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Short Communication

Synthesis of SnO_2 Hollow Microspheres with Efficient Photocatalytic Activity for Tetracycline Hydrochloride

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Antibiotic residues lead to serious environment pollution and provoke many health problems. Among all the antibiotics, Tetracycline hydrochloride (TC-HCl) in surface and drinking waters around the world has attracted widespread attention. Large-scale SnO_2 with hollow microspheres were synthesized via one-step hydrothermal approach as a high-efficiency photocatalyst to degrade TC-HCl. These synthesized series of SnO_2 materials with various molar ratios were characterized by XRD, SEM and EIS in terms of crystal structure, morphology, and electronic resistance. SnO_2 hollow microspheres synthesized with $SnCl_2 \cdot 2H_2O$ to $Na_3C_6H_5O_7 \cdot 2H_2O$ at the molar ratio of 1:4 showed the best photocatalytic degradation activity of TC-HCl under UV light illumination. The high photocatalytic property was considered to be benefit from the unique hollow microstructure, and the updated SnO_2 hollow microspheres were good candidates for synthesis of composite photocatalysts in area of photo degradation, such as C_3N_4-SnO_2, etc.

Keywords: SnO_2, hollow microsphere, Tetracycline hydrochloride, Photocatalytic degradation

1. INTRODUCTION

Tetracycline hydrochloride (TC-HCl) is a widely used antibiotic drug around the world, and it has become a typical organic pollutants in water environment.[1] This chemical has been harmful to the environmental due to its higher water solubility and difficulty of biodegradation.[1] Therefore, the photocatalytic degradation has been an effective solution for water pollutant treatment, and numerous materials has been developed or synthesized as one of significant subjects for research in the field of water treatment.[2-4]

In recent years, many research groups have been making great efforts to synthesize semiconductors, such as TiO_2, MnO_2, V_2O_5, NiO, ZnO and SnO_2.[5, 6] As a widely used semiconductor material, SnO_2 are excellent photocatalyst for the degradation of organic pollutants in aqueous solution due to their good chemical stability, low cost and environmental friendly, with non-toxicity.[6, 7] SnO_2 has been researched and widely used in photocatalysts, gas sensors, energy storage.[8, 9] It has also been developed in various geometrical morphologies like flower, rods, hierarchical, spherical and many others structures.[5, 8] However, it is a stable n-type semiconductor with a wide band gap (Eg = 3.5-3.8 eV), [5] which makes the SnO_2 difficult to be activated by visible light. This disadvantage leads to relative low light utilization efficiency and practical applications potential of SnO_2.[10]

In order to make the photodegradation highly efficient, substantial research have been undertaken to develop SnO_2 composites with a relative lower band gap to degrade different types of environmental pollutants, such as SnO_2-MoS_2 composite heterostructure,[11] FeS_2/SnO_2 quantum dots,[12] Ce-Doped SnO_2 nanoparticles,[13] and SnO_2/conjugated polyvinyl alcohol derivative nanohybrid.[14] As an important materials, the quality of SnO_2 can affect the photocatalytic properties of composite materials. [15] However, there have only few reports concerning the excellent photocatalytic activities of SnO_2 hollow microspheres. Most researches interests were in the combination of SnO_2 with other materials, some research developed the SnO_2 nanoparticles recently and photodegradation of methyl violet, [6] but very few studies delved into the enhancement of SnO_2 with hollow structures. Therefore, if SnO_2 can be updated with hollow structure and with more efficient photocatalytic activity, it is of great significance for the development of composite materials containing SnO_2 in the future [16-19].

