Controlled morphological synthesis of temperature-dependent CuO nanostructures and their effect on photocatalytic performance

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Abstract
With the development of the times, more and more pollutants such as dyes produced by industry have inevitably caused harm to human health. Dyes are complex and stable in structure, and traditional methods of physically and chemically processing dyes have been proven to be inefficient. The heterogeneous photocatalytic technology has been widely regarded as one of the most promising processes for the treatment of harmful organic wastewater. In this paper, copper oxide (CuO) nanomaterials were synthesized via a hydrothermal method and it was found that the stirring temperature can regulate its morphology and structure, which in turn affects the optical, electrical and catalytic properties of the final product. By controlling the stirring temperature, CuO nanomaterials in the range of ∼30–500 nm were obtained. The as-prepared composites were characterized using x-ray diffraction, transmission electron microscope, scanning electron microscopy, and ultraviolet-visible spectroscopy techniques, among others. After a possible mechanism was proposed according to the above data, the photocatalytic performance of the CuO nanomaterials was evaluated by measuring the decomposition rate of rhodamine B (RhB) solutions. The results indicated that the CuO obtained at 100 °C exhibited excellent photocatalytic activity in comparison to other samples, with around 93% degradation of the RhB solution after 80 min. Finally, the recycling performance of the CuO nanomaterials was also tested and found to be extremely stable, with a high degradation level of 78% maintained after five cycles. In conclusion, the CuO nanomaterials are efficient catalysts for the complete degradation of RhB.

1. Introduction

With the development of modern industry, large quantities of dyes have been widely applied in a variety of products such as textiles, foodstuffs and leather [1, 2]. Consequently, dyes have inevitably been leached from factories in industrial wastewater into the environment, where they present a hazard to human health. As dyes have complex structures and are stable, traditional physical and chemical treatments of dye effluents have proven to be inefficient [3, 4]. Heterogeneous photocatalysis technology has been widely recognized as a promising process for the treatment of hazardous organic wastewater [5–7]. Hence, the fabrication of novel materials with high removal capacity that function as photocatalysts is urgently required to deal with dye pollutants.

In past decades, the synthesis and properties of metal oxide nanostructures with controllable sizes and shapes have attracted increasing attention due to their potential applications in electronchemistry, water purification, and photocatalysis under visible light [8–11]. As a promising material, copper oxide (CuO), an important p-type semiconductor with a narrow band-gap of 1.4 eV, has many excellent characteristics, such as that it is an abundant resource, non-toxic, and can be easily prepared in diverse shapes of nano-sized dimensions. In recent years, increasingly more studies have focused on the applications of CuO in...
Table 1. Comparison table of photocatalytic performance with earlier reported literature.

| Photocatalyst | Synthesis method | Structure          | Co-catalyst | Performance                                                                 | References |
|--------------|------------------|--------------------|-------------|-----------------------------------------------------------------------------|------------|
| CuO/TiO$_2$-F | sol-gel method   | nanoparticles      | TiO$_2$-F   | 90% caffeine removal in 180 min under 4.4 mW UV radiation                   | [12]       |
| CuO-SnO$_2$  | Hydrothermal and high temperature treatment | Hydrogel           | SnO$_2$     | The highest reaction rate constant ($k_{\text{app}}$) for the degradation of methylene blue is 1.2944 min$^{-1}$ | [14]       |
| CuO-SiO$_2$  | wet-impregnation method | hierarchical porous Monolithic materials | SiO$_2$     | 90.5% rhodamine-B removal in 180 min under 45 W UV-visible radiation        | [16]       |
| CuO          | —                | nanoparticles      | —           | 99.99% chemical oxygen demand removal in 60 min under 30 W UV radiation     | [18]       |
| CuO          | Hydrothermal method | nanoparticles      | —           | 93% rhodamine-B removal in 80 min under 350 W UV-visible radiation          | This work |
photocatalysis, most of which have focused on its role as a sensitizer in composite photocatalysts, such as CuO/TiO$_2$ [12, 13], CuO/SnO$_2$ [14], CuO/ZnO [15], CuO/SiO$_2$ [16], and CuO/zeolite [17] rather than its use as an independent photocatalyst. Moreover, even though there have been a few reports on the use of CuO as an independent photocatalyst since 2008, most only focused on the light absorption (table 1), and did not study the effect of the morphology and structure of CuO on the optical, electrical and catalytic properties [18–20]. In this regard, there were obvious disadvantages to the materials studied, for example, the prices of the resources consumed in the studies were high, and moreover, protective measures were necessary in the case of harmful wavelengths. Taking all of the above into account, it is significant to synthesize CuO that can be effectively used in the visible light.

