Int. J. Electrochem. Sci., 12 **(2017)** 6282 – 6291, doi: 10.20964/2017.07.25

International Journal of
ELECTROCHEMICAL
SCIENCE
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Short Communication

A Comprehensive Investigation on Photocatalytic Properties of Macroporous Silicon

Chuan Lai[1,2,*], *Bin Xie*[2,*], *Like Zou*[2], *Xiao Ma*[2], *Chenglong Deng*[2], *Wan Gou*[1], *Jianhai Hu*[1]

[1] School of Chemistry and Chemical Engineering, Sichuan University of Arts and Science, Dazhou, 635000, PR China
[2] Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Environmental Engineering, Institute of Functional Materials, Sichuan University of Science and Engineering, Zigong, 643000, PR China
[*]E-mail: laichuanemail@163.com, xiebinsuse@126.com

Received: 3 April 2017 / *Accepted:* 6 May 2017 / *Published:* 12 June 2017

Here, the macroporous silicon (macro-pSi) was successfully prepared by electrochemical anodization silicon wafers in the etching solution of 1:1 HF(40%)/EtOH(99.5%)(v/v). Results show that macro-pSi with different thickness and porosity exhibit the different photocatalytic activity for methyl orange degradation, and the maximum value of decolorization efficiency is 66.62%. Especially, the influence factors including photocatalysts dosage, current density, thermal treatment temperature, pH and recyclability for photocatalytic activity of macro-pSi as photocatalysts slice were systematically investigated. Furthermore, the decolorization kinetic equation is also presented in this work.

Keywords: Electrochemical anodization; Macroporous silicon; Photocatalytic activity.

1. INTRODUCTION

As an attractive porous material, porous silicon (pSi) was reported by Uhlir in 1956[1] and attracted considerable attention since observation of photoluminescence phenomenon by Canham in 1990[2]. After that, as a fact, the pSi was successful prepared with different methods and applied in many important fields including electronics, photonics, semiconductor material, biomaterial, micromachining, solar cell material fields[3-6] because of numerous excellent characteristics, such as excellent electronic and optical properties, the high specific surface area, biodegradability, biocompatibility and low toxicity, etc[3-6,7-9].

It is well known that the photocatalysts in powder form usually possess relatively high photocatalytic activity, due to their small size and large specific surface area. However, powders of

photocatalysts are difficult to recycle from suspension following the photocatalytic process, adding to secondary pollution and catalyst loss [10-11]. In order to use photocatalysts in practical applications, the photocatalysts need to be immobilized or coated onto a substrate or pelleted for easy recovery [12]. As a fact, pSi sample as a large specific surface area porous material prepared on silicon wafers substrate, which may be act as an excellent recycle photocatalysts. Meanwhile, there are few works focusing on pSi as photocatalysts for photocatalytic activity evaluating.

Considering the importance for development a novel recycle photocatalysts, the aim of this work is to investigate the photocatalytic properties of pSi sample as photocatalysts slice for degradation of methyl orange. First, several pSi samples were prepared by electrochemical anodization with different current densities for 25 min. Second, the pSi with different thickness and porosity were characterized weight loss measurement and scanning electron microscope (SEM). Then the influence factors for photocatalytic activity of pSi photocatalysts slice were systematically analyzed in the present work.

2. EXPERIMENTAL SECTION

2.1 Reagents and materials

All the reagents including hydrofluoric acid (40%, HF), ethanol (99.5%, EtOH), acetone, sodium hydroxide (NaOH), perchloric acid ($HClO_4$) and methyl orange, were purchased from aladdin reagents (shanghai) co., ltd, which were analytical grade and used without further purification. Silicon wafers, a phosphorus doped n-type wafer with a resistivity of 2-4 Ω cm, (100) oriented and 500-550 μm thick, was purchased from Emei Semiconductor Material Factory & Institute (China).