Therefore, this study developed modified SnO_2 with hollow sphere with one-step hydrothermal method of synthesis of $SnCl_2\cdot 2H_2O$ to $Na_3C_6H_5O_7\cdot 2H_2O$ with various blended ratios at 1:3 to 1:6. Among different methods of synthesis SnO_2 particles, the hydrothermal method is preferred due to its simplicity, high efficiency and non-pollution [17]. After characterization, some of the as-prepared catalysts contained hollow microspheres. These SnO_2 were characterized with XRD, SEM and EIS. Then the photo degradation of TCl-HCl was studied with the as-prepared SnO_2 synthesized. SnO_2 with hollow structure exhibited enhanced photocatalytic activities for TCl-HCl degradation. This synthesized SnO_2 have shown the efficient photocatalytic degradation and electro chemical properties, and it can be adopted into other combined with nano-materials in the field in future [20-21].

2. EXPERIMENTS

2.1. Synthesis of SnO_2 hollow microspheres

SnO_2 hollow microspheres were prepared by a hydrothermal methods follows: 0.4890g $SnCl_2\cdot 2H_2O$ and $Na_3C_6H_5O_7\cdot 2H_2O$ with different molar ratios of 1:x (where x can be varied from 3 to 6, denoted with SnO_2-1:3, SnO_2-1:4, SnO_2-1:5 and SnO_2-1:6) were dissolved in 12.5 ml distilled water to form a homogeneous solution A. 0.30g NaOH was dissolved in 12.5 ml distilled water to form solution B. Then solution B was added into solution A slowly with continuous stirring for 24 h. The previous mixture was transferred to a 50 ml Teflon-lined stainless-steel autoclave, and heated at 180 °C for 12 h.

The samples were cooled down to room temperature and centrifuged alternately with distilled water and ethanol for several times. The final precipitate was dried in an oven at 60 °C overnight.

2.2. Characterization methods

XRD patterns were investigated on a Rigaku D/MAX-2495VB/PC Diffractionmeter under the following conditions: θ–2θ mode, Cu Kα1 radiation ($\lambda = 1.5406$ Å). SEM images were recorded using an FEI XL-30 scanning electron microscope, 25 kV. Electro-chemical impedance spectroscopy (EIS) tests were performed on the CHI660E electrochemical workstation (Chenhua Instruments Co. Shanghai china) at open circuit potential over the frequency range between 100 kHz and 0.1 Hz. The detailed operation parameters were set as follow, initial E = 0.221 V, 0.243 V, 0.272 V, 0.298 V, High Frequency = 10^{+5} Hz, Low frequency = 0.1 Hz. Amplitude = 0.005 V. Quiet time = 2 sec. Cycles = 1 Hz.

2.3. Photocatalytic activity experiments

Photocatalytic activity experiments were performed under a Mercury Hg Lamp, with irradiation wavelength of 365 nm, the reaction temperature was kept at 25°C. The photocatalytic degradation activity of SnO_2 was evaluated with a TC-HCl as target molecules. The TC-HCl solution was prepared as 50 mg/L and executed ultrasonic processing for half an hour. The photocatalyst SnO_2 of 50 mg was evenly dispersed into 40 ml TC-HCl solution (50 mg/L). Then, the solution was stirred for half an hour under dark conditions to reach adsorption and desorption equilibrium between TC-HCl and SnO_2. At the time interval of 20 minutes, the sample of 2 ml pipetted and diluted with 2ml distilled water and centrifuged twice to remove sediment. The overall photo degradation was tested for 140 minutes. The residual concentration of TC-HCl was determined by UV-vis spectrometer at 360 nm.

3. RESULTS AND DISCUSSION

To determine the crystal structure and phase composition, the prepared SnO_2 samples were characterized by XRD. In Fig. 1, the diffraction peaks were located at 27.6°, 33.9°, 37.9° and 51.8°, which belongs to the (110), (101), (200) and (211) lattice plane of SnO_2. The XRD pattern of SnO_2 in Fig. 1 is consistent with the standard card (JPDF NO. 41-1445). No other crystal phase derived peaks exist, which indicated the synthesized SnO_2 has high purity. From Fig. 1 the SnO_2 synthesized at different molar ratios were similar to each other, which indicated the same Tin oxides for the series.

