Photocatalytic activities of TiO_2 nanoparticles modified by nanoclusters of copper oxides prepared by atomic layer deposition

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Received 21 Aug 2022; Revised 14 Sep 2022; Accepted 07 Nov 2022; Published 18 Nov 2022.
DOI: https://doi.org/10.54939/1859-1043.j.mst.83.2022.30-39

ABSTRACT

We employed atomic layer deposition to deposit nanoclusters of Cu_2O on TiO_2 nanoparticles to produce TiO_2/Cu_2O photocatalysts with the Cu concentration in the range of 0.4 - 4.6%. By annealing the TiO_2/Cu_2O photocatalysts in the air at 400 ℃ for 4 h, the oxidation of Cu_2O resulted in the formation of TiO_2/CuO photocatalysts having the same Cu concentration. Transmission electron microscopy and X-ray diffraction characterizations demonstrated the successful deposition of Cu_2O nanoclusters with an average diameter in the range of 1.3 - 2.0 nm and a face-centered cubic crystalline structure, whereas a weak signal of the monoclinic structure of CuO was detected for the TiO_2/Cu_2O catalysts. The photocatalytic activity of the TiO_2/Cu_2O and the TiO_2/CuO photocatalysts was investigated by the degradation of RhB under UV radiation. The results show that the presence of Cu_2O and CuO nanoclusters could improve the photocatalytic activity of TiO_2, and for the same Cu concentration, the TiO_2/Cu_2O photocatalyst provided higher catalytic activity than the TiO_2/CuO counterpart.

Keywords: Atomic layer deposition; Surface modification; TiO_2/Cu_2O; TiO_2/CuO; Photocatalysis.

1. INTRODUCTION

Due to its high catalytic activity, high chemical stability, and abundance in nature, TiO_2 is one of the most used photocatalytic materials for applications in environmental and energy related fields, such as water and air pollution treatment, water-splitting for hydrogen production and energy conversion and storage.[1–3] However, one of the major disadvantages of this material is the rapid recombination of the photogenerated electron-hole pairs, which reduces the catalytic efficiency. Therefore, to enhance the photocatalytic performance, TiO_2 is often modified by nanoparticles of noble metals, such as Au, Ag, Pt, and Ru, or semiconductor metal oxides (SMOs), such as Fe_2O_3, SnO_2, CuO, and NiO.[2] The coupling of the nanoparticles with TiO_2 promotes the transfer of electrons/holes between the two materials due to their difference in energy band structure. This reduces the recombination of the photogenerated carriers, which consequently enhances the photocatalytic activity of TiO_2.

Copper oxides exist in two popular compounds in nature, i.e., CuO and Cu_2O. Both compounds are semiconductors with bandgaps of about 1.3 eV and 2.2 eV, respectively.[4,5] Many studies have shown that the deposition of copper oxide nanoparticles (i.e., CuO_x NPs) on the surface of TiO_2 nanomaterials could enhance the photocatalytic activity of TiO_2.[4,6–8] Until now, TiO_2/CuO_x nanomaterials have been synthesized mainly by wet-chemistry methods, such as hydrothermal, co-precipitation and sol-gel thanks to their advantages of simplicity, low cost, and the ability to synthesize a wide range of materials. However, these methods have limitations in controlling the size of CuO_x nanoparticles, especially in the range of a few nanometers, or smaller.

Atomic layer deposition (ALD) is a gas-phase deposition technique that was developed in the 1970s, with the focus on the applications in microelectronics.[9,10] Recently, ALD has been applied in catalysis to deposit thin films or nanoparticles of catalytic materials, including metals such as Pt, Pd, Ag, Au, Ru and oxides such as CuO_x, VO_x, TiO_2, SnO_2, WO_x, MnO_x.[11–13] By ALD, the thickness of the films and the size of the nanoparticles can be controlled with an accuracy in the sub-nanometer range, even at the single-atom level.[14,15]

In this work, we study and compare the photocatalytic activities of TiO_2 nanoparticles modified by nanoclusters of copper oxides, i.e., TiO_2/Cu_2O and TiO_2/CuO. The Cu_2O nanoclusters were deposited onto TiO_2 nanoparticles by ALD to realize the TiO_2/Cu_2O photocatalysts, while the TiO_2/CuO photocatalysts were obtained from the oxidation of TiO_2/Cu_2O in the air at 400 °C. The photocatalytic properties of the materials were investigated by the decomposition of Rhodamine B (RhB) solution under ultraviolet irradiation.