2.2 Preparation of macro-pSi

Macro-pSi were prepared by electrochemical anodization in 1:1 HF(40%)/EtOH(99.5%)(v/v) solution at room temperature. Silicon wafers were cut and rinsed with double distilled water, ethanol and acetone for 5 min successively, then dried in nitrogen atmosphere. The preparation of macro-pSi was performed with different constant current densities (10, 30, 60, 90 and 120 mA cm^{-2}) at 25 min using a Pt gauze as the counter electrode, and the etching process was illuminated by a 150 W high pressure mercury lamp. After preparation, the fresh macro-pSi as the total surface area of 0.95 cm^2 was rinsed and stored in ethanol. If the pore diameter of prepared porous silicon more than 50 nm that the porous silicon is the macro-pSi[5]. The detail procedures for macro-pSi fabrication were described in previous work [5, 13-15].

2.3 Characterization

The key properties of porosity and thickness for macro-pSi were estimated by weight loss method based on $porosity(\%)=(m_1-m_2)/(m_1-m_3)\times100$ and $thickness(\%)=(m_1-m_2)/\rho S\times100$ [5,13,15,16],

where m_1 and m_2 are the mass of the silicon substrate sample before and after electrochemical anodization, m_3 is the mass of the macro-pSi sample after macro-pSi layer completely removed by 1.0 M NaOH with 20% EtOH at room temperature, ρ is the density of substrate wafer(2.328 g cm^{-3}), and S is the total surface area of the macro-pSi(0.95 cm^2). Furthermore, the morphology image of macro-pSi was analyzed by JSM-6510 scanning electron microscope (SEM, JEOL).

2.4 Photocatalytic activity evaluation

In present work, photocatalytic activity evaluation experiments were performed in a simple and easily operated photochemical reactor [17], methyl orange was selected as a probe pollutant to study the catalytic activities of the macro-pSi. The detail procedures for photocatalytic experiments were described in references [18-20]. The different pieces of specimens were put into 300 mL methyl orange solution (10 mg L^{-1}) under intense magnetic stirring with 25 W UV lamp (λ=365 nm) irradiating at 30℃. The initial mass concentration of methyl orange was 10 mg L^{-1}, and initial pH value of methyl orange solution was controlled at 7.00. At each regular interval, approximately 5 mL of reaction mixture solution was sampled for absorbance measurements at 463 nm by using a UV-vis spectrophotometer (PerkinElmer Lambda 35). The decolorization efficiency was calculated according to equation of $\eta_t(\%)=(A_0-A_t)/A_0\times100$ by Lambert-Beer law, in this equation η_t is the decolorization efficiency, A_0 is the initial absorbance of methyl orange solution (10 mg L^{-1}), and A_t is the absorbance of methyl orange solution after UV irradiation at different conditions. In addition, the stabilization macro-pSi through thermal treatment of freshly prepared macro-pSi in a muffle furnace at different temperatures (120℃, 400℃, 600℃ and 800℃) for 2.0 hours were used to effect the temperature of thermal treatment on photocatalytic activity, and the various pH value was adjusted by 1.0 M $HClO_4$ and 1.0 M NaOH.

3. RESULTS AND DISCUSSION

3.1 Characterization of photocatalysts

In this work, the porosity and thickness of macro-pSi can be easily estimated by weight loss measurement [5, 16]. Based on this measurement, the porosity and thickness of macro-pSi fabrication with different current densities at 25 min were estimated and presented in figure 1. It can be clearly seen that the current density has a significant effect on porosity and thickness of macro-pSi. For fixed anodization time (25 min), the porosity increases with anodization current density increasing, and the linear fitting result further indicates that the dissolution of n-type silicon wafers in 1:1 HF(40%)/ EtOH(99.5%)(v/v) solution at room temperature obeys Faraday's laws of electrolysis[5]. The porosity and thickness of macro-pSi prepared with 60 mA cm^{-2} at 25 min are 38.68% and 170.47μm, respectively.