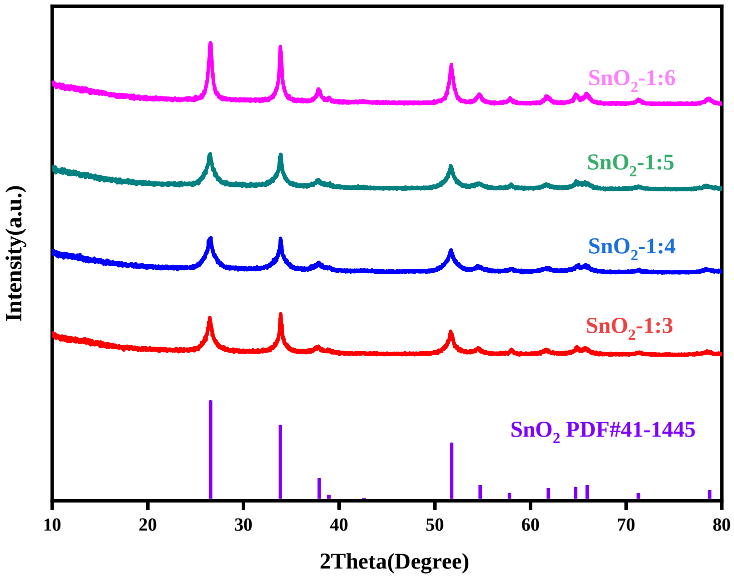

Figure 1. XRD patterns of SnO_2 hollow microspheres prepared in of SnO_2-1:3, SnO_2-1:4 SnO_2-1:5 and SnO_2-1:6.

The morphology of the SnO_2 samples synthesized by hydrothermal method at different ration were revealed by the SEM (Fig. 2). It is found that the structure of SnO_2 are significantly influenced by molar ratio. From SEM images at a low magnification (Fig. 2a, 2c, 2e & 2g), it can be seen that only SnO_2-1:4 sample show the best dispersity and morphology. Besides, it can be observed from magnified images (Fig. 2b, 2d, 2f & 2h) that SnO_2-1:4 sample with an average diameter of ~1 μm, and interestingly, almost every SnO_2 microsphere owned obvious hollow structure with sizes ranging from ~200 nm to ~500 nm. In addition, although SnO_2-1:5 exhibit hollow structure to some extent, but it owns large difference in size. Other samples exhibit worse dispersity or apparent fragmentation of structure.

The electrochemical impedance spectra (EIS) of SnO_2 was displayed in Fig. 3 and the EIS parameters were estimated and categorized into Table 1. Since SnO_2 has very huge energy gap, their Nyquist arc radius was very huge due to poor electro conductivity. Different studies reported different results, from 20 Ohm as nanoparticles [6], to 1250 Ohm [14]. For our synthesized samples, the Nyquist arc radius were even larger and the Rct has to be estimated based on the plot. From Fig. 3, the R_{Ω} was negligible, and the charge transfer resistance (R_{ct}) was the focus. The trends of estimated R_{ct} was clear, that the prepared SnO_2 with hollow spheres (SnO_2-1:4 < SnO_2-1:5) has smaller R_{ct} than those without hollow spheres (SnO_2-1:3 < SnO_2-1:6.) The order of estimated R_{ct} was SnO_2-1:4 (5800 ohm) < SnO_2-1:5 (6300 ohm) < SnO_2-1:3 (8100 ohm) < SnO_2-1:6 (8300 ohm). The R_{ct} of SnO_2-1:4 was 5800 ohm, higher than other study[14], while it is the smallest among the other as-prepared SnO_2 samples. The EIS plot and Table 1 indicated that the interfacial charge transfer resistance (R_{ct}) is relatively low for synthesized SnO_2 with hollow microsphere among 1:4 to 1:5. The hollow spheres within the samples help to reduce the interfacial charge transfer resistance, and result in enhanced transfer and separation of electrons and holes. [19]

