

SnO₂纳米棒的生长过程、发光性能及光催化活性

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摘要: 在柠檬酸的调控下, 采用水热法合成 SnO₂ 纳米棒。利用高分辨透射电子显微镜、X 射线衍射、傅里叶变换红外光谱、Brunauer-Emmett-Teller 氮吸附、紫外可见漫反射光谱和光致发光光谱研究了 SnO₂ 样品在生长过程中的结构特征。结果表明, SnO₂ 纳米晶体的生长可进一步分为 2 个阶段: 早期 SnO₂ 纳米晶遵循定向附着模式生长, 而后期采取 Ostwald 熟化模式沿 [001] 方向缓慢生长。SnO₂ 纳米粒子在不同阶段的光致发光性能和光催化活性显示: 在晶体的生长过程中, 这 2 种性能变化趋势几乎相似, 即生长前期性能迅速增加, 随后性能逐渐降低。

关键词: 二氧化锡; 定向生长; 奥斯特瓦尔德熟化; 光催化; 光致发光

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Growth Process, Photoluminescence Property and Photocatalytic Activity of SnO₂ Nanorods

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Abstract: In this work, under the regulation of citric acid, SnO₂ nanorods were synthesized by hydrothermal method. The structural characteristics of SnO₂ samples during the growth process was investigated by using high-resolution transmission electron microscope, X-ray diffraction, infrared spectra Fourier transform spectra, Brunauer-Emmett-Teller nitrogen physisorption, UV-visible diffuse reflection spectrum, and photoluminescence spectra. The results reveal that the overall crystal growth can further be divided into two stages: the oriented attachment of SnO₂ nanocrystals at the early stage and subsequently a slow crystal growth along the [001] direction following the Ostwald ripening mode. Photoluminescence property and photocatalytic activity of SnO₂ nanoparticles at the different stages was also investigated, which show a similar changing trend with the crystal growing: greatly increased at the former stage and gradually decreased at the latter stage.

Keywords: SnO₂; oriented attachment; Ostwald ripening; photocatalytic activity; photoluminescence

0 Introduction

Tin dioxide (SnO₂) is a direct wide band gap semiconductor ($E_g=3.6$ eV) with excellent photoelectronic

properties, gas sensitivity, and superior chemical stability^[1-2], which has already been used in sensors^[3-5], solar cells^[6-7], lithium-ion batteries^[8-9]. It has aroused great interest to study SnO₂ nanostructures in recent years. Re-

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searchers have already realized that the physicochemical properties are closely associated with the sizes, surface states, and lattice defects^[10-15]. Among these factors, the defect is regarded as a crucial factor in the photocatalytic activity and photoluminescence (PL) property of SnO_2 nanocrystals. However, universal knowledge about how to control the formation and disappearance of defects is absent.

Over the past decades, considerable efforts have been made to improve the properties of SnO_2 nanomaterials. (1) Doping method: N-doped SnO_2 nanoparticles have been prepared by Wang et al. for lithium storage properties^[16]. (2) Morphological control: The octahedral SnO_2 particles were synthesized by Han et al. and show excellent gas - sensing performance due to the high chemical activity of the exposed (221) facets^[17]. Five atomic-layer-thick SnO_2 sheets were successfully synthesized for remarkably improved CO catalytic performances^[18]. Uniform SnO_2 nanorod arrays have been produced for the highly selective H_2 sensors^[19]. (3) Heterojunction hybridization: It was reported by Li et al. that 3D hierarchical electrode composed of porous SnO_2 nanosheets on flexible carbon cloth was used for the electroreduction of CO_2 to formate^[20]. (4) Growth mechanism: The aggregation - induced fast crystal growth mechanism was proposed to explain the steep growth mode of SnO_2 nanocrystals^[21]. A mixed growth mode was also discovered by Zhang et al.^[22]. In recent years, researchers have already realized that PL property and photocatalytic activity are closely associated with the defects and structure. In fact, both defects and structure are closely related to the growth process. Although some researchers have done the works about the growth trajectory of SnO_2 nanocrystals, there are few reports about the correlation between property, defects and growth evolution of SnO_2 nanorods.