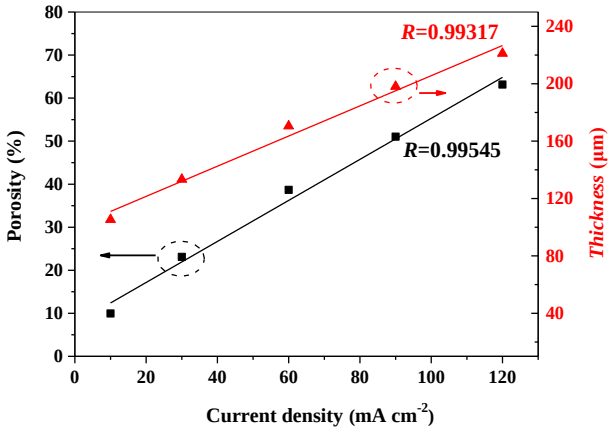

Figure 1. The influence of current density on porosity and thickness of macro-pSi; anodization time is 25 min

The thickness and porosity are the macroscopic parameters to help in discussing trends, the microscopic information on the morphology of prepared macro-pSi was analyzed by SEM, which show in figure 2(a)-(d).

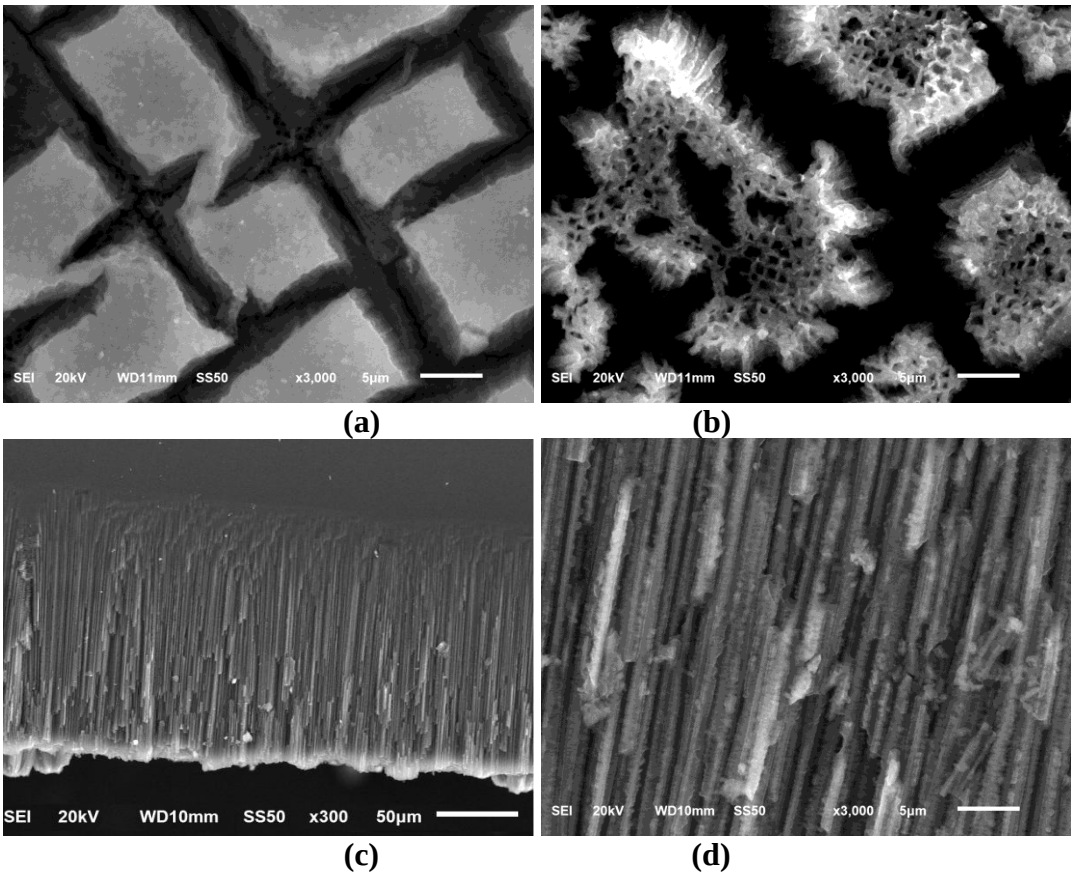

Figure 2. The top view and cross-sectional SEM images of photocatalysts; (a): the top view of macro-pSi preparation with 10 mA cm^{-2} at 3000x, (b): the top view of macro-pSi preparation with 60 mA cm^{-2} at 3000x, (c): the cross-sectional of macro-pSi preparation with 60 mA cm^{-2} at 300x, (d): the cross-sectional of macro-pSi preparation with 60 mA cm^{-2} at 3000x