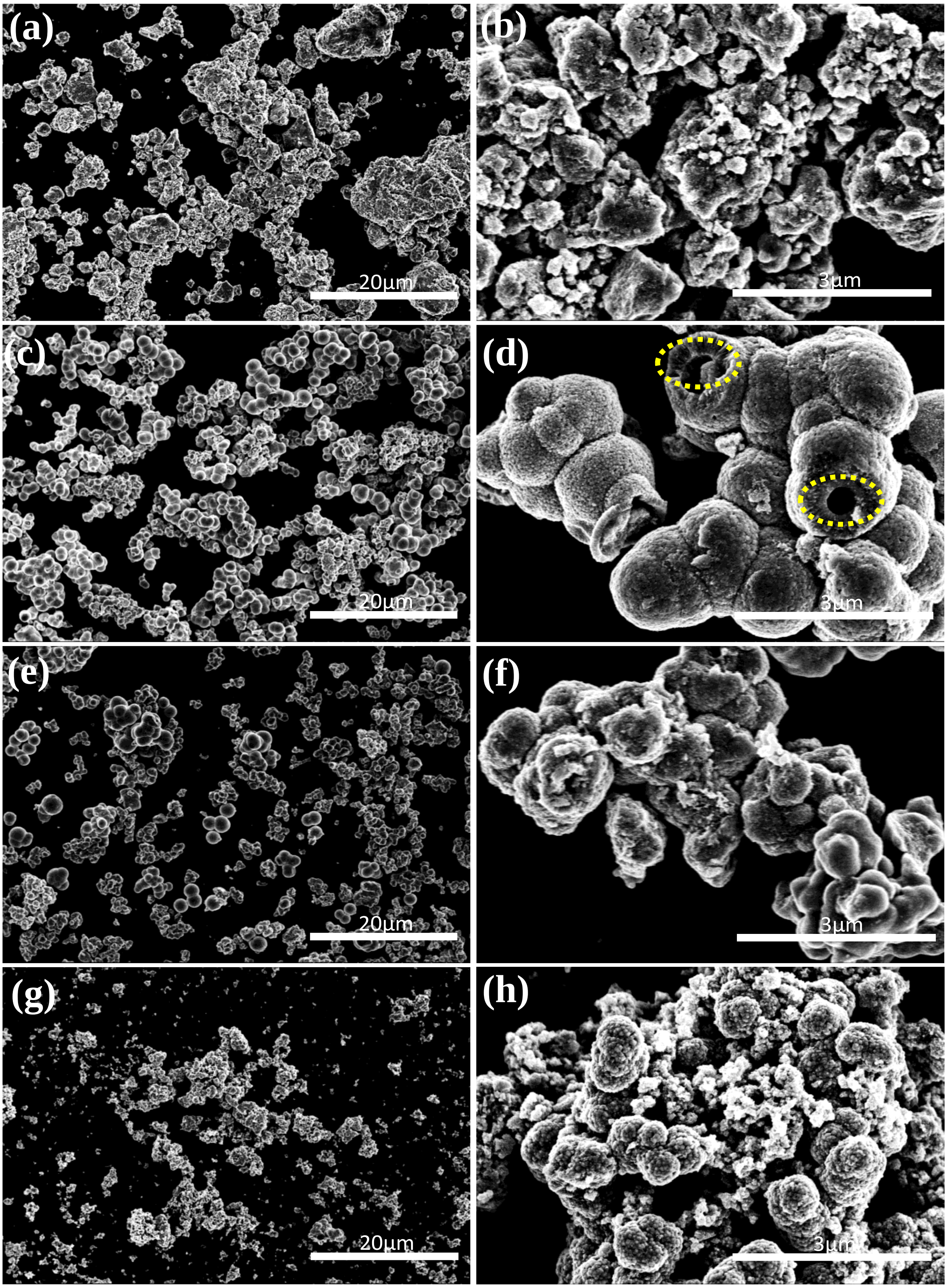

Figure 2. FESEM images of the prepared catalysts of SnO_2-1:3 (a-b), SnO_2-1:4(c-d hollow sphere), SnO_2-1:5(e-f hollow sphere), SnO_2-1:6(g-h).