2. EXPERIMENTAL

2.1. ALD of Cu_2O

The ALD of Cu_2O was carried out in a fluidized bed reactor operating at atmospheric pressure as described in ref.[16,17] Commercial P25 TiO_2 powder with a mean diameter of 21 nm and a specific surface area of 54 $m^2\ g^{-1}$ was used as the substrate. Cu_2O nanoparticles were deposited at 250 °C using Cu(I)(hfac)(TMVS) as the precursor and H_2O as the reactant. An ALD cycle consisted of sequential exposures of the TiO_2 powder to Cu(I)(hfac)(TMVS) vapor and water vapor, which were separated by a purge of N_2 to remove the reaction by products. TiO_2/CuO powder was obtained by annealing the TiO_2/Cu_2O in the air at 400 °C for 4 h.

2.2. Materials characterization

The morphology of the deposited materials was characterized by transmission electron microcopy (TEM) using a JEOL JEM1400 transmission electron microscope. The concentration of Cu was determined by ICP-OES using a PerkinElmer Optima 5300 DV ICP-OES Spectrometer. X-ray diffraction patterns of the materials were recorded using a Bruker D8 Advance diffractometer equipped with a Cu-Kα X-ray source (λ = 0.154 nm).

2.3. Photocatalytic test

The photocatalytic activity of the catalysts was investigated by the degradation of RhB solutions under UV radiation generated by a mercury lamp (25 W). For each test, 10 mg of the catalyst was dispersed in an 80 ml aqueous RhB solution (10 mg l^{-1}) contained in a 200 ml glass beaker. The solution was stirred in the dark for 30 min to reach the adsorption-desorption equilibrium and uniform suspension. Thereafter, the suspension was exposed to the UV radiation for different exposure times. The suspension was then centrifuged to separate the solid catalyst from the solution. Finally, the solution was analyzed by UV–visible spectroscopy using a Jenway's 6800 double beam spectrophotometer to determine the residual concentration of the RhB in the solution. The catalytic activity was analyzed by the first-order kinetics, where the slope of $\ln(C_t/C_0)$ versus time gives the kinetic constant.

3. RESULTS AND DISCUSSION

Figure 1 shows the TEM images of the TiO_2/Cu_2O with Cu atomic concentrations of 0.4%, 1.2%, 1.7% and 4.6%. The images demonstrate the presence of ultrasmall Cu_2O clusters on the surface of TiO_2 nanoparticles. For the TiO_2/Cu_2O with Cu concentrations of 0.4%, the average cluster size was 1.3 nm, which increased gradually to 1.7 nm, 1.8 nm, and 2.0 nm, respectively, for the higher Cu concentrations. The change in the particle size