To date, various methods have been reported to synthesize CuO with different morphologies, such as hydrothermal treatment [21], thermal oxidation [22], electrodeposition [23], thermal evaporation [24], and solution preparation [25], among which hydrothermal treatment was found to be the most attractive method due to its safety, simple operation, and low cost. In this work, a facile hydrothermal synthesis of CuO is prepared, and the effects of stirring temperature on its formation and morphology of the CuO are discussed in detail, with a formation mechanism proposed. The photocatalytic properties of the products were evaluated by the photodegradation of RhB in the presence of a small amount of hydrogen peroxide ($\text{H}_2\text{O}_2$) under the irradiation of a 350 W Xenon lamp. As a control experiment, the degradation capability of P25 was also studied under the same conditions.

2. Experimental

2.1. Reagents

Copper nitrate [Cu(NO$_3$)$_2$, 99%, China Medicine Company], ammonia (25%, China Medicine Company), commercial TiO$_2$ (Degussa P25, Degussa Chemical, Germany), Rhodamine B (RhB, 99%, China Medicine Company), H$_2$O$_2$ (30%, aladdin) and absolute ethanol (99%, Shanghai Chemical Industrial Co. Ltd.) were used throughout the study. All of the chemical reagents were of analytical grade and purchased from Sinopharm Chemical Reagents Company, China, and used without further purification.

2.2. Synthesis of CuO nanomaterials

A typical synthesis was as follows. First, copper nitrate (0.5 g) was ultrasonically dissolved in distilled water (100 mL). Then, ammonia solution (0.3 M, 20 mL) was added to the above solution under constant stirring at different temperatures in the range of 30 °C–100 °C, using plastic wrap, keeping the solution in a closed environment. After stirring for 15 min, the resultant solution was sealed in a 100 mL Teflon container and heated at 80 °C for 4 h. The CuO powders, labeled as CuO stirring temperature (e.g., CuO$_{30}$, CuO$_{50}$, CuO$_{75}$ and CuO$_{100}$) were then centrifuged, washed several times with ethanol-distilled water, and finally dried by freeze-drying.

2.3. Characterization

The structural properties and morphology of the products were investigated using field emission scanning electron microscopy (SEM; JEOL JSM-6700F), transmission electron microscopy (JEOL JEM-200CX), and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010F). A powder x-ray diffractometer (XRD; Rigaku D/max-2200) equipped with a Cu–Kα radiation source ($\lambda = 1.50405$ Å) was used to characterize the crystalline structures and compositions of the as-prepared samples. The specific surface areas and pore size distributions of the samples were obtained via N$_2$ adsorption–desorption analysis conducted at 77 K on a Quadrasorb SI instrument. Ultraviolet–visible (UV–vis) diffuse reflectance spectra were recorded using a Hitachi U-3010 spectrophotometer to detect the concentration of RhB.

2.4. Photocatalytic properties

The photocatalytic activities of the CuO nanomaterials were tested by degrading RhB in an aqueous solution under visible light irradiation. All of the photocatalysis experiments were carried out in an SGY-IB photochemical reactor. In a typical photocatalysis experiment, the as-prepared CuO nanomaterial in powder form (25 mg) was added into an RhB solution with an initial concentration of 15 mg L$^{-1}$. The mixture was then placed in an ultrasonic water bath for a few minutes to ensure good dispersion of CuO, followed by ventilation in the dark at ambient temperature for 0.5 h to achieve adsorption–desorption equilibrium of RhB. After that, the suspension was transferred into a 50 ml quartz tube and illuminated under a 350 W Xenon lamp. Over 80 min, aliquots of around 3–5 ml of the suspension were sampled every 20 min. After immediate centrifugation of the samples to separate out any suspended solids, the upper solution in the centrifuge tube was analyzed by UV–vis spectroscopy using a Hitachi U-3010 UV–vis spectrophotometer to determine the concentration of the
remaining RhB in solution over time. The degradation efficiency (C) of RhB was calculated using the following equation, conversion \( = \frac{A_i}{A_0} \times 100\% \), where \( A_0 \) is the absorbance of undegraded RhB and \( A_i \) is the absorbance of the extracted solution. For comparison, a mixture of P25 was also investigated under the same conditions.