Figure 2 shows the top view (a-b) and cross-sectional (c-d) SEM images of photocatalysts prepared with 10 mA cm^{-2}(a) and 60 mA cm^{-2}(c-d) at 25 min. Based on figure 1 and 2, it can be found that the porosity of macro-pSi prepared with 10 mA cm^{-2} and 60 mA cm^{-2} at 25 min are 9.96% and 38.68%, respectively, and the current density has a significant influence on porosity and morphology of photocatalysts. Obviously, there are some cracks and no pores on the surface of macro-pSi in figure 2(a), while with current density increase, the macropores appear on surface of photocatalysts in figure 2(b). Referring to the cross-sectional (c) and (d) SEM images of macro-pSi fabricated by the constant current density of 60 mA cm^{-2} at 25 min, the thickness of the porous layer measuring by weight loss measurement is 170.47μm, which is confirmed by cross-sectional SEM images present in figure 2(c). In addition, from figure 2(d), the porous microstructure were clearly seen this figure, which exhibits a more ordered vertical pore structure, it further confirm that the prepared porous silicon belong to macro-pSi, and the average pore diameter of porous silicon is about 1μm.

3.2 Photocatalytic activity

In order to evaluate the photocatalytic activity of macro-pSi, the blank experiments were performed, which shows that the photodecomposition of methyl orange (10 mg L^{-1}) with illumination after 30 min is inappreciable. Meanwhile, the adsorption ability of the different macro-pSi samples toward methyl orange after 30 min in dark is found to be almost less than 5%, which indicates that the efficient photo-generated charge separation plays an important role in photocatalytic activity of macro-pSi for methyl orange decolorization.

3.2.1 Effect of photocatalysts dosage

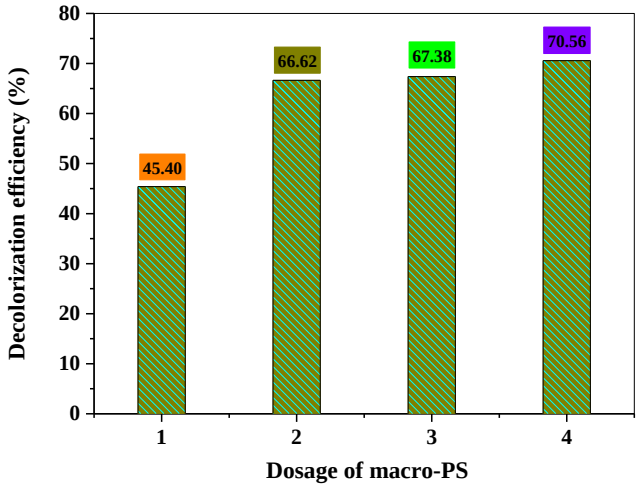

Figure 3. Relationship between decolorization efficiency and dosage of macro-pSi; the initial concentration of methyl orange was 10 mg L^{-1}, the initial volume of methyl orange solution, the initial pH of methyl orange was 7.00, the macro-pSi fabricated with 60 mA cm^{-2} at 25 min.

The photocatalytic activities of macro-pSi is evaluated and displayed in figure 3, in which the relationships between decolorization efficiency and dosage of macro-pSi was presented. It is clearly seen from figure 3 that the decolorization efficiency increase from 45.40% to 66.62% for two piece of macro-pSi samples in 300 mL methyl orange solution and is stable thereafter. Based on the results, the dosage of two pieces of macro-pSi samples in 300 mL methyl orange solution was selected to investigate the influence of photocatalytic activity by other factors. Comparison with Puangpetch [21], Gu [17], Huang [20] and Wang [22] reported, which show that the macro-pSi can act as an excellent photocatalyst.