In this work, through the effect of citric acid, the growth process of SnO_2 nanorods under the hydrothermal condition was investigated. It was discovered that the growth behavior of SnO_2 nanorods followed an oriented attachment (OA) mode at the beginning stage and then occurs an Ostwald ripening (OR) mode in the subsequent growth process. With the growth mode

changing, the defects concentration also changed with the growth process and resulted in the different PL property and photocatalytic activity.

1 Experimental

1.1 Synthesis

SnO_2 nanorods were prepared by a hydrothermal method with stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, analytical grade). The method was as follows: 3.15 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 30 mL deionized water, and subsequently added 1 g citric acid to keep the pH value at ~ 0.5 . The suspension was uniformly stirred and finally transferred into a 60 mL Teflon-lined autoclave for consequence hydrothermal reaction. The hydrothermal reaction was conducted at 220 °C in an oven for different durations, ranging from 2 h to 7 days. When the reaction was completed, the autoclave was removed from the oven and cooled down to room temperature. The samples were centrifugally separated and sufficiently washed by deionized water and ethanol to remove the residual impurities. Finally, the products were placed into a desiccator for drying at 60 °C for 24 h.

1.2 Characterization

The structural characteristic of as - synthesized products was performed using X-ray diffraction (XRD) by Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) on a Rigaku D/MAX 2200 VPC diffractometer, operating at 40 kV and 20 mA, with steps of 0.02° at $10^\circ \cdot \text{min}^{-1}$ in a 2θ range from 15° to 75° . Transmission electron microscopic (TEM) and high resolution transmission electron microscopy (HRTEM) (TEM, JEM - 2010HR electron microscope equipped with a Gatan GIF system) with an acceleration voltage of 200 kV were used to determine the morphological, structural, and chemical characteristics of synthesized products. The Brunauer-Emmett-Teller (BET) nitrogen physisorption experiments were carried out on a Micromeritics ASAP 2010 system. The pore size distributions of synthesized products were determined by using the Barrett-Joyner-Halenda (BJH) algorithm according to the desorption data of the N_2 isotherms. For photoluminescence measurements, using a Renishaw micro-Raman model via Reflex spectrograph with the excitation wavelength of 325 nm, the spectrum

range was extended to 380~800 nm. The UV-Vis absorption was recorded using Lamda850 spectrophotometer in total reflection mode by the integration sphere in the region of 200~800 nm. Infrared spectra Fourier transform (FT-IR) spectroscopy was performed using a Nicolet 560 spectrophotometer.

1.3 Photocatalytic activity evaluation

The photocatalytic activity for the degradation of methyl orange (MO) was performed in a Pyrex reactor in which 200 mg of the photocatalysts was suspended in 200 mL of MO aqueous solution ($10 \text{ mg} \cdot \text{L}^{-1}$). A 250 W mercury lamp (Beijing Perfect Co. Ltd., the wavelength within the range of 365 nm) as an ultraviolet light source was positioned inside a cylindrical Pyrex vessel. Prior to irradiation, the suspension of the photocatalyst in MO aqueous solution was stirred in the dark for 30 min to secure an adsorption/desorption equilibrium. At the given irradiation time intervals of 5 min, 4 mL of reaction suspension was sampled and separated by centrifugation. The absorption spectra of the centrifuged reaction solution were measured on a T6 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.). The concentration of MO was determined by monitoring the change in the absorbance at 464 nm.

2 Results and discussion

2.1 XRD analysis

The powder X-ray diffraction (XRD) pattern of the prepared products by hydrothermal method with different reaction time is shown in Fig.1. As can be seen, the peaks correspond to the characteristic diffraction of (110), (101) and (211) crystal planes respectively, which can be indexed as tetragonal rutile structure of SnO₂ (PDF No.41-1445). With the extension of time, the diffraction peaks of SnO₂ products became obviously stronger. After the nucleation incubation time about 2 h, the weak diffraction peak appeared and SnO₂ nanocrystalline phase were gradually formed. With the hydrothermal reaction continuing, the intensity of characteristic diffraction peak was gradually enhanced and the width of the diffraction peak became narrower, which reveal that the nanoparticles size is enlarged and the crystallization degree is increased.