3. Results and discussion

3.1. Formation mechanism

During the synthesis process (scheme 1), the color of CuO_{30} and CuO_{50} solutions remained blue after the addition of an aqueous solution of ammonia \((\text{NH}_3 \cdot \text{H}_2\text{O})\), while CuO_{75} and CuO_{100} solutions rapidly turned black. This phenomenon was mainly because of the high temperature that accelerated the hydrolysis process of Cu(OH)_2 \([26]\). Furthermore, the nucleation rate of the CuO nanoparticles was much greater than the growth rate under stirring, thus, the size of the CuO became smaller with an increase in the stirring temperature. Based on the following evolution of the temperature-dependent morphologies and compositions, it could be concluded that the formation mechanism of the CuO nanomaterials underwent hydrolysis→thermal decomposition→growth→self-assembly processes. This is consistent with what is shown in figure 1, where the shuttle-shaped CuO nanomaterial shown in (a) is probably formed from the stacking of the rod-like shapes shown in (d); \( \text{Cu(NO}_3)_2 \) acted as a Cu source in the present reaction system, with \( \text{Cu}^{2+} \) ions being continuously released from the Cu(NO_3)_2, which were then immediately captured via coordination with NH_3 to form Cu(NH_3)_4^{2+} complexes that are transformed into Cu(OH)_2 under alkaline conditions. Orthorhombic Cu(OH)_2 can be easily transformed to monoclinic CuO in solution. In conclusion, the chemical reactions involved in the formation of the complexes are as follows:

\[
\begin{align*}
\text{NH}_3 \cdot \text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{NH}_4^+ \\
\text{Cu}^{2+} + 2\text{NH}_3 \cdot \text{H}_2\text{O} & \rightarrow \text{Cu(OH)}_2 + 2\text{NH}_4^+ \\
\text{Cu(OH)}_2 + 4\text{NH}_3 \cdot \text{H}_2\text{O} & \rightarrow (\text{Cu(NH}_3)_4)^{2+} + 4\text{H}_2\text{O} + 2\text{OH}^- \\
(\text{Cu(NH}_3)_4)^{2+} & \rightarrow \text{Cu}^{2+} + 4\text{NH}_3 \\
\text{Cu(OH)}_2 & \rightarrow \text{CuO} + \text{H}_2\text{O}
\end{align*}
\]

3.2. Structure and morphology

The morphologies of the products were characterized using SEM and TEM techniques. Figure 1 shows typical TEM micrographs of the as-prepared products. As can be seen, notable differences in morphology and particle size were observed between samples obtained at different stirring temperatures. As shown in figure 1(a), the sample features big particles with a regular shuttle-like morphology and a size in the range of 400–500 nm. According to what is shown in figures 1(b) and (c), with an increase in the stirring temperature, the size of CuO became increasingly smaller and maintained a similar morphology. However, at a stirring temperature of 100 °C, the morphology of CuO rapidly changed to being rod-like, with a decrease in size to 30–40 nm. In
Figure 1. TEM images of the variations in the morphologies of the CuO nanostructures synthesized at different stirring temperatures of (a) 30 °C, (b) 50 °C, (c) 75 °C and (d) 100 °C.

Figure 2. SEM images of variations in the morphologies of the CuO nanostructures synthesized at different stirring temperatures of (a) 30 °C, (b) 50 °C, (c) 75 °C and (d) 100 °C.
particular, from what can be seen in figure 2(a), it was observed that there were even some rod-like shapes found on the shuttle-like CuO particles. According to the data presented in figures 1 and 2, a mechanism was proposed. It was observed that a relatively low stirring temperature benefited the stacking of small CuO particles, and the rod CuO particles aggregate together and grow in the same direction to form a uniform morphology. In conclusion, the stirring temperature is critical in controlling the size of the CuO nanoparticles.