3.2.2 Effect of current density

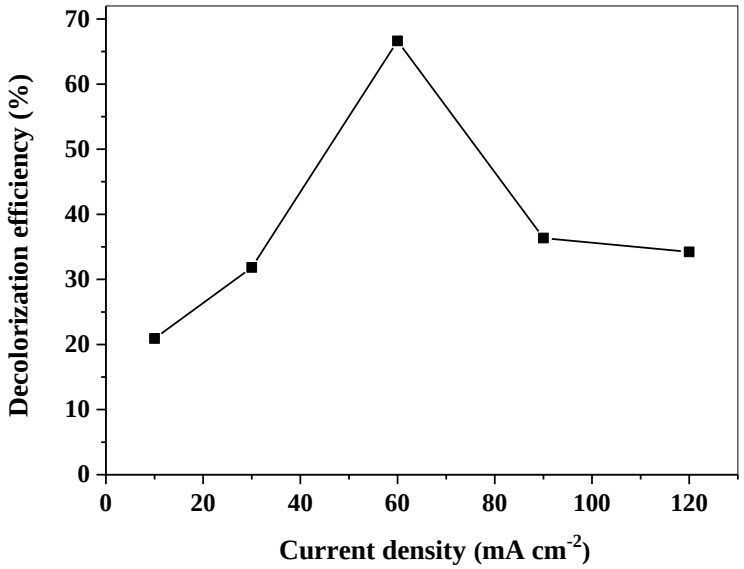

Figure 4. Relationship between decolorization efficiency and current density; the initial concentration of methyl orange was 10 mg L^{-1}, the initial pH of methyl orange was 7.00, the dosage of photocatalysts was two pieces of macro-pSi samples in 300 mL methyl orange solution.

The effect of current density on decolorization efficiency is shown in figure 4. Clearly, decolorization efficiency increase with the current density increasing, which can be attributed to the fact that the porosity increase with the current density from 10 mA cm^{-2} to 60 mA cm^{-2}. But on the contrary, with continually increase in current density from 60 mA cm^{-2} to 120 mA cm^{-2}, the decolorization efficiency has dropped from 66.62% to 34.23%. We suspect that, the increase of decolorization efficiency is duo to the porosity and thickness of macro-pSi sample increase with current density from 10 mA cm^{-2} to 60 mA cm^{-2}, and the decrease of decolorization efficiency is duo to the rack increase with current density higher than 60 mA cm^{-2}[5,23].

3.2.3 Effect of temperature

The effect of thermal treatment temperature on photocatalytic activity of macro-pSi shows in figure 5. It is obvious that the decolorization efficiency decrease with thermal treatment temperature increasing, and which decrease from 66.62% to 36.78% when thermal treatment temperature increase from room temperature to 400℃ and is stable thereafter. Based on the results, it is evident that the decolorization efficiency of fresh macro-pSi is higher than the decolorization efficiency of fresh macro-pSi treatment at different temperature. The results further reveal that thermal treatment stabilization can't enhance the photocatalytic activity of macro-pSi, which may due to the fresh macro-pSi was oxidized by thermal treatment.

