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Photocatalytic Performance of CPC Photoreactor in Presence of Anatase/Rutile TiO_2 Mixed Phase

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Abstract

Titanium dioxide mixed phase of anatase and rutile was prepared via sol-gel process with ultrasound assistance then calcined at different temperatures to obtain mixed phase TiO_2. The mixed phase TiO_2 with specific ratio was used as photocatalyst in compound parabolic collecting (CPC) photoreactor. X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the phase transformation of TiO_2. Photoactivities of the prepared photocatalysts were performed to decolorize the organic dye solution by coating on solid glass spherical beads which were packed in CPC photoreactor to study the performance of photodegradation. The results indicate that the system can be practically utilized and the cleaning is required for the next use.

Keywords: Titanium dioxide, Sonochemical, CPC reactor

1. Introduction

In the photocatalytic application, TiO_2 is one of the most attractive semiconductor with great effective role as photocatalyst. Naturally, there are three different structures of TiO_2 including anatase, rutile and brookite with its slight difference on band-gap energy. Due to the flat band potential, TiO_2 is one of most photoreactive semiconductor materials for producing the reactive radicals. Furthermore, TiO_2 has been used in various fields of applications; for instance solar cell technology, sensor technology, surface coating and photocatalyst [1,2]. Among those different polymorphs, anatase and rutile phase are most effective in photocatalytic application. However pure phase of anatase or rutile can be improved to obtain greater performance in photocatalytic activity. Some of researches have reported that the mixed phase between anatase and rutile phase in specific fraction can potentially enhance the photocatalytic performance by retarding the rate of electron-hole recombination after excitation process and also enhance the life time of excited state of electron which can be migrate to the surface of material and react with absorbed molecules. For material preparation, there are many alternative way to produce the mixed phase TiO_2 particles. A great method to synthesize the TiO_2 nanoparticles is ultrasound assisted sol-gel process as known as sonochemical process by produce fine particles with low aggregation of the particles [3,4]. In the use as photocatalyst in the photoreactor, TiO_2 particles were coated on spherical transparent solid substrate. For coating process, many methods have been used. Most well-known and uncomplicated methods for coating the TiO_2 on substrate is dip-coating process. It is known as a low energy requiring process, simply system and large production process [5].

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In this work, TiO_2 mixed phase was prepared by sonochemical process then calcined at different temperatures. The anatase to rutile phase transformation of prepared titanium dioxide was investigated by x-ray photoelectron spectroscopy (XPS) and x-ray adsorption spectroscopy (XAS) to study the chemical properties and the change in transition state. The anatase and rutile mixed phase of TiO_2 nanoparticles at specific ratio were also coated on solid glass substrate by dip coating process for using in photocatalytic application with CPC reactor.

2. Experimental details

2.1 Preparation of TiO_2 mixed phase particles

Titanium dioxide particles were synthesized using titanium tetraisopropoxide (TTIP) designated as the starting precursor. Firstly, 0.5 mol of titanium tetraisopropoxide (TTIP) was mixed with 20 ml ethanol following by stirring for 2 h. Deionized water was then added into the solution until total volume was 100 ml. The mixed solution was further stirred for 2 h. The prepared precursor was irradiated under intense ultrasound operated at, 750 W 20 kHz for 30 min during sol-gel process until the precipitated product was obtained, The precipitated materials was dried followed by calcination process calcined for 5 h at 500°C to 800°C.

2.2 Preparation of coated TiO_2

The mixed phase TiO_2 particles were coated on spherical glass beads whose diameter of 0.6 mm used as substrate to embed the TiO_2 particles using dip coating process. For dip coating process, the spherical substrates were cleaned then dipped in the titanium aqueous for 10 min. The dipping step was conducted for 10 times followed by drying process in each cycle coating. The coated glass beads were proceeded to heat treatment process at 400°C for 1 h.

2.3 Characterization

The main characterization is to investigate the anatase and rutile mixed phase and phase transformation of as-prepared TiO_2 by using x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). Photocatalytic process of mixed phase TiO_2 coated glass beads was carried out in the designated CPC photoreactor under light illumination.

3. Results and Discussion

3.1 Phase identification by X-ray diffraction technique

Fig.1 reveals the main peaks of x-ray diffraction patterns of as-prepared TiO_2. It is clearly indicated that the mixed phase of as-prepared TiO_2 occur at the annealed temperature range of 600°C -700°C. The main peak that according to anatase phase is appeared at 2θ = 25.5°, corresponding to its (101) plane. Meanwhile the peak of rutile phase is situated at 2θ = 27.8° that is corresponded to its (110) plane. Therefore, the mixed phase of as-prepared TiO_2 can be obtained at calcination temperature in range of 600°C -700°C. The as-prepared TiO_2 could be completely transformed to rutile phase at heating temperature beyond 800°C [6].

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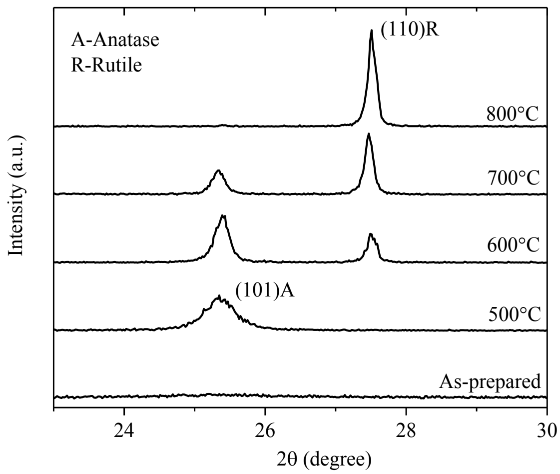

Fig. 1. XRD patterns of different TiO_2 phases of prepared TiO_2 particles calcined at different temperatures.

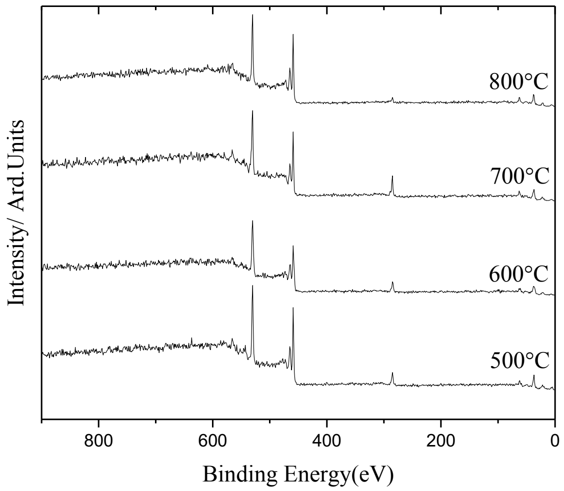

Fig. 2. X-ray photoelectron spectra of prepared TiO_2 particles calcined at different temperature.

3.2 X-ray Photoelectron Spectroscopy (XPS)

Fig. 2. illustrate the survey scan of x-ray photoelectron spectra of TiO_2 particles calcined at different temperatures. The main appeared peaks are corresponded to C1s, Ti2p and O1s peaks located at 286 eV, 258.9 eV and 530 eV, respectively [7]. Fig. 3. shows O1s XPS spectra of prepared TiO_2 calcined at different temperatures. The peak consists of two closely located components. The peak at higher energy can be attributed to O-H or O-C bonds and the peak located at lower energy can be attributed to O-Ti bond.

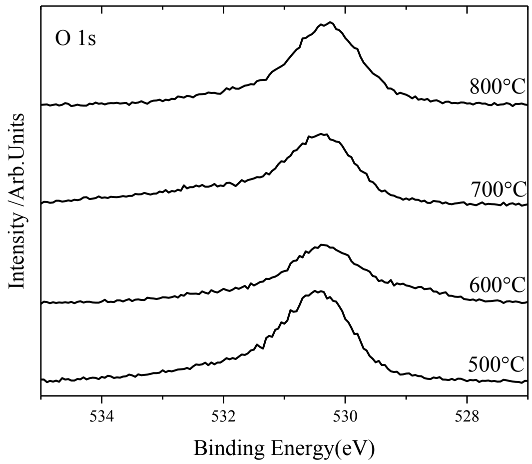

Fig. 3. O1s XPS spectra of prepared TiO_2 particles calcined at different temperature.

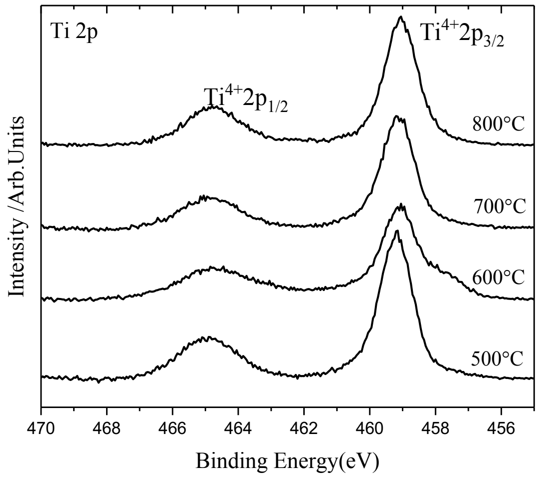

Fig. 4. Ti 2p XPS spectra of TiO_2 powders calcined at different temperature.

The Ti2p XPS spectra of prepared TiO_2 that were calcined at different temperatures are illustrated in Fig. 4**.** The peaks indicating the spin orbital splitting locate at 464 eV and 458 eV relating to Ti^{4+} $2p_{1/2}$ and Ti^{4+} $2p_{3/2}$, respectively [8,9].

3.3 X-ray Absorption Spectroscopy (XAS)

To investigate the mixed phase of prepared TiO_2 at different calcined temperatures, x-ray absorption spectroscopy was employed to study the anatase to rutile phase transformation of prepared TiO_2. The Ti K-edge XANES spectra of prepared TiO_2 with different calcined temperatures is shown in Fig.5. the XANES patterns of as-prepared sample and the sample calcined at 500°C are identical to the anatase standard sample.

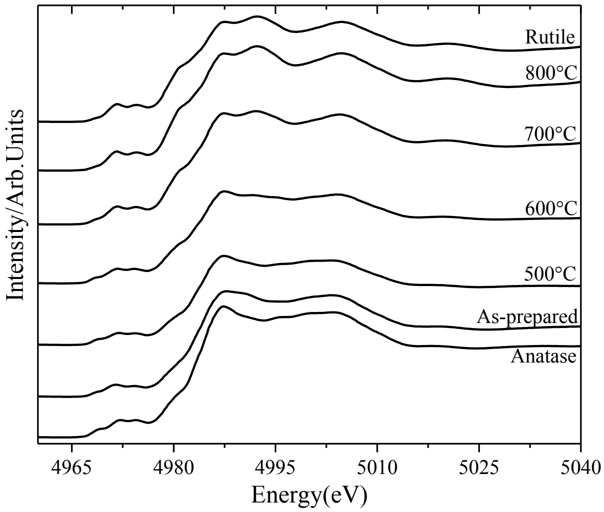

Fig. 5. Ti K-edge XANES spectra of TiO_2 particles calcined at different temperatures.

At calcined temperature of 600°C, the corresponding XANES spectrum exhibits the specific featured patterns combined with anatase and rutile peaks meanwhile those patterns of the samples calcined at higher temperatures are in the same feature of rutile standard sample. This result affirms that the prepared TiO_2 particles are transformed from anatase to rutile phase at high temperature which also corresponding to x-ray diffraction results [10].

3.4 Photocatalytic Performance

Photocatalytic activities of coated TiO_2 mixed phase were measured by decolorization of rhodamine B organic dye solution. The coated glass spheres were loaded in the reactor tube of compound parabolic collector. The system was carried under solar irradiation then dye solution was withdrawn for 3 ml every 30 min for 4 hr. Finally, water was flowed throughout the system to clean the residue of dye solution out of the system. The collected dye solution was evaluated by UV-Visible spectrophotometer. Degradation reaction percentage of coated glass spheres can be determined as follow the equation [11].

$$\%Degradation = \frac{C_0 - C_t}{C_0} x100 \quad (1)$$

Where C_0 and C_t is the concentration of dye solution at initial and concentration of dye solution at time t, respectively. The photodegradation performance of coated TiO_2 mixed phase on glass sphere has shown in Fig. 6. The decolorization of rhodamine B dye solution by TiO_2 mixed phase calcined at 700°C indicates the highest photodegradation performance due to mixed phase of anatase and rutile in suitable fraction and the interfaces between both phases. Some of ratio of TiO_2 mixed phase could not maximize the photocatalytic performance because it is also depend on interface between phases.

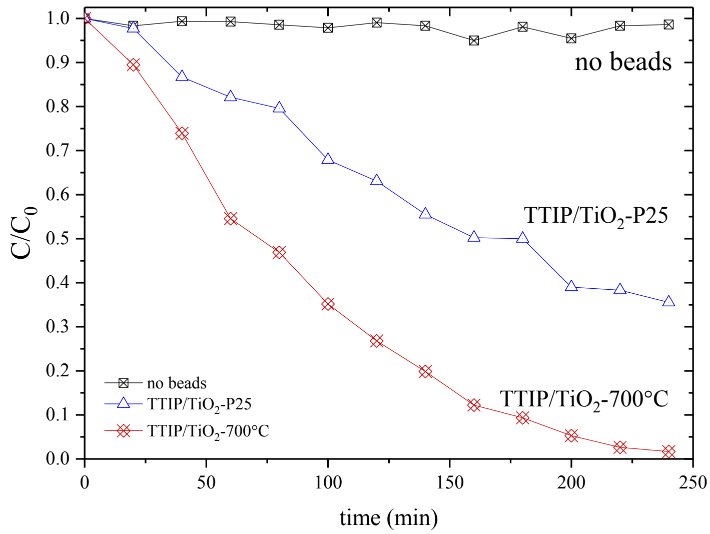

Fig. 6. Photocatalytic activities of different coated glass sphere in CPC photoreactor under solar irradiation.

According to our previous work, the phase ratio of this sample is 24 and 76 of anatase phase and rutile phase, respectively[12]. By mixing of anatase and rutile TiO_2 in proper fraction, the excited electron and hole can be transfer to the other states instead of lead to rapid recombination [3]. Furthermore, it can be increased lifetime to react with organic molecules on the surface of materials resulting to more reactivity to degrade the organic dye molecules. The black line photodegradation of dye solution without coated glass beads, it's show the slightly degradation which due to its photolysis process of dye solution meanwhile the glass beads coated with TiO_2-P25 are show clear for photodegradation as it's the commercial grade of mixed phase TiO_2 powders with ratio is 70 and 20 of anatase and rutile phase, respectively. However, as above description the photocatalytic performance of mixed phase TiO_2 are depend on various parameters such as method of preparation, precursor and interface of each phase which can transfer the excited charge to the other phase before recombine.

4. CONCLUSION

Anatase/Rutile mixed phase titanium dioxide was prepared via sonochemical process following by calcination process at different temperatures to obtain the mixed phase between anatase and rutile for using as photocatalyst. The XPS result indicates the slight difference in Ti2p corresponding to different phases of TiO_2 when calcined at different temperatures. XAS result clearly illustrates the change in K-edge peak of prepared TiO_2 when calcined at different temperatures indicating that it is absolutely transformed from anatase phase at calcined at below 500° C to rutile phase at calcination temperature over 700° C. The photocatalytic result indicates the TiO_2 mixed phase calcined at 700° C show highest performance compare to other sample. The mixing phase of anatase and rutile in proper ratio can be increase in photodegradation performance due to excited charge can move to other phase prior recombine. With this idea, increase in lifetime to react with molecules on the surface. However, it is not only mixing phase of anatase and rutile that can be improve its photocatalyst performance. It is also depend on preparation method and interface of each phase.

Acknowledgments

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