Figure 3(a) shows XRD patterns of the prepared samples grown at different stirring temperatures in the range of 30 °C–100 °C. In the powder patterns of the nanocomposite samples, the peaks at 35.42°, 38.90°, 48.72°, 53.48°, 58.26°, 61.52°, 66.22° and 68.12° can be indexed to the (002)/(111), (200)/(111), (20–2), (020), (202), (11–3), (31–1) and (220) planes of monoclinic CuO (JCPDS 48–1548), respectively. No other diffraction peaks can be observed in the patterns, such as those of Cu(NO₃)₂ and Cu(OH)₂, suggesting the high purity of the as-prepared samples. With an increase in the stirring temperature, the (002) and (200) peaks sharpened, which indicated the good crystallization of the CuO nanomaterials, consistent with the good photocatalytic performance of CuO₁₀₀.

The specific surface areas of the as-prepared CuO nanomaterials were further determined by carrying out nitrogen adsorption–desorption measurements, the results of which are shown in figure 3(b). The measured Brunauer–Emmett–Teller specific surface areas of CuO₃₀, CuO₅₀, CuO₇₅, and CuO₁₀₀ were found to be 15.522, 19.756, 19.893, and 29.877 m² g⁻¹, respectively. These results are in good accordance with the SEM images shown in figure 2. A higher stirring temperature accelerates the dehydration rate of Cu(OH)₂ generated by the reaction between Cu(NO₃)₂ and ammonia, leading to the formation of more dehydration products (CuO) in the solution. With the growth of the CuO crystals, steric hindrance affects the morphology of the CuO growing. And more growing spots of CuO lead to a smaller size of the CuO nanostructure. Herein, the CuO nanostructure size decreased upon an increase in the stirring temperature from 30 °C to 100 °C. Using the Scherrer formula, the average thickness of CuO₁₀₀ grains perpendicular to the crystal plane direction is obtained as 176.43 Å.

Figure 4 shows representative HRTEM images of CuO₁₀₀ and the corresponding fast Fourier transform image. The crystal lattice resolved fringes with a spacing of 0.254 nm correspond to the 002 and 111 planes of orthorhombic CuO₁₀₀, similar to the results in the literature [27]; we also observed the behavior of building units in this work. Based on the aforementioned data, it can be determined that the surfaces of CuO₁₀₀ are rough, which confirms an OA growth mechanism. The XRD patterns of the sample shown in figure 3(a) indicate that all of the peaks can be indexed to orthorhombic CuO (JCPDS 48–1548).

3.3. Photocatalytic properties

To date, many studies have been published in the literature on the excellent photocatalytic properties of CuO and its use in many practical applications [28–30]. To investigate the potential capability of CuO to remove contaminants from wastewater, RhB was selected as a target pollutant at room temperature under visible light. Prior to irradiation, catalyst (0.05 g) was combined with 50 ml of a 25 mg l⁻¹ of RhB solution containing 0.01 M H₂O₂. Since the characteristic absorption peak of RhB is 554 nm, this wavelength was used to detect the photocatalytic degradation process. The transient absorption spectra were obtained in neutral solution (pH = 7) in the wavelength range of 300–800 nm, with the results shown in figure 5. After ventilation in the dark at ambient temperature for 0.5 h to ensure that the adsorption–desorption equilibrium of RhB was reached, the suspension was sampled every 20 min to record the degradation process of RhB.

The catalytic activities of CuO nanomaterials were examined via the degradation of RhB in the presence of H₂O₂ under >400 nm visible light using UV–vis spectroscopy, with the results shown in figure 5. Figure 5(a) of

**Figure 3.** (a) XRD patterns of the samples synthesized at different stirring temperatures. (b) Nitrogen absorption–desorption isotherms of the samples.
The degradation of RhB in the presence of the CuO100 nanomaterial shows the decrease in the intensity of the absorption peaks of RhB with respect to the reaction time, wherein it can be seen that the color of the dye solution obviously changed from dark red to almost colorless. Moreover, based on the data shown in figure 5(b), the conclusion could be drawn that CuO100 exhibits superior photocatalytic activity in comparison to the other photocatalysts (CuO30, CuO50, and CuO75). This catalyst converts 67.78% of RhB in 30 min, with the conversion increasing in line with an increase in the visible light irradiation time, finally reaching a maximum value of 91.18% after 80 min of irradiation. The catalytic activity of the nanocomposites was found to be in the following ascending order: CuO30 (58.63%) < CuO50 (77.73%) < CuO75 (83.86%) < CuO100 (91.18%). The higher photocatalytic activity of the CuO100 nanomaterial over those of the other catalysts could be explained by it having relatively more capacious interspaces, meaning that it provides more active sites and readily accessible porosity for the photocatalytic degradation of RhB molecules. Besides this, the specific surface area of CuO nanomaterials is also a very important parameter in the photocatalysis process. A decrease in the specific surface area leads to a decrease in hydrophilicity and adsorption performance. Overall, in particular, for small-sized
particles, photogenerated electrons undergo rapid transfer from the interior of the material to the surface, which further improves the separation efficiency of electrons and holes as well as leading to the generation of more ·OH as a result of the reaction between H2O2 and O2 in the solution.