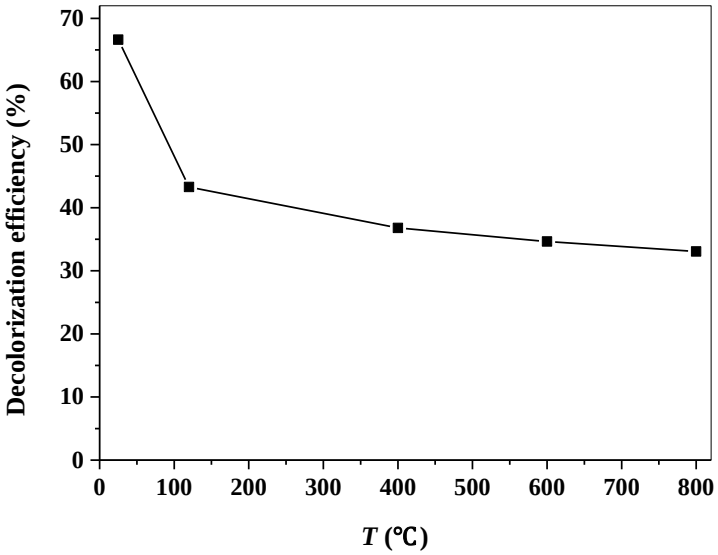

Figure 5. Relationship between decolorization efficiency and thermal treatment temperature (*T*); the initial concentration of methyl orange was 10 mg L^{-1}, the initial pH of methyl orange was 7.00, the dosage of photocatalysts was two piece of macro-pSi samples in 300 mL methyl orange solution , the macro-pSi fabricated with 60 mA cm^{-2} at 25 min.

3.2.4 Effect of pH

Figure 6 provides an influence of pH on decolorization efficiency, the comparative experiments were performed at seven pH values: 2, 4, 6, 7, 8, 10 and 12. This given figure presents that the decolorization efficiency decrease with pH values increasing at acid pH(pH＜7). The maximum value of decolorization efficiency is 66.62% when pH value reach to neutral pH (pH=7). For pH values higher than neutral pH, the decolorization efficiency sharply decrease from 66.62% to 32.55% with pH values from neutral pH to basic pH (pH=8). The result is probably attributed to the basic pH (pH＞7) solution cause the fresh macro-pSi chemical stabilization as a result of fresh macro-pSi oxidized by hydroxide ion (OH^-)[23].

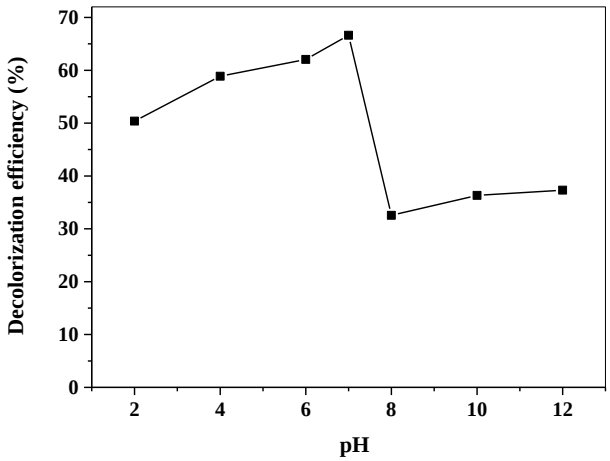

Figure 6. Relationship between decolorization efficiency and pH of methyl orange solution; the initial concentration of methyl orange was 10 mg L^{-1}, the dosage of photocatalysts was two piece of macro-pSi samples in 300 mL methyl orange solution, the macro-pSi fabricated with 60 mA cm^{-2} at 25 min.

3.2.5 Effect of recycling times

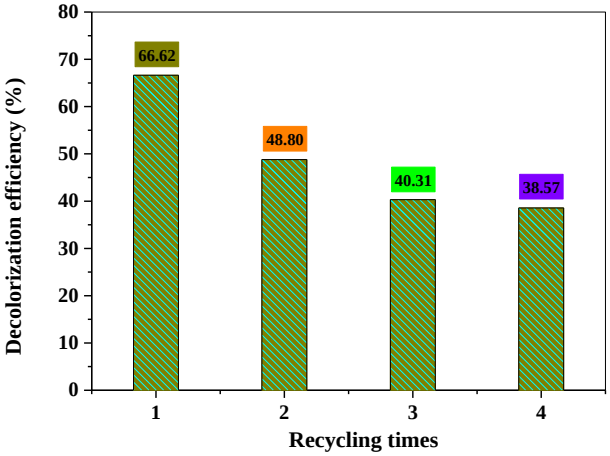

Figure 7. Relationship between decolorization efficiency and recycling times; the initial concentration of methyl orange was 10 mg L^{-1}, the initial pH of methyl orange was 7.00, the dosage of photocatalysts was two piece of macro-pSi samples in 300 mL methyl orange solution, the macro-pSi fabricated with 60 mA cm^{-2} at 25 min.

