Preparation and performances of nanosized Ta_2O_5 powder photocatalyst

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Abstract

Nanosized-Ta_2O_5 powder photocatalyst was successfully synthesized by using sol–gel method via $TaCl_5$ butanol solution as a precursor. Ta_2O_5 species can be formed under 500 °C via the decomposition of the precursor. The crystalline phase of Ta_2O_5 powder photocatalyst can be obtained after being calcined above 600 °C for 4 h. The crystal size and particle size of Ta_2O_5 powder photocatalyst was about 50 nm. A good photocatalytic performance for the degradation of gaseous formaldehyde was obtained for the nanosized-Ta_2O_5 powder. The Ta_2O_5 powder formed at 700 °C for 4 h and at 650 °C for 12 h showed the best performance. The calcination temperature and time play an important role in the crystallization and photocatalytical performance of nanosized-Ta_2O_5 powder.

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1. Introduction

Ta_2O_5 oxide has been widely used as key material of dynamic random access memory, antireflective coating layer, and impedance under high temperature, gas sensor and capacitor due to its high dielectric constant, high refractive index and high chemical stabilization [1,2].

Ta_2O_5 is a semi-conducting material with band gap of 3.0 eV, which also has shown photocatalytic activities. The organic compounds such as 2-propanol can be photodegraded under irradiation of UV light [3]. In addition, the composite-oxide based on tantalum such as $InTaO_4$ is an efficient photocatalyst for splitting water to form hydrogen [4–7]. Nanosized-Ta_2O_5 powder can be prepared by the solvothermal reaction of tantalum pentabutoxide (TPB) [3] or tantalum oxide gel [8]. But, the precursor is not easy to be obtained and is also very expensive. Besides, the mesoporous structure of Ta_2O_5 can be obtained via the ligand-assisted templating method [7,9,10]. Thus, nanosized Ta_2O_5 and tantalate photocatalyst have attracted many researchers [11,12]. The knowledge of nanosized Ta_2O_5 as a photocatalyst is limited, it is still important to reveal the relationship between structure and photocatalytical performance.

In this work, nanosized-Ta_2O_5 powder photocatalyst was synthesized using sol–gel method via $TaCl_5$ as a precursor. The structure and photocatalytic performance have been investigated. A good photocatalytic activity was obtained for nanosized-Ta_2O_5 powder.

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2. Experimental

2.1. Preparation of nanosized-Ta_2O_5 photocatalyst

All of the chemicals were of analytical grade. $TaCl_5$ (1.0 ml) was slowly added dropwise into 10 ml ethanol at room temperature. Then, 0.1 ml diethanolamine was added as stabilizer and 0.1 ml water was added as a hydrolyzing agent. A light yellow solution was obtained and gelatinized for 24 h to form sol–gel. Then, the sol–gel solution was vaporized at 80 °C until a dry-gel was obtained. The dry-gel precursor was calcined at different temperatures for a definite time in air to form Ta_2O_5 powders. In order to promote the decomposition of organic components in the precursor, the initial heating rate was maintained at 5 °C/min.

2.2. Instrumental

IR spectra were obtained in Perkin-Elmer 2000 FT–IR spectrometer. The Raman spectra were recorded on a Renishaw RM1000 spectrometer, and the wavelength of the laser light was 514 nm. XRD experiments were carried out on a D8 Advance Bruker X-ray Diffractometer with monochromatized $CuK\alpha$ ($\lambda =$ 1.5418 Å) radiation. The morphology and particle size were measured using a Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of electron beam was 200 kV. TGA and DTA analyses were performed on a Dupond 1090 thermal analyzer. The atmosphere was air, and the heating rate was maintained at 10 °C/min.

An 8 W lamp was used as a light source with its main wavelength at 254 nm. The photoreactor used was a 250 ml cylindrical quartz vessel, which consisted of an inlet, an outlet and a sample port. Ta_2O_5 powder was dispersed on the surface of glass plate with $2 \times 3\,cm^2$ area homogeneously. The glass slide with Ta_2O_5 powder was tested in the vessel perpendicular to the light beam. The distance between the sample and the light source was 5 cm, where the light intensity was measured to be 1840 $\mu W/cm^2$ at 254 nm, 113 $\mu W/cm^2$ at 365 nm and 333 $\mu W/cm^2$ at 420 nm. The gaseous formaldehyde in the contaminated atmosphere was obtained by vaporization of formaldehyde liquid using predetermined values of flow rate controlled by mass flow controllers. The mixture was then forced to flow through the photoreactor for 1 h. Then the photoreactor was sealed and the photocatalytic reaction was started by switching on the lamp. Subsequently, the concentration of formaldehyde in the photoreactor, obtained by a gastight syringe from the sample port, was measured with a SP-502 gas chromatograph (GC) equipped with a flame ionization detector and a 2 m stainless-steel column (GDX-403) at 100 °C.