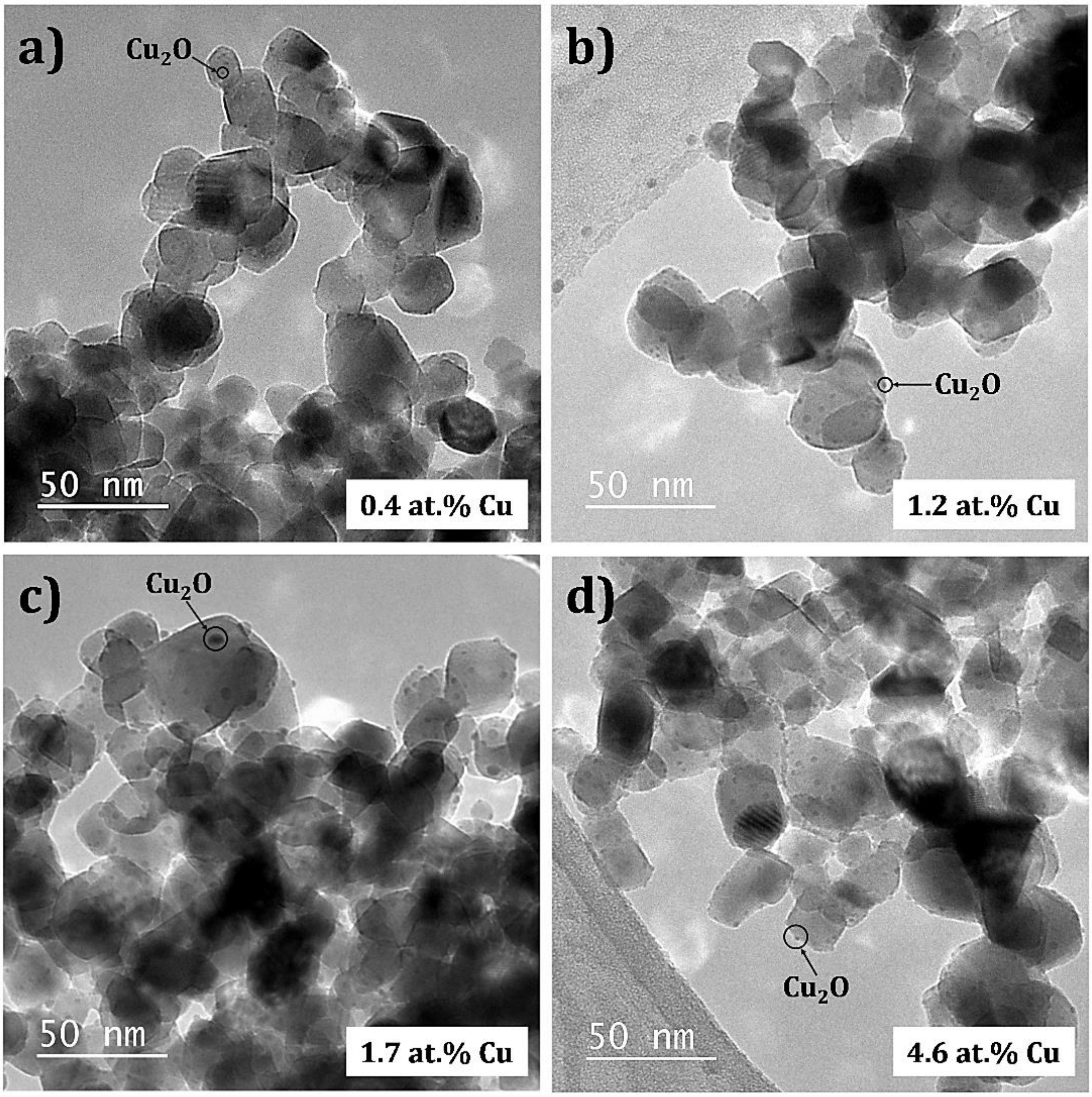

Figure 1. *TEM images of the TiO_2/Cu_2O powders with Cu atomic concentrations (at.%) of (a) 0.7 %, (b) 1.2%, (c) 1.7% and (d) 4.6%.*

is insignificant compared to the change in Cu_2O loading. This indicates that during the deposition, new nuclei are constantly formed on the surface of TiO_2, resulting in a higher cluster density with increasing Cu_2O loading. This can be seen from the TEM images.

XPS analysis confirmed the Cu_2O phase of the copper oxide clusters.[16] This is further indicated by the XRD diffractograms shown in figure 2a, which were obtained for the initial P25 TiO_2, the TiO_2/Cu_2O with Cu concentration of 4.6% before (i.e., as-deposited) and after annealing in the air at 400 °C for 4 h. The bottom pattern represents the typical XRD pattern of P25 TiO_2 that consists of the diffraction peaks of both anatase (red circles) and rutile (blue squares) phases. These peaks remain unaffected after the deposition of Cu_2O and the subsequent annealing, indicating that the deposition and the annealing processes did not cause any change in the crystalline structure of the host material. The XRD pattern of the as-deposited TiO_2/Cu_2O shows the appearance of two new peaks at 43.3° and 74.1°. These peaks represent the diffraction on the (200) and (311) crystal planes of the face-centered cubic (FCC) structure of Cu_2O (JCPDS 05-0667). It should be noted that the diffractogram of the FCC Cu_2O should also contain two additional peaks at 36.1° and 62.1°, which correspond to the diffraction on the (111) and (220) planes, respectively (JCPDS 05-0667).[18] However, these two peaks are not visible in the pattern due to their superposition with the peaks of the TiO_2. After the annealing, the peaks of the Cu_2O phase disappear, and a new weak peak is found at 35.5°, which can be seen more clearly in figure 4b. The disappearance of the Cu_2O peaks indicates that Cu_2O has been oxidized upon annealing, whereas the new peak at 35.5° fits well with the diffraction on the (002) crystal plane of the monoclinic structure of