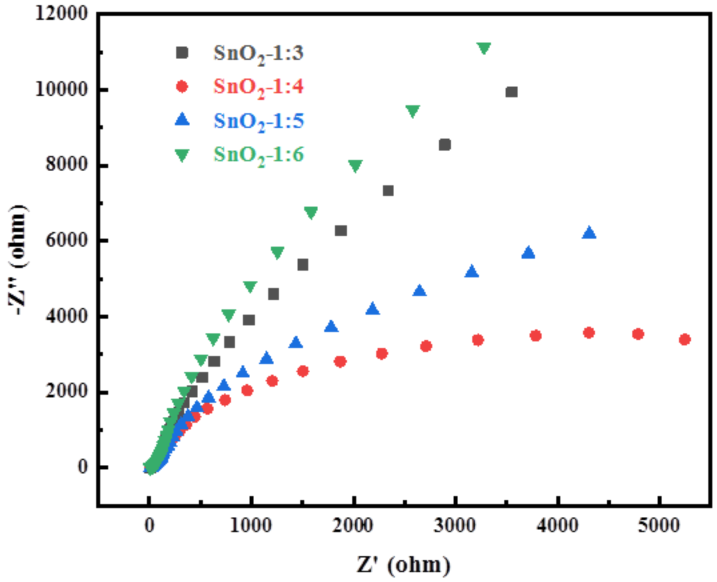

Figure 3. The Nyquist plots of as-synthesized samples: SnO_2-1:3,SnO_2-1:4 SnO_2-1:5 and SnO_2-1:6.

Table 1. The EIS parameters of SnO_2 hollow microspheres prepared in different proportions. [a]

Samples with / without hollow sphere	Initial E (V)	High Frequency (Hz)	Low Frequency (Hz)	Amplitude (V)	Quiet Time (sec)	Cycles (0.1-1Hz)	R_{ct} estimated (ohm)
SnO_2-1:3 (none)	0.221	10^{+5}	0.1	0.005	2	1	8100
SnO_2-1:4 (hollow)	0.243	10^{+5}	0.1	0.005	2	1	5800
SnO_2-1:5 (hollow)	0.272	10^{+5}	0.1	0.005	2	1	6300
SnO_2-1:6 (none)	0.298	10^{+5}	0.1	0.005	2	1	8300

a. From the plot, $R_\Omega = 0$.

The photocatalytic degradation with SnO_2 has been studied intensively, and the mechanism in terms of chemical reaction was listed as follows. The photons from the UV light source converts into the charge carriers (electrons and holes), and these electrons were transferred to the conduction band of SnO_2. The charge carriers then reacts with O_2 and ·OH resulting energetic superoxide and hydroxide radicals. [18] These radicals react with TCl-HCl.

$SnO_2 + hv \rightarrow e^- (SnO_2) + h^+$ (1)
$h^+ + H_2O \rightarrow \cdot OH + H^+$ (2)
$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$ (3)
$e^- (SnO_2) + O_2 \rightarrow \cdot O_2$ (4)
$H_2O_2 + \cdot O_2 \rightarrow \cdot OH + O_2$ (5)
$H^+ + e^- + \cdot OH \rightarrow H_2O$ (6)
$\cdot OH/ H_2O_2/\cdot O_2$ + TCl-HCl → Mineralized Products (7)

The photocatalytic activity of the prepared SnO_2 materials at different ratios was evaluated by the photodegradation of TC-HCl under the UV light irradiation. 50 mg SnO_2 was dispersed and stirred for 30 min in the dark in 40 ml TC-HCl solution (50 ml/L) before the illumination to attain the equilibrium of adsorption-desorption. Fig. 4a indicated the highest ratio of adsorption is 8%, the adsorption efficiency of TC-HCl was relatively low.