As it is a catalyst, it is also necessary to investigate the reusability of the prepared CuO. As shown in figure 5(c), with an increase in the number of cycles, the CuO100 catalyst maintains high activity after five photodegradation cycles of RhB solution. The degradation efficiency of RhB solution was found to be around 91.18% in the first cycle, and after being reused five times still retained a degradation efficiency of around 73.86%.

Figure 6(a) exhibited the UV–vis diffuse reflectance spectroscopy (DRS) spectra of different samples, which reflect their optical properties in the wavelength range of 300–800 nm. Obviously, these composites showed an enhanced light absorption ability in visible light range (400–800 nm), and the absorption ability increased with the stirring temperature raised. Moreover, the band gap energy (Eg) values of different samples can be calculated according to Kubelka-Munk function. And the results showed in figure 6(b), the respective band gaps of the samples were calculated about 1.58 eV. In short, all tests indicated that CuO100 can be excited to generate more photoinduced electron–holes, and it is promoted to enhance the photocatalytic performance.

Figure 7(a) shows a plot of degradation versus reaction time, based on the data taken from the UV–vis profiles of H2O2 in the degradation of RhB. It was observed that RhB was almost unaffected by H2O2 alone, with only 16.73% of degradation being detected in the presence of 3 ml of H2O2, and that different amounts of H2O2 had no effect on the degradation of RhB. Moreover, as shown in figure 7(b), the conversion ratio of RhB was merely 17.73% in the presence of CuO alone, with neither separate dosing of CuO nor H2O2 found to accelerate the degradation of RhB. However, in the case of the addition of H2O2 together with the catalyst, the RhB solution rapidly turned from a dark color to almost colorless. This can be explained as H2O2 in the photocatalytic system
mainly acts as the electron acceptor instead of the -OH radical donor, a small portion of which was decomposed in the experiment. The proposed mechanism of the photodegradation process is shown below.

\[
\begin{align*}
\text{CuO} + h\nu &\rightarrow \text{CuO}(e^- + h) \\
\text{CuO}(h) + OH^- &\rightarrow \text{CuO} + OH \\
e^-_{\text{aq}} + H_2O_2 &\rightarrow OH + OH^- \\
e^-_{\text{aq}} + O_2 &\rightarrow O_2^- \\
-O_2^- + H_2O_2 &\rightarrow OH^- + OH + O_2 \\
-H + H_2O_2 &\rightarrow OH + H_2O \\
\text{RhB} + OH + O_2^- &\rightarrow CO_2 + H_2O + \text{degradation products}
\end{align*}
\]

As is well known, the separation and recombination rate of photoinduced electron–holes are one of the most important factors that influence the photocatalytic activity of photocatalysts [31]. In this process, firstly, electrons and holes are generated on the surface of CuO. Secondly, the separation of photogenerated electron–hole pairs is markedly promoted as the electrons can be scavenged by H2O2 and O2 to generate -OH and -O2-, respectively. Furthermore, H2O2 in the solution also reacts with -O2- and -H to generate -OH. Finally, the degradation of RhB is realized by -OH and -O2-.