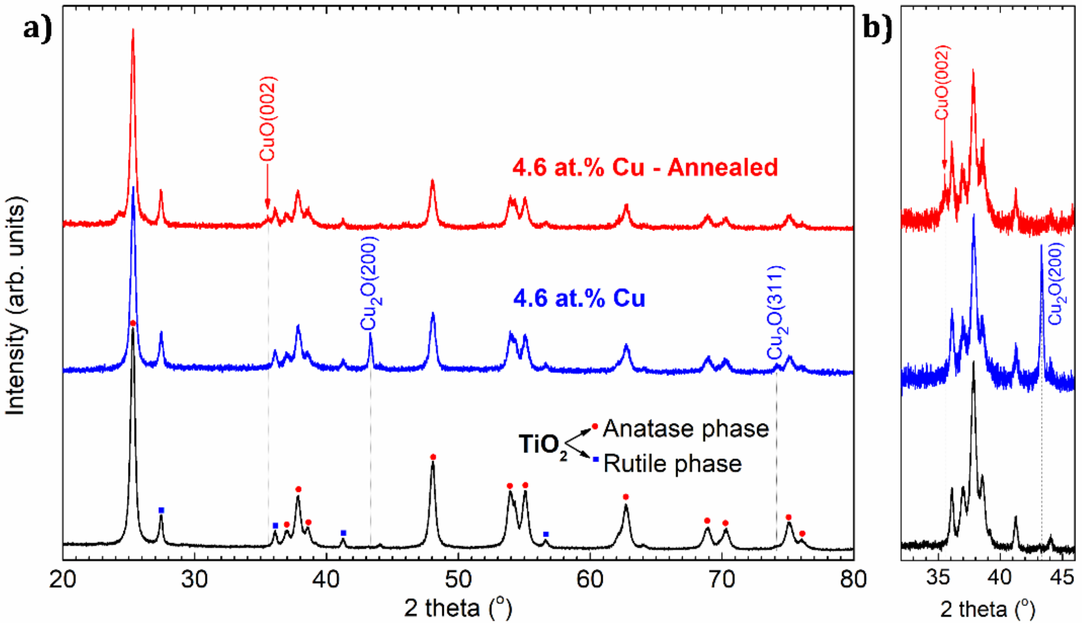

Figure 2. *(a) XRD diffractograms of the initial TiO_2 powder, the TiO_2/Cu_2O with Cu atomic concentration of 4.6% before and after annealing in the air at 400 ℃ for 4 h; (b) A zoomed-in view of the diffractograms in (a) for the 2θ angle range of 32–46°.*

CuO.[18] The transformation from Cu_2O to CuO due to thermal oxidation observed in our work is very consistent with the results reported by Yang *et al.*[18] Therefore, we conclude that Cu_2O nanoclusters were successfully deposited on TiO_2 nanoparticles by ALD to produce the TiO_2/Cu_2O photocatalyst, and converted into CuO by the thermal annealing, resulting in the TiO_2/CuO photocatalyst.

The photocatalytic performances of the materials are investigated by the degradation of RhB solution under the UV irradiation. The photocatalytic activity of the TiO_2/Cu_2O photocatalysts in the degradation of RhB with different Cu loadings was previously reported.[16] In this work, with the purpose of comparing the photocatalytic activities of TiO_2/Cu_2O and TiO_2/CuO, three pairs of the two photocatalysts having the same Cu concentration (i.e., 0.4%, 0.7%, and 1.2%) are studied and compared.

Figure 3a shows the photodegradation of RhB as a function of irradiation time by the P25 TiO_2, TiO_2/Cu_2O and TiO_2/CuO photocatalysts. From these degradation curves, the kinetics of the degradation can be derived by applying the kinetic equation:[19]

$$C = C_0\exp(-k_{app}.t) \text{ or } ln\left(\frac{C_0}{C}\right) = k_{app}.t \qquad (1)$$

where C_0 is the concentration of the RhB solution before irradiation, C is the concentration of RhB at the irradiation time t, k_{app} is the apparent first-order rate constant that represents the degradation rate of RhB. The kinetic plots describing the relationship between $ln\left(\frac{C_0}{C}\right)$ and t are shown in figure 3b. The linear regression of these plots allows for the determination of the degradation rate, k_{app}, which can be used to compare the photodegradation efficiency of the catalysts. The obtained k_{app} values are presented in table 1. The results demonstrate that the deposition of both Cu_2O and CuO nanoclusters with a small Cu concentration can enhance the photocatalytic activity of TiO_2. Particularly, for the TiO_2/Cu_2O photocatalysts, an enhancement factor of 2.3 and 1.7 is obtained for the catalyst with a Cu concentration of 0.4 and 0.7%, respectively. With a

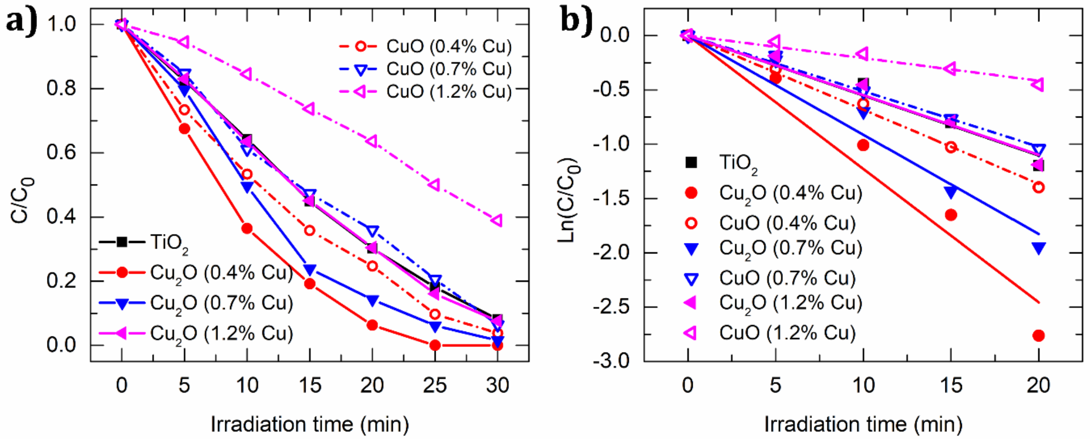

Figure 3. *(a) Photodegradation of RhB by P25 TiO_2, TiO_2/Cu_2O and TiO_2/CuO photocatalysts as a function of irradiation time, and (b) the corresponding kinetic plots.*

Cu concentration of 1.2%, the photocatalytic activities of P25 TiO_2 and TiO_2/Cu_2O are comparable. For the TiO_2/CuO photocatalysts, an enhancement (i.e., 1.3 times) is only achieved for the photocatalyst with the Cu concentration of 0.4%. With the higher Cu concentrations (i.e., 0.7% and 1.2%), the degradation rate obtained for TiO_2/CuO is comparable to/lower than that obtained for P25 TiO_2. The decrease in photocatalytic performance with increasing Cu concentration could be due to the light-shielding effect, in which the presence of the copper oxide nanoclusters on the surface screens the light absorption of TiO_2.[20] The obtained results demonstrate that for the same Cu concentration, the photocatalytic activity of TiO_2/CuO is considerably lower than that of TiO_2/Cu_2O.

Table 1. *Degradation rates of the RhB by P25 TiO_2, TiO_2/Cu_2O and TiO_2/CuO photocatalysts with different Cu concentrations.*

Cu concentration	**Photocatalyst**	**k_{app} (min^{-1})**	**R^2**
0%	P25 TiO_2	0.053 ± 0.003	0.98
0.4%	Cu_2O/TiO_2	0.123 ± 0.009	0.98
	CuO/TiO_2	0.068 ± 0.001	0.99
0.7%	Cu_2O/TiO_2	0.091 ± 0.006	0.98
	CuO/TiO_2	0.051 ± 0.001	0.99
1.2%	Cu_2O/TiO_2	0.055 ± 0.003	0.98
	CuO/TiO_2	0.021 ± 0.001	0.98

Several mechanisms have been proposed to explain the improved photocatalytic activity of TiO_2 due to the Cu_2O and CuO nanoclusters. Xu *et al.* studied the photocatalytic properties of TiO_2/Cu_2O in the degradation of methylene blue (MB) solution.[21] The results showed that when modified by Cu_2O nanoparticles with a very small concentration (<0.32%), the catalytic activity of TiO_2 was enhanced. It was explained that the deposition of Cu_2O nanoparticles caused the formation of Ti–O–Cu bonds on the TiO_2 surface, and the copper ions acted as trapping centers of photogenerated electrons. This led to an increase in the hole lifetime and consequently enhanced the photocatalytic activity.[21] Li *et al.* studied the photocatalytic properties of TiO_2/Cu_2O in the hydrogen reduction reaction and observed an enhanced performance compared with the unmodified TiO_2 material. This was explained by the formation of a p-n junction between Cu_2O (p-type semiconductor) and TiO_2 (n-type semiconductor). At this junction, the recombination process between the electrons of TiO_2 and the hole of Cu_2O occurred. This mechanism is also known as the "Z-scheme" mechanism.[22,23] This process reduces the recombination rate of the photogenerated electron-hole pairs, thereby increasing the lifetime of holes and increasing the photocatalytic efficiency. A