The degradation of ofloxacin obeys the first order reaction law, and the degradation efficiency constantly increases with extending illumination time. After 50 min of reaction, photocatalytic degradation efficiencies
on the nonporous and porous CeTi$_2$O$_6$ samples are 38.1% and 70.5%, respectively. At this time, 92.5% of the initial ofloxacin molecules are removed from the solution by adsorption and photocatalytic degradation on the porous sample. The first order reaction rate constant is 9.60×10$^{-3}$ min$^{-1}$ on the nonporous CeTi$_2$O$_6$, while the reaction rate constant is as large as 2.44×10$^{-2}$ min$^{-1}$ on the porous CeTi$_2$O$_6$.

The porous CeTi$_2$O$_6$ sample was reused to examine its recycling performance on ofloxacin degradation. Photocatalytic reaction under illumination was performed in each cycle, and then the ofloxacin solution was restored to its initial concentration. Photocatalytic degradation efficiency after 50 min of irradiation is 70.5% in the first cycle, and the efficiency can be 65.3% in the fifth cycle.

Fig. (6). Photocatalytic degradation of ofloxacin with prolonged irradiation time on the nonporous and porous CeTi$_2$O$_6$ samples. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (7) shows HPLC analyses of ofloxacin solution during photocatalytic degradation on the nonporous and porous CeTi$_2$O$_6$ samples. The original ofloxacin solution is chromatographically pure and has a solely peak at a retention time of 4.55 min. The peak intensity decreases with extending irradiation time, while the solution containing porous CeTi$_2$O$_6$ undergoes a faster dropping off of HPLC peak intensity. There are several small peaks at shorter retention time in the chromatograms, indicating the formation of degradation intermediates during the photocatalytic oxidation process.

Fig. (8) illustrates the photocatalytic degradation mechanism of ofloxacin on the porous CeTi$_2$O$_6$ material. The initial step for photocatalytic degradation is the photogeneration of electron-hole pairs, which are involved in the subsequent production of hydroxyl and peroxyl radicals. The oxidative radicals are responsible for the degradation of organic pollutants into CO$_2$ and H$_2$O. The band edges of the porous CeTi$_2$O$_6$ material are calculated through the following equations 1 & 2 [43, 44]:

\[
E_{CB} = X - E^c - \frac{1}{2}E_g
\]

\[
E_{VB} = E_{CB} + E_g
\]

Where, $E_{CB}$ is the conduction band edge, $E_{VB}$ is the valence band edge, $X$ is the absolute electronegativity of CeTi$_2$O$_6$, $E^c$ is the energy of the free electrons on the hydrogen scale (about 4.5 eV), and $E_g$ is the band gap energy of the sample.

The valence band edge and conduction band edge of the porous CeTi$_2$O$_6$ material are 2.81 and -0.37 eV, respectively. The oxidation potential is 2.72 V for the oxidation of H$_2$O to produce hydroxyl radical [45], and the reduction potential is -0.13 V for the reduction of O$_2$ to produce •O$_2$ [46]. In this case, the valence band potential of the porous CeTi$_2$O$_6$ material is higher than the oxidation potential of H$_2$O, and the conduction band potential is lower than the reduction potential of O$_2$.

Fig. (7). High performance liquid chromatography analyses of ofloxacin solution during photocatalytic degradation on (a) nonporous CeTi$_2$O$_6$ and (b) porous CeTi$_2$O$_6$. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
CONCLUSION

The effects of CTAB on the properties of CeTi$_2$O$_6$ material were investigated. The CeTi$_2$O$_6$ samples were composed majorly of brannerite CeTi$_2$O$_6$, and CeTi$_2$O$_6$ crystallite sizes for the nonporous and porous samples were 38.1 and 43.2 nm, respectively. The burning up of CTAB during calcination produced abundant pores in the porous material. The absorption edge of the porous sample had a slight blue shift as compared to the nonporous sample. Cerium was mainly in its Ce$^{4+}$ oxidation state in both the samples, and the addition of CTAB can strengthen this tendency. After 50 min of reaction, photocatalytic degradation efficiencies on the nonporous and porous CeTi$_2$O$_6$ samples were 38.1 and 70.5%, respectively. The valence band edge and conduction band edge of the porous CeTi$_2$O$_6$ material were 2.81 and -0.37 eV, respectively.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data supporting the findings of the article is available from the corresponding author [W.Z] on reasonable request.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

REFERENCES


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