3. Results and discussion

3.1. Thermal decomposition processes of precursor

Fig. 1 shows a typical TGA result of $TaCl_5$ precursor gelatinized for 24 h. The change of residual weight with temperature was shown by the real line and the differential of the weight loss was shown by the broken line. Four weight-loss regions were observed on the TGA curve. Based on the quantitative calculation of the weight loss in each region, the thermal decomposition processes were distinguished as following. The weight loss region from 30 to 40 °C resulted from the loss of solvent. The regions of weight loss from 198 to 290 °C and from 320 to 340 °C were attributed to the elimination of OH group and the decomposition of the organic compound diethanolamine. The organic groups were all nearly eliminated at about 490 °C. The weight loss region at about 500 °C was attributed to the loss of Cl^-. The sample kept its weight at about 600 °C, which was 40.3% of the original weight.

The thermal decomposition processes of the dried precursor calcined at different temperature were investigated using IR analysis. The peaks of organic compound became weaker as the calcination temperature rose, implying that the organic groups were gradually eliminated as the calcination temperature increased. The higher the calcination temperature was, the more similar the IR peaks position and shape of sample was to that of pure reference Ta_2O_5. After the precursor sample calcined at 600 °C for 4 h, IR cannot detect any organic group and the spectrum is similar to that of pure Ta_2O_5 sample, implying that pure Ta_2O_5 species formed.
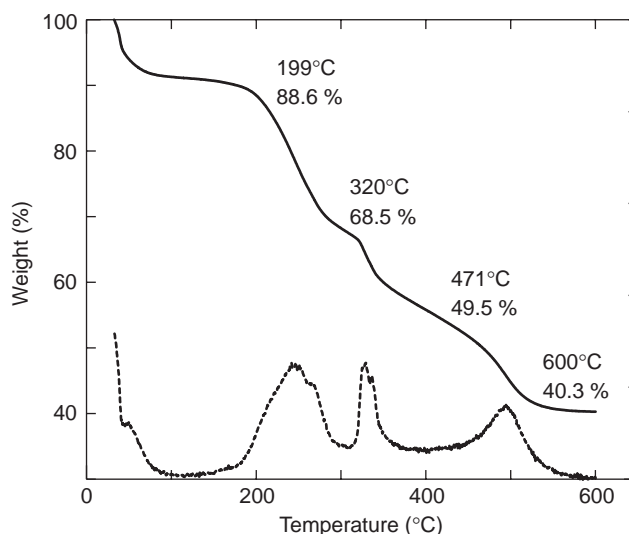

Fig. 1. The TGA result of Ta_2O_5 precursor gelatinized for 24 h.

3.2. Influence of calcination on crystalline phase

The influence of the calcination temperature on the formation of Ta_2O_5 crystalline phase has been investigated using XRD. The XRD patterns of Ta_2O_5 precursor samples calcined at different temperatures for 4 h are shown in Fig. 2. After the precursor was calcined at 500 °C for 4 h, the XRD pattern showed that the sample was still amorphous. Several sharp peaks were observed after the precursor was calcined at 600 °C for 4 h. Based on the XRD standard spectra of Ta_2O_5 crystal, these peaks were attributed to the pure Ta_2O_5 crystal. This result indicated that Ta_2O_5 with crystal structure could be synthesized in this way at 600 °C for 4 h. However, the crystal phase was not perfect and was mainly amorphous. With increasing the calcination temperature to 700 °C, on XRD peak was intensified significantly and also became much sharper. This indicated that the crystalline phase of Ta_2O_5 became more perfect with rising the calcination temperature.