It is necessary to measure the recyclability of macro-pSi as an efficient photocatalyst for methyl orange decomposition. Figure 7 shows that the decolorization efficiency decreased from 66.62% at the first recycling times to 40.31% at the third cycling, and a slight decline (<3%) can be detected after four cycles. Based on this result, the decolorization efficiency decreased with increasing

of recycling times, it is reasonable to conclude that the fresh macro-pSi were gradually oxidation in the process of recycling.

3.2.6 Decolorization kinetic

The relationship between $\ln(C_0/C_t)$ and irradiation time is displayed in figure 8, which is evident that $\ln(C_0/C_t)$ versus irradiation time (t) is in linear form. This result demonstrates that the decolorization process of methyl orange with macro-pSi as catalysts match well a first-order model, $\ln(C_0/C_t)= k_{drc}t$ fits the tendency, where C_0 is the initial concentration, C_t is the concentration of methyl orange at different irradiation time, and k_{drc} is the decolorization rate constants. The fitting result reveal that the decolorization kinetic process obeys $\ln(C_0/C_t)=0.00361t$ (k_{drc}=0.00361 min^{-1}, R=0.99827), and the strong correlation (R>0.998) suggests that the decolorization process observes first-order model.

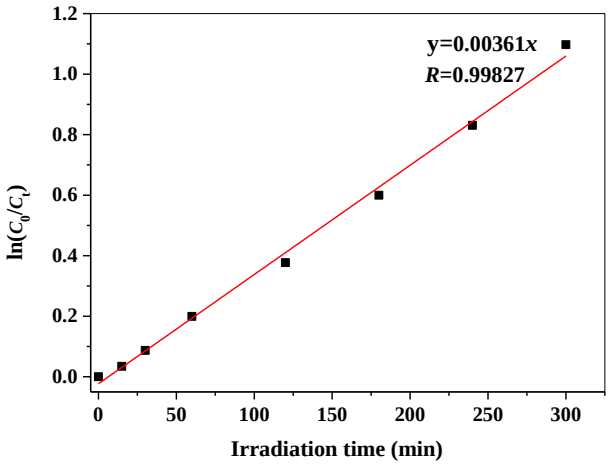

Figure 8. Relationship between $\ln(C_0/C_t)$ and irradiation time; the initial concentration of methyl orange was 10 mg L^{-1}, the initial pH of methyl orange was 7.00, the dosage of photocatalysts was two piece of macro-pSi samples in 300 mL methyl orange solution, the macro-pSi fabricated with 60 mA cm^{-2} at 25 min.

4. CONCLUSIONS

In this contribution, the photocatalyst slice of macroporous silicon was successfully fabricated by electrochemical anodization in the solution of 1:1 HF(40%)/EtOH(99.5%)(v/v). The results demonstrate that macro-pSi with different thickness and porosity exhibit the different photocatalytic activity for methyl orange degradation, and the maximum value of decolorization efficiency is 66.62% by macro-pSi preparing with 60 mA cm^{-2} at 25 min. The decolorization efficiency decrease with thermal treatment temperature and recycling times increasing, and which increase with photocatalysts dosage and acid pH (pH＜7) increasing. Furthermore, the decolorization kinetic process obeys $\ln(C_0/C_t)=0.00361t$ (k_{drc}=0.00361 min^{-1}, R=0.99827).

ACKNOWLEDGEMENTS
This project is supported financially by the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of Higher Education (No. LYJ1503, LYJ1605), the Program of Education Department of Sichuan Province (No. 16ZA0358), the Program of Science and Technology Department of Sichuan Province (No. 2017JY0180), the Project of Dazhou City (No. KJJ2016002).

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