Fig. 4a-d showed the time resolved degradation curves TC-HCl with irradiation time over the SnO_2 synthesized with different molar ratio of 1:3 to 1:6. The degradation rates were different for SnO_2 synthesized at different ratios. From the curve of Fig. 4a, at the optimized ratio of SnO_2-1:4, the degradation rates reached the optimum of 76% at 140 minutes. At ration of SnO_2-1:6 the degradation rates was reduced to 61.0 %. The degradation rate followed the order of SnO_2-1:4 > SnO_2-1:5 > SnO_2-1:3 > SnO_2-1:6. The results indicted the synthesized SnO_2 hollow microspheres (1:4 and 1:5) were better than those without hollow microspheres (1:3 and 1:6).

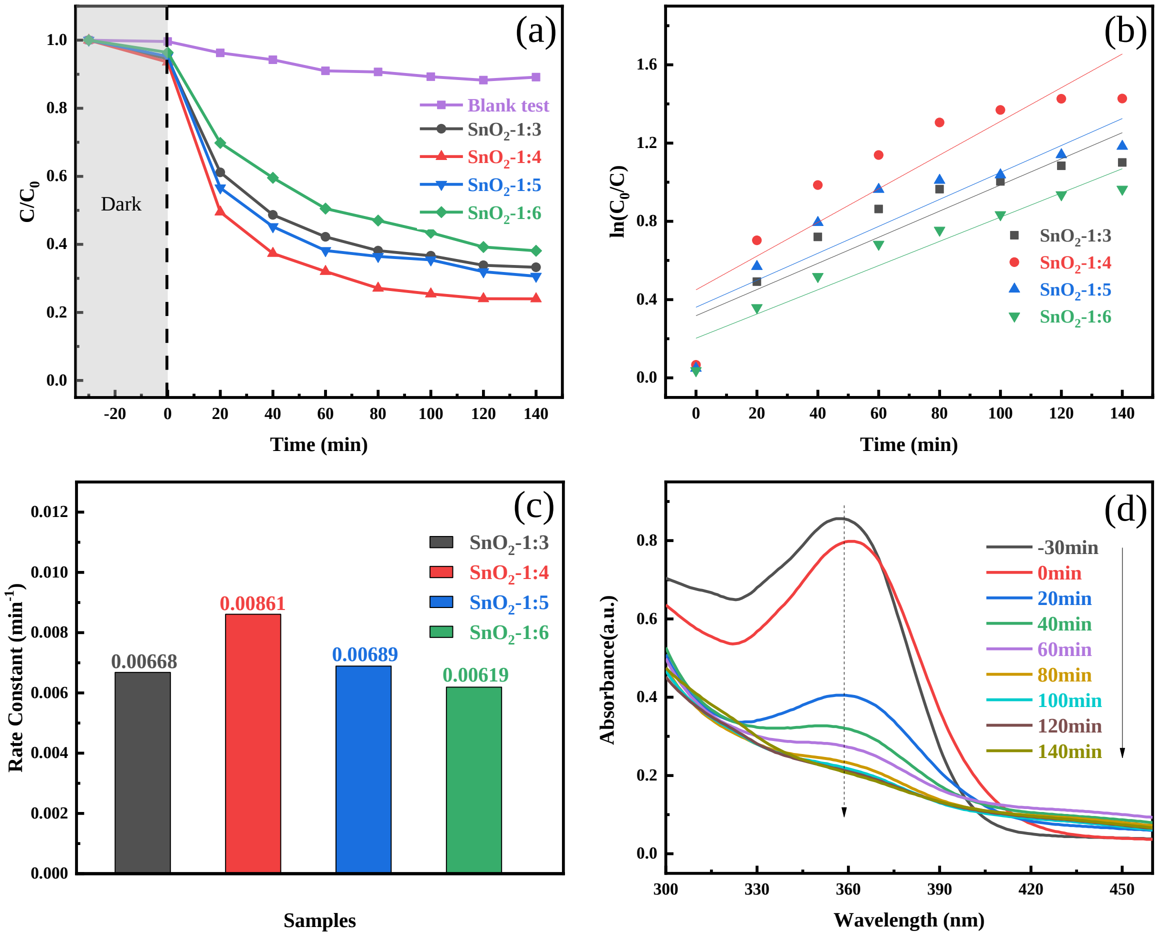

Figure 4. Dark absorption and UV photocatalytic activity of SnO_2 catalysts for the degradation of TCl-HCl (a) dynamic curves of 140 minutes, (b) Pseudo-first order kinetic plots of $\ln(C_0/C)$ versus time of SnO_2-1:3, 1:4 1:5 and 1:6, (c) Bar graph of rate constants of SnO_2-1:3, 1:4 1:5 and 1:6, (d) Determination of TC-HCl concentration during photo degradation with time-dependent UV spectrum during dark (-30 to 0 min) and irradiation (0-140 minutes).

The synthesized SnO_2 with hollow structure (1:4) was better than that with poor hollow microstructure (1:5). The improvement of photocatalytic performance was due to the hollow structure which increases the scattering rate of light in the holes, thereby improving the light utilization efficiency. The conclusion was consistent with the SEM results above mentioned. To our knowledge, there are very few relevant reports about photocatalytic degradation of TC-HCl by SnO_2 correlative materials, only Zhou et. al[22] investigated the photocatalytic degradation pathway of tetracycline hydrochloride with cubic structured ZnO/SnO_2 heterojunction nanocatalyst. In the work, the degradation efficiencies of different ZnO-SnO_2 composites vary from 60%-90%. Compared with this ZnO/SnO_2 heterostructured material, our designed and synthesized material SnO_2 hollow microsphere although did not show the better catalytic performance, but the preparation process was simpler and more economical. However, if our synthesized SnO_2 catalyst with hollow spheres were adopted and synthesized with ZnO to generate new composites ZnO-SnO_2, the photo degradation effect may be better.