The average crystal sizes of Ta_2O_5 powder samples have be measured via XRD pattern parameters based on Scherrer equation: $D_c = K\lambda/\beta\cos\theta$. D_c is the average crystal size, K is the Scherrer constant equal to 0.89, λ is the X-ray wavelength equal to 0.15406 nm, β is the full-width at half-maximum (FWHM) and θ is the diffraction angle. The average crystal size of the sample synthesized at 700 and 800 °C was the same as 50 nm, implying that the effect of calcination
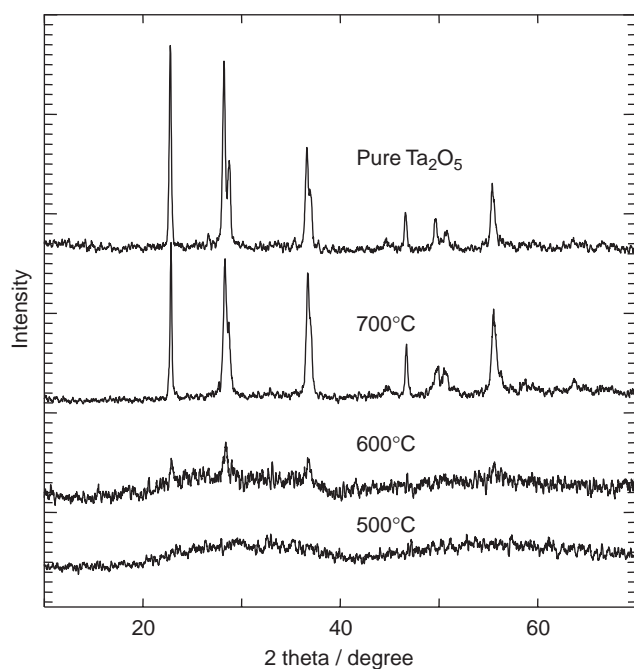
temperature on the crystalline size was very small under 800 °C.

The influence of calcination time on the formation of Ta_2O_5 crystalline phase was also studied by XRD. As it was shown in Fig. 3, no crystal was formed for Ta_2O_5 powder when the precursor was calcined at 650 °C for 2 h. The crystalline phase of Ta_2O_5 was formed after the precursor was calcined at 650 °C for 4 h. However, the crystal phase was not perfect and was mostly amorphous. All diffraction peaks of Ta_2O_5 were observed after the precursor was calcined at 650 °C for 8 h, indicating that the perfect crystal of Ta_2O_5 can be synthesized at 650 °C for 8 h. XRD peaks only became a little and became much sharper with prolonging the calcination time. This indicated that the crystalline phase of Ta_2O_5 can become more perfect on prolonging the calcination time.

The Raman spectra of Ta_2O_5 samples calcined at various temperatures were shown in Fig. 4. The Raman spectrum of Ta_2O_5 calcined at 500 °C only showed the strong fluorescence absorbtion, indicating that no crystalline structure was formed. After the calcination temperature increased to 600 °C, several Raman peaks appear though the fluorescence absorbtion still existed. It can be deduced that the crystal structure of Ta_2O_5 powder formed at 600 °C was not perfect. After the sample was calcined at 700 °C for 4 h, the Raman spectrum of sample is almost similar to that of pure
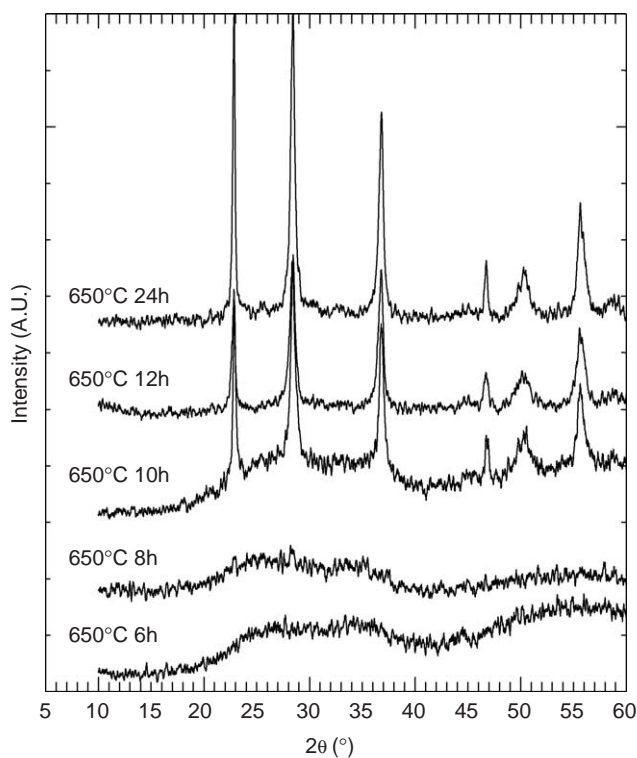

Fig. 2. The XRD spectra of the precursor calcined at various temperatures for 4 h.