4. Conclusions

In this work, CuO nanomaterials were prepared via a convenient one-step hydrothermal method. The TEM and SEM results showed that the stirring temperature played a crucial factor in the formation of the CuO nanomaterials. On the basis of the experiment results, the formation process of the products was also investigated. The photodegradation of RhB results indicated that the CuO prepared from rotating at 100 °C exhibited excellent photocatalytic activity, that is, the degradation rate of RhB was about 93% after 80 min of illumination. Taking all the results into account, it can be concluded that the stirring temperature has an important effect on the synthesis of the CuO nanomaterials. Considering the mild reaction conditions of the synthetic route, large-scale production of CuO can be carried out at a low cost. Moreover, the present synthesis system may also be applicable to the preparation of other metal oxides.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Ding X X, Gutierrez L, Croue J P, Li M R, Wang L J and Wang Y R 2020 Chemosphere 253 126655
[2] Gonzalez-Crisostomo J C, Lopez-Juarez R and Petranovskii V 2021 Processes 9 1736
[3] Kenfoud H, Baaloudj O, Nasrallah N, Bagtache R, Assadi A A and Trari M 2021 J. Mater. Sci., Mater. Electron. 32 16411
[4] Wang J W, Li C L, Rauf M, Luo H J, Sun X and Jiang Y Q 2021 Sci. Total Environ. 759 134359
[5] Sun Q B, Zhao C Y, Frankcombe T J, Liu H and Liu Y 2020 Crit. Rev. Environ. Sci. Technol. 50 523
[6] Ibbadon A O and Fitzpatrick P 2013 Catalysts 3 189
[7] de Assis G C, Silva I M A, dos Santos T V, Meneghetti M R and Meneghetti S M P 2021 Catal. Sci. Technol. 11 2354
[8] Jiang B et al 2022 Nanomicro lett. 14 40
[9] Pashkevich A V et al 2022 J. Alloys Compd. 895 162621
[10] Ansari J R, Singh N, Anwar S, Mohapatra S and Datta A 2022 Colloid. Surface. A 635 128102
[11] Murugalakshmi M, Mamba G, Ansari S A, Muthuraj V and Nkambule T I T 2022 Colloid. Surface. A 634 127969
[12] Castaneda C, Martinez J J, Santos L, Rojas H, Osman S M, Gomez R and Luque R 2022 Chemosphere 288 132506
[13] Redjeki A S, Sukirno S and Slamet S 2022 Chem. React. Eng. Catal. 16 816
[14] Khan S B, Akhtar K, Bakhsh E M, Kamal T and Asiri A M 2021 Chemosphere 291 132811
[15] Bykkam S, Prasad D N, Maurya M R, Sadasivuni K K and Cabibihan J J 2021 *Sustainability* 13 7685
[16] Sharma S and Basu S 2021 *Sep. Purif. Technol.* 279 119759
[17] Zilfa, Arifin B, Zein R, Rahmayeni, Umni S and Ramadhan S 2021 *Desalin. Water Treat.* 226 400
[18] Amirian P, Bazrafshan E and Payandeh A 2017 *Desalin. Water Treat.* 65 274
[19] Cho Y S and Huh Y D 2008 *Bull. Korean Chem. Soc.* 29 2325
[20] Zhang X, Wang G, Liu X and Wu H 2008 *Mater. Chem. Phys.* 112 726
[21] Sun L, Zhang Z Y, Wang F L, Bai M J, Deng X Y and Wang L Y 2022 *Environ. Res.* 205 112529
[22] Wang X Q, Deng M T, Zhao Z Y, Zhang Q and Wang Y Q 2022 *Mater. Chem. Phys.* 276 125305
[23] Cuong H N, Pansambal S, Ghotekar S, Ota R, Hai N T T, Viet N M and Nguyen V H 2022 *Environ. Res.* 203 111858
[24] Feng Y M, Lv X Y, Ran X, Jia C F, Qin L J, Chen M S, Qi R J, Peng H and Lin H C 2022 *J. Colloid Interface Sci.* 608 749
[25] Govender K, Boyle D S, Kenway P B and O’Brien P 2004 *J. Mater. Chem.* 14 2575
[26] Govender K, Boyle D S, Kenway P B and Brien P O 2004 *J. Mater. Chem.* 14 2575
[27] Dmitry A S, Tatyana Y K, Olga A S, Elena M S, Andrey I S, Sergei V K, Alexei P C and Andrei I B 2013 *J. Phys. Chem. C* 117 14588
[28] Li J P, Sun F Q, Gu K Y, Wu T X, Zhai W, Li W S and Huang S F 2011 *Appl. Catal. A-Gen.* 406 51
[29] Yang M and He J 2011 *J. Colloid Interface Sci.* 355 15
[30] Hoffmann M, Martin S T, Choi W and Bahnemann D W 1995 *Chem. Rev.* 95 69
[31] Nagaveni K, Hegde M, Ravishankar N, Subbanna G and Madras G 2004 *Langmuir* 20 2900