Furthermore, the kinetic equation of pseudo-first order kinetic equation was adopted in Fig.4b to obtain the reaction rate constant (k) of photocatalytic degradation of TC-HCl. According to the kinetics plots in Fig. 4b, the rate constant k were calculated and plotted into bar graph Fig. 4c. The k values was listed in Fig. 4c. For SnO_2-1:4, k was the largest value of 0.00861 min^{-1}. The rest three were 0.00689, 0.00668 and 0.00619 min^{-1} for SnO_2-1:5, SnO_2-1:3 and SnO_2-1:6, respectively. This rate constant k of SnO_2-1:4 was almost 1.39 times of that of SnO_2-1:6. Fig. 4d clearly demonstrated the normalized degradation plot of TC-HCl with existence of SnO_2. The time-dependent UV-vis absorbance spectrum of TC-HCl displayed the max absorbance peak at 360 nm, which is the signature peak of the TCl-HCl. The absorbance of TC-HCl solutions decreased clearly at the section of 330-400 m after the degradation process, with respect to irradiation time. This absorbance verified the decomposition of TCl-HCl into small organic/inorganic molecules. [1, 19]

4. CONCLUSION

A UV light responsive SnO_2 hollow microsphere photocatalyst was prepared from $SnCl_2\cdot 2H_2O+Na_3C_6H_5O_7\cdot 2H_2O$ at blended molar ratio of 1:4 and 1:5 by a thermal one-step approach. The prepared SnO_2 photocatalyst containing unique structure demonstrated better photocatalytic activity than SnO_2 without hollow morphology in the degradation of TCl-HCl under UV-light irradiation. The degradation rate follows the order of SnO_2-1:4 (micropore) > SnO_2-1:5 (poor micropore) > SnO_2-1:3 (none) > SnO_2-1:6 (none), and rate constant k of SnO_2-1:4 was 0.00861 min^{-1}, almost 1.39 times of that of SnO_2-1:6 (0.00619 min^{-1}). This newly developed SnO_2 can cope with other materials such as C_3N_4-SnO_2, SnO_2-CPVA, Ce-SnO_2, SnO_2-MoS_2, etc. to develop superior composite photocatalysts.

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