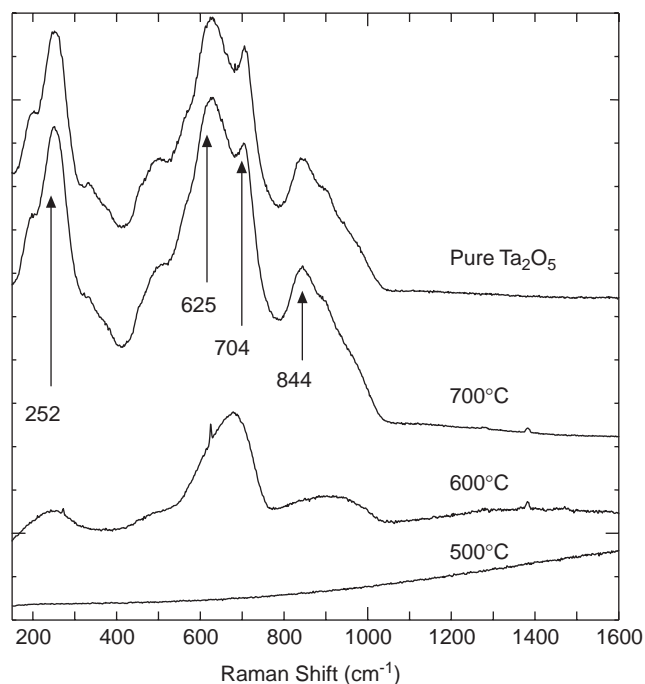Fig. 3. The XRD spectra of the precursor calcined at 650 °C for various time.

Fig. 4. The Raman spectra of Ta_2O_5 powder calcined at various temperatures for 4 h.

Ta_2O_5 powder, indicating that the perfect crystalline Ta_2O_5 powder was obtained.

The above results indicated that Ta_2O_5 crystalline phase can be formed at a relatively low temperature (600 °C). The calcination temperature and time play an important role on the formation of crystal structure of Ta_2O_5 powder.

3.3. Morphology of Ta_2O_5 nanosized photocatalyst

The morphology and grain size of Ta_2O_5 powder photocatalysts, which varied with calcination temperature have been studied using TEM as shown in Fig. 5. The grain size of the sample calcined at 500 °C was uniform and about 50 nm as shown in Fig. 5a. Some polycrystalline rings are found in the diffraction pattern but no single crystal diffraction dots are found. It means that polycrystalline Ta_2O_5 was formed at this temperature though XRD did not show any diffraction patterns. It can be explained that Ta_2O_5 tiny crystal can be formed after the precursor was calcined at 500 °C for 4 h. The particle size of Ta_2O_5 sample formed at 600 °C was about 50 nm as well, but the dimensional uniform is not good as shown in Fig. 5b. Some cubic crystal can be observed in certain parts. Both polycrystalline diffraction rings and single crystal diffraction dots are found in the diffraction patterns, indicating that single crystal of Ta_2O_5 was formed. After the precursor was calcined at 700 °C for 4 h, most Ta_2O_5 particles existed as single

crystal and the grain size grew up to 100 nm. The grain sizes grew up on the increasing the calcinations temperature of the precursors. TEM results also indicate that the particles size of Ta_2O_5 powder grew up from 50 to 100 nm on prolonging the calcination time from 2 to 24 h at 650 °C.

3.4. Photocatalytic performance of nanosized Ta_2O_5 powder

The evaluation of photocatalytic activity was carried out on gas chromatograph system. Fig. 6 shows he result of photocatalytic activity of nanosized-Ta_2O_5 photocatalyst calcinated at 650 °C for 8 h. The result indicated that the concentration of gaseous formaldehyde reduced from 1100 to 50 ppm in 40 min. After UV light was turned on for about 60 min, formaldehyde was degraded completely, implying that nanosized Ta_2O_5 is a good photocatalyst under UV irradiation. The photocatalytical reaction of gaseous formaldehyde can be considered as a zero grade reaction.