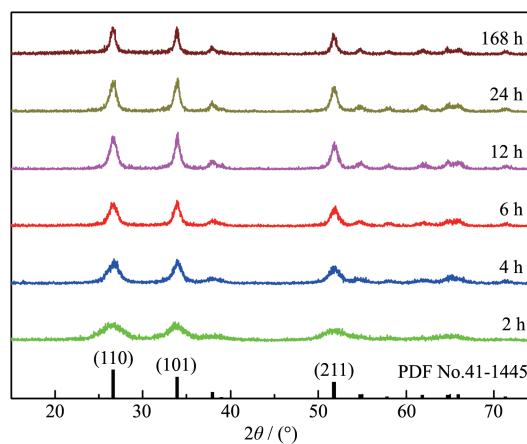


Fig.1 XRD patterns of SnO₂ samples synthesized at 220 °C with different reaction times ranging from 2 to 168 h

2.2 FT-IR analysis

As shown in Fig. 2, FT-IR spectra were used to analyze the surface absorbed citric acid and the structure of SnO₂ nanoparticles. The FT-IR spectra of the samples showed strong absorption occurring between 400 and 750 cm^{-1} with two main maxima observed near 660 and 520 cm^{-1} . These features are typical of SnO₂ nanoparticles and are related to asymmetric and symmetric Sn - O stretching vibrations^[15]. The two strong bands around 3 430 and 1 630 cm^{-1} were attributed to the O-H stretching vibrations of H₂O adsorbed in the samples, indicating the presence of adsorbed H₂O. With the reaction proceeding, the two bands were gradually decreased, suggesting that the adsorbed water reduced. The absorption band at 1 380 cm^{-1} was

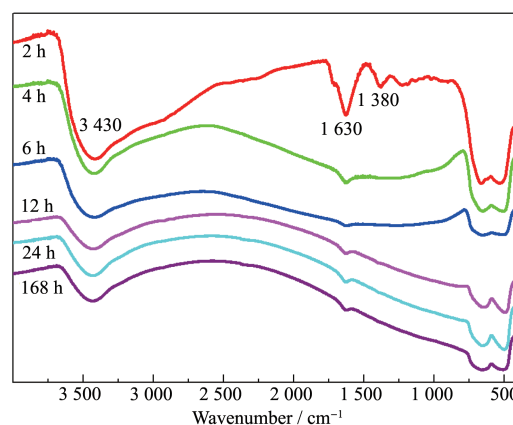


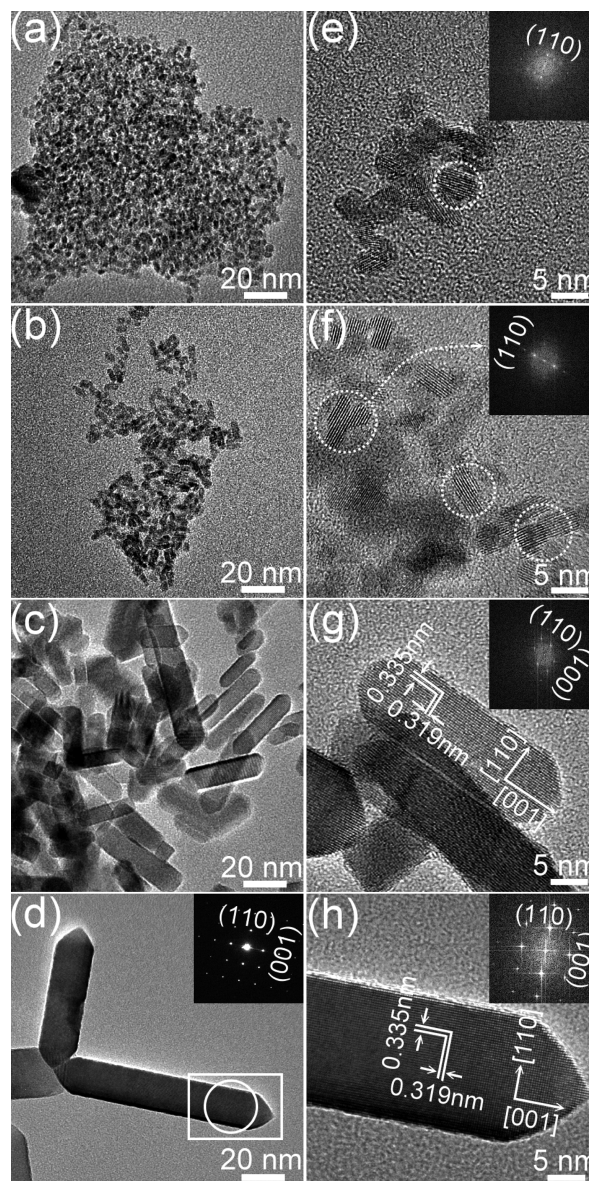
Fig.2 FT-IR spectra of SnO₂ samples synthesized at 220 °C with different reaction times ranging from 2 to 168 h