Fig. 7 shows the degradation curve of gaseous formaldehyde degraded by Ta_2O_5 powder calcined at various temperatures for 4 h. As is shown, the apparent reaction constant of Ta_2O_5 powder formed at 600 °C for 4 h is about 0.0098. The photocatalytical performance is not so good because the crystal structure of nanosized Ta_2O_5 powder is not perfect due to low calcination temperature. Although XRD showed that crystalline structure was not perfectly calcined at 600 °C for 4 h, LRS and electron diffraction pattern indicated the formation of crystalline Ta_2O_5. The photoactivities of Ta_2O_5 increased with the calcination temperature increasing due to more perfect crystal structure. When the calcination temperature reached 700 °C, the photocatalytical performance reached the best and the apparent reaction constant reached 0.0326. After the calcination temperature increased to 800 °C, the apparent reaction constant decreased again. The significant increase of crystal size due to high calcination temperature resulted in the decrease of photoreactivity though the crystal structure became more perfect. It is in concordance to the results of XRD patterns and TEM.

Fig. 8 shows the degradation curve of gaseous formaldehyde degraded by Ta_2O_5 powder which was calcined at 650 °C various time. The apparent reaction constant of Ta_2O_5 powder formed at 650 °C for 4 h is about 0.0109. With the prolonging of the calcination time, the crystal structure became more perfect, resulting in the raising of photoactivities. When the calcination time prolonged to 12 h, the photocatalytical performance reached the best and the apparent reaction constant reached 0.0453. After the calcination time prolonged to 24 h, the apparent reaction constant decreased to 0.0167.The growth of crystal size resulted
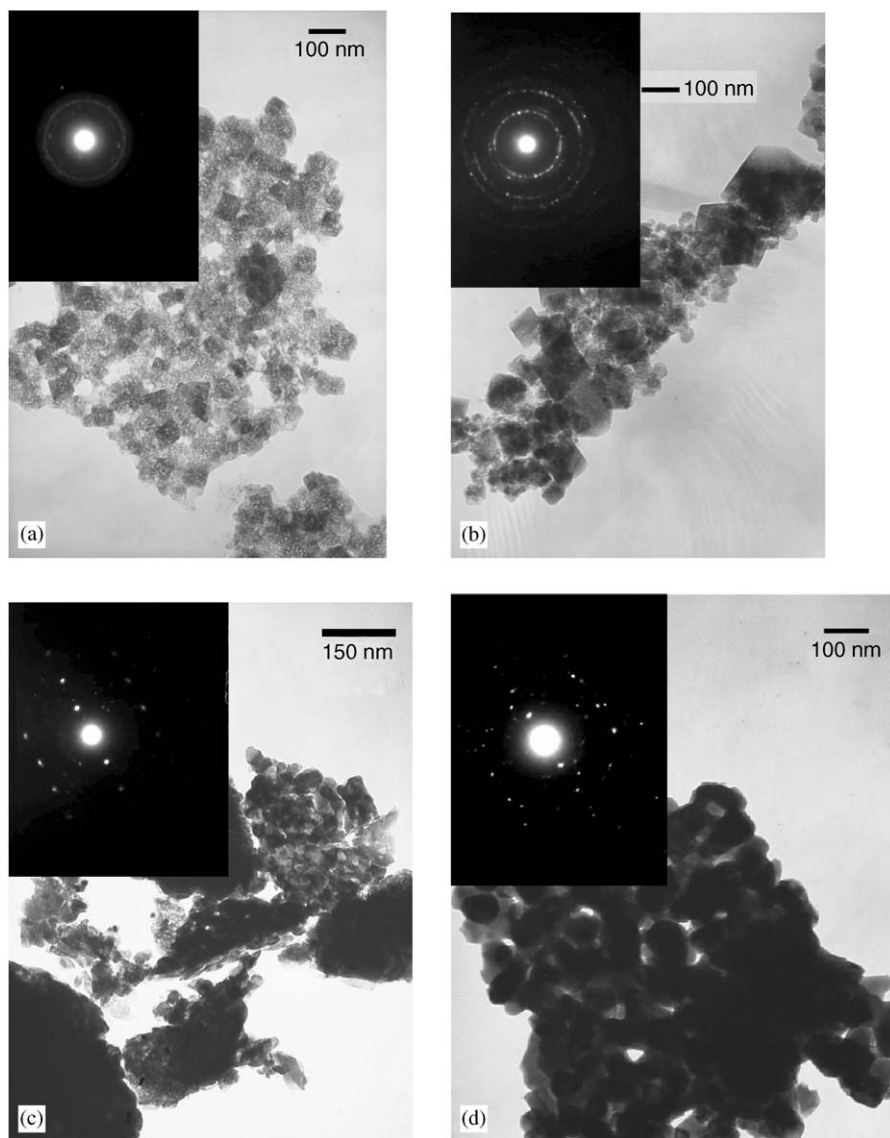
Fig. 5. The TEM spectra of the precursor calcined at various temperatures for 4 h. (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C.
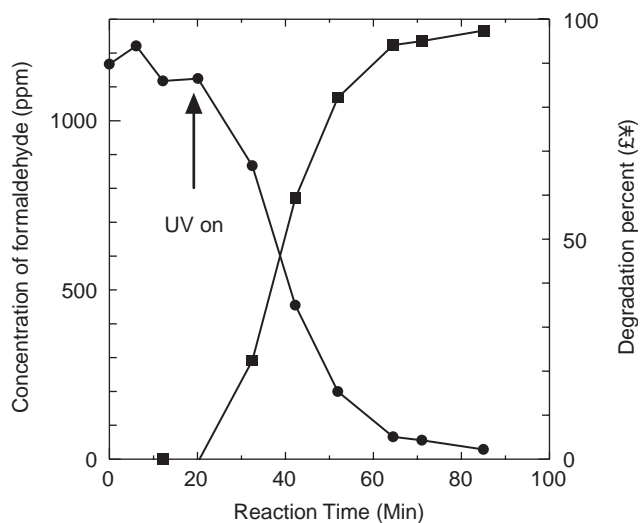