assigned to the symmetric stretching motions of the carboxylate group and the weaker band around $1\,200\text{ cm}^{-1}$ corresponded to the coupled C-(OH) stretching and C-O-H bending motions^[23]. These spectra provide useful information about adsorbed citric acid onto SnO_2 nanoparticles. After 2 h, the bands at $1\,380$ and $1\,200\text{ cm}^{-1}$ have disappeared from the spectrum and were no longer present. Obviously, the adsorbed citric acid desorbed from the surface of SnO_2 nanoparticles.

2.3 Morphology characterizations

In order to further reveal the growth mode and crystal structure of SnO_2 samples, TEM and HRTEM were characterized. Fig.3 shows the TEM and HRTEM images of the typical products synthesized from different reaction times, and the corresponding fast Fourier transform (FFT) patterns and the selected area electron diffraction (SAED) pattern are given in the insets. As the crystallizing time continuing, the morphology and growth of SnO_2 samples also changed. Fig.3a is the TEM image of the sample synthesized for 2 h, from which the nanoparticles about 2 nm were loosely aggregated together. These nanoparticles characteristics including the irregular morphology, rough surface, and weak crystallization are further illustrated by HRTEM and FFT in Fig.3e. Under prolonging the crystallization time to 6 h, the crystal morphology was changed from irregular sphere to an elongated shape described in Fig.3b. HRTEM image in Fig.3f shows the detailed microstructure of the sample reacting for 6 h. Clearly, the particle was composed of several sub-nanocrystals. The sub-nanocrystals have smooth (110) plane and attach together along [001] crystallographic orientation. The FFT pattern in the upper right corner of Fig.3f reveals that the aggregated-nanocrystal had single-crystal feature, which agrees well with the OA growth^[24-25]. Due to OA between sub-nanocrystals, the OA-induced interface defect such as dislocation, misorientations, and interface defects can be obviously formed. When the reaction time reached to 12 h (Fig. 3c), SnO_2 nanorods with length ($\sim 40\text{ nm}$) and diameter ($\sim 8\text{ nm}$) begin to appear. As shown in Fig.3g, the nanorods have enhanced crystallization and smooth surface. The continuous lattice fringes discovered that

the OA-induced defects almost disappeared, which is ascribed to the self-integration between nanocrystals. Therefore, at this stage, the growth mode is different from OA and accords well with OR. As shown in Fig. 3d, with the reaction going on, the perfect SnO_2 nanorods can be obtained, which have $\sim 100\text{ nm}$ length



Insets in e, f, g and h are the corresponding FFT patterns, obtained from their HRTEM images; Inset in d is the corresponding SAED patterns of the area circled by the line; Edge area marked by a rectangle was further investigated by HRTEM, as shown in h

Fig.3 TEM (a~d) and HRTEM (e~h) images of SnO_2 samples synthesized at $220\text{ }^{\circ}\text{C}$ for different reaction duration: (a, e) 2 h, (b, f) 6 h, (c, g) 12 h, (d, h) 168 h

and ~15 nm diameter. The SAED and FFT patterns in Fig. 3d and 3h discovered that the nanorods have smooth (110) plane and grow along [001] direction.

According to the analysis, SnO₂ crystal growth is based on OA in the early stage, While OR plays a dominant role during the latter period. The surface charge of nanoparticles plays a key role in the interactions between nanoparticles. Previous study indicated that the isoelectric point of SnO₂ nanocrystals was ~3.1^[26]. In our results, the pH value of reaction solution was ~0.5 and the OA of SnO₂ nanoparticles should be easy to do. According to the previous reports, SnO₂ spherical aggregated-nanoparticles were easily produced under OA^[27]. However, SnO₂ nanorods can be obtained in this result. So, it is sure that citric acid could play a critical role on the formation of SnO₂ nanorods. The surface energies of SnO₂ in different crystallographic orientations have been reported by several groups^[28]. Their calculations exhibited the same general trends, *i. e.*, in order of increasing energy, the planes form the sequence (110)<(100)<(101)<(001). Since the (110) and (001) planes are suggested to have the lowest and the highest surface energies, respectively, the (110) crystal plane is easy to appear and the [001] direction is the favored growth direction. As soon as the SnO₂ nanocrystals formed, citric acid can rapidly absorb on its (110) plane. The absorption reduced the surface energy of (110) plane and accelerated the OA between SnO₂ nanocrystals along the [001] direction. Through the latter ripening, SnO₂ nanorods could be formed.

2.4 Schematic diagram

Based on the above analysis, the structural evolution of SnO₂ nanorod is illustrated in Fig.4. In the initial stage of hydrothermal reaction, citric acid can rapidly adsorb on the surface of SnO₂ crystal nucleus (as shown in Fig.4a). Under the low surface charge (due to the acid solution) and the action of citric acid, SnO₂ nanocrystals easily attached together along the [001] direction when the reaction time continues. As shown in Fig.4b, a lot of OA-induced crystal defects can be detected, which were good for PL and photocatalytic activity. As the reaction progresses, due to the self-integration between SnO₂ nanocrystals, the OA-

induced defects almost disappear and SnO₂ nanorods come into being, as shown in Fig.4c. Finally, after a long time of OR, the perfect SnO₂ nanorod along the [001] direction is shown in Fig.4d.

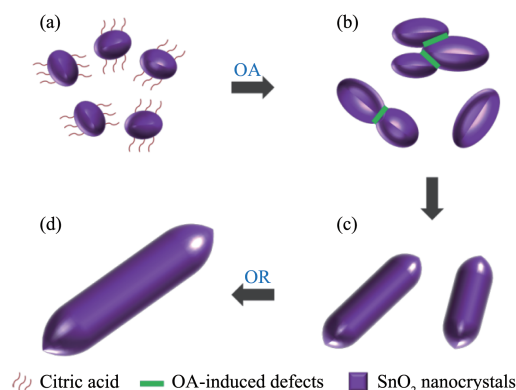


Fig.4 Schematic drawing to show the growth evolution of SnO₂ nanorods

2.5 BET surface area analysis

To evaluate the specific surface of the synthesized SnO₂, the isothermal curve and BJH pore-size distribution are used, and the results are shown in Fig.5. As can be seen, the nitrogen adsorption/desorption isotherms reflect the typical IV - model adsorption isotherms, and the adsorption capacity improves with increasing the relative pressure. The sorption data also indicated the systematic decrease of BET surface area (S_{BET}) from 174 to 23 m²·g⁻¹ with increasing the reaction time. The results show that the samples produced at 2 h have not only the largest surface area and small-

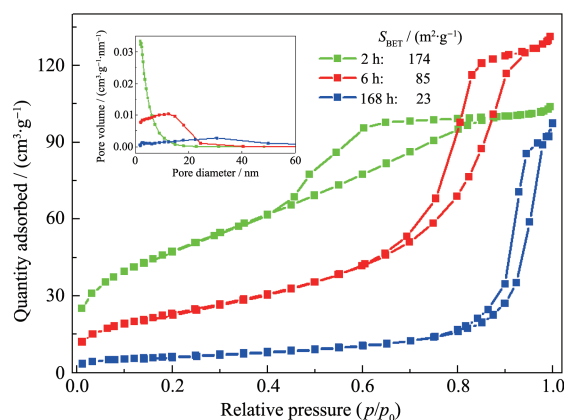


Fig.5 Nitrogen adsorption/desorption isotherms and BJH pore size distribution plots of SnO₂ samples synthesized at 220 °C for different reaction durations

er particle size but also a mesoporous structure centered at 2.0 nm.

2.6 UV-Vis absorption

As shown in Fig.6a, the UV-visible diffuse reflection spectra were used to understand the optical response of SnO₂ samples. The strong absorption peak around 280 nm represents the characteristic absorption of SnO₂ in UV-Vis spectrum. With the hydrothermal reaction proceeding, the absorption bands tend to be

broadened and red-shifted, which is maybe the result of the increasing of particle size and the enhancing of crystallization. The curve of $(\alpha h\nu)^2$ versus photon energy are described in Fig.6b and the corresponding band gap of SnO₂ became narrow with the reaction time, which can be calculated by Wood and Tauc method^[29]. The result means that the excitation energy required for the electron transition is gradually reduced, which is favorable for light absorption and photocatalysis.

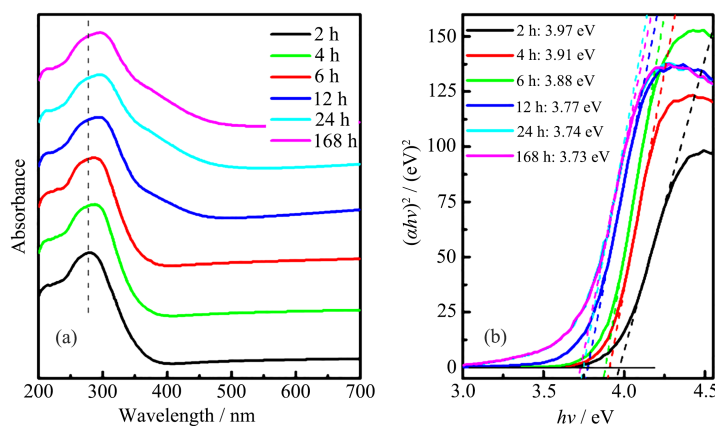


Fig.6 (a) UV-visible diffuse reflection spectra of SnO₂ samples synthesized at 220 °C for different reaction durations; (b) Band gap (E_g) of SnO₂ samples that estimated by the corresponding curve of $(\alpha h\nu)^2$ versus photon energy

2.7 Photoluminescence spectra

Fig.7 is the PL spectra of SnO₂ samples under excitation at 325 nm. It is well-known that PL properties are attributed to the imperfections degree of the crystal structure^[11,30-31]. As can be seen, the PL behaviors can change with the crystal growing, which indicates that the different structure defects produced during the growth process. According to the PL results shown in Fig.7, the entire process can be divided into two stages. At the first stage from 2 to 6 h, PL intensity was greatly

enhanced with the reaction time increasing. When the reaction time was 2 h, the PL curve of the sample was very flat and there were no any peaks appeared, which is due to the poor crystallization of SnO₂ samples. When the time reached 4 h, the distinct emission peak around 500 nm was observed, which was attributed to the high crystallinity and the structural defects such as dislocation, or dangling bonds produced during the crystallization process. With increasing time to 6 h, the strongest emission peak around 515 nm also appeared

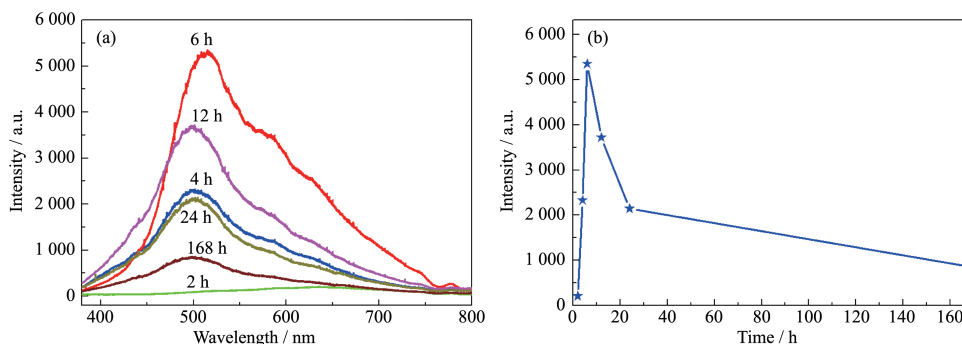


Fig.7 (a) Evolution characteristics of the PL spectra of SnO₂ nanocrystals synthesized at 220 °C for different reaction durations; (b) Comparison of PL intensities of the typical SnO₂ samples

and had the obvious red-shift. During the period, the aggregation growth of more SnO₂ nanoparticles can result in a high concentration of OA-induced defects such as dislocation, misorientations, and interface defects. Therefore, the PL intensity is substantially improved by these OA-induced defects. The shoulder peaks at ~580 nm was also revealed in the spectrum of the sample reacting for 6 h, which was derived from the oxygen vacancies defects formed in SnO₂ surface^[11]. At the second stage (after 6 h), with the crystallization going on, the nanoparticles grow perfectly and the reduced defects decreased the PL emission. In brief, during the SnO₂ growth, PL intensity increased rapidly at the initial stage and then decreased slowly at the later stage.

2.8 Photocatalytic analysis

As depicted in Fig.8, the photocatalytic properties of the SnO₂ nanocrystals are evaluated in terms of the photodegradation of MO in aqueous solution at ultraviolet light excitation. It can be seen that SnO₂ nanoparticles at different stages exhibited obvious different photocatalytic activities: In the first stage (2~6 h), the degradation ability to MO rapidly increased with prolonging the reaction time. While in the second stage (6~168 h), the photocatalytic activity of SnO₂ samples show a slow decreasing with increasing the time. Obviously, the photocatalytic results of SnO₂ samples show a clear corresponding relationship and similar changing trend with the PL analysis.

It is well noted that the photocatalytic properties depend on the surface area, defects and microstructure of SnO₂ nanocrystals^[10,15]. As described in Fig.5, the 2 h

sample had the largest specific surface area which can provide more adsorption of reactant molecule. Especially, the special mesoporous structure of the sample reacting for 2 h can accelerate the charge separation and migration of photogenerated carriers^[29]. Therefore, although having low crystallization, the the sample reacting for 2 h showed better photocatalytic activity than the the sample reacting for 168 h with high crystallization. With the crystallization going on, the surface area of SnO₂ nanoparticles decreased, while the OA-induced defects concentration increased rapidly, which can facilitate the separation of the e⁻/h⁺ pairs and improve the photocatalytic activity. Finally, the sample reacting for 6 h with the highest concentration of OA-induced defects presents the best catalytic performance. After reacting for 6 h, due to the self-integration and ripening of SnO₂ crystals, the surface area and the defect concentration gradually decreased, and the degradation rate of MO was seriously weakened.

Due to OA-induced defects, the photoinduced charge carriers can be effectively separated, and accordingly their recombination was slowed down. The efficient charge separation can increase the lifetime of the charge carriers and enhance the efficiency of the interfacial charge transfer to adsorbed substrates^[32-34]. So, it is reasonable that the SnO₂ nanocrystals with the highest concentration of OA-induced defects have higher photocatalytic efficiencies. The cycling experiments for the photocatalytic degradation of MO were further carried out and the results suggested the photocatalytic stability of the prepared SnO₂ samples.

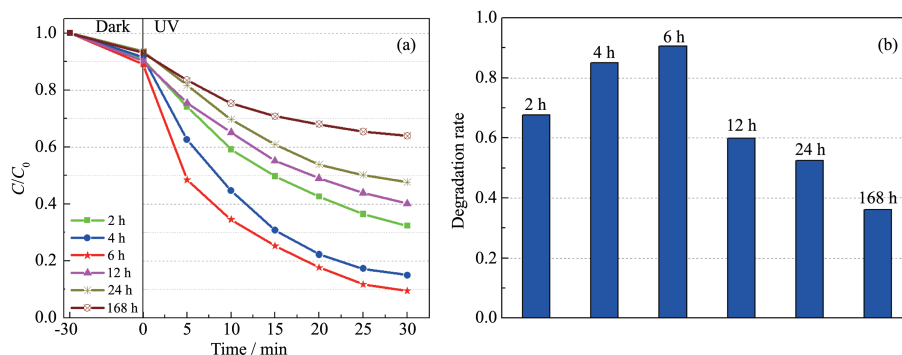


Fig.8 (a) Photocatalytic activities of SnO₂ samples synthesized at 220 °C; (b) Degradation rate of MO in the presence of SnO₂ nanocrystals synthesized for different reaction durations

3 Conclusions

SnO₂ nanorods were synthesized by the simple one-step hydrothermal method. The results reveal that the growth of SnO₂ nanorods follows “Oriented Attachment (OA)+Ostwald Ripening (OR)”. The adsorbed citric acid promoted the oriented attachment of SnO₂ nanocrystals at the early stage and subsequently a slow Ostwald ripening resulted in nanorod-like crystal along the [001] direction. The photocatalytic degradation of methyl orange indicates that SnO₂ nanocrystals at different stages exhibited obvious different photocatalytic activities. Especially, the aggregated-nanoparticles synthesized at 6 h showed the best catalytic performance and the strongest PL emission, which is ascribed to a lot of OA-induced defects. This study provides a new idea for the excellent performance photocatalyst.

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