in the decrease of photoreactivity though the crystal structure become more perfect with the prolonging of calcination time.

4. Conclusion

(a) Nanosized-Ta_2O_5 powder of 50 nm was successfully prepared by sol–gel methods via $TaCl_5$ as precursor.

(b) The crystalline phase of Ta_2O_5 was formed at 600 °C and became perfect above 700 °C.

(c) The calcination temperature and time have an important role on the crystal structure and photo activities of Ta_2O_5 powder.

(d) Nanosized-Ta_2O_5 powder showed a good photocatalytic activity under UV light radiation.

Fig. 6. The photocatalytically performance of Ta_2O_5 powders calcined at 650 °C for 8 h.
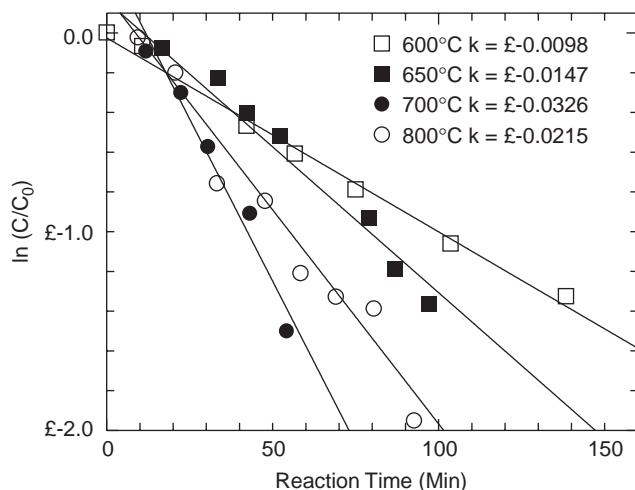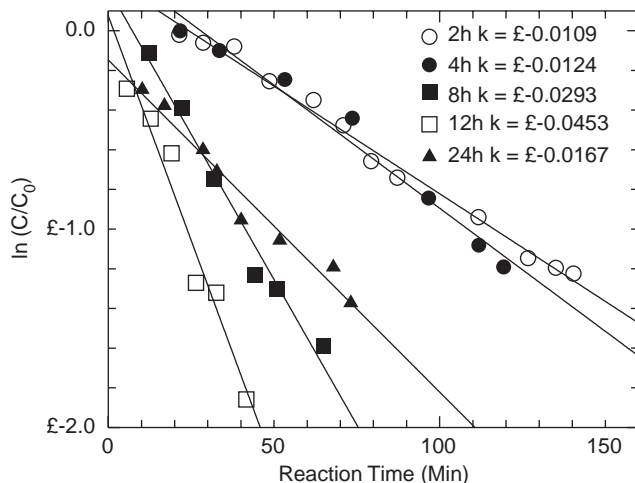
Fig. 7. The photocatalytically performance of Ta_2O_5 powders calcined at varied temperature for 4 h.

Fig. 8. The photocatalytically performance of Ta_2O_5 powders calcined at 650 °C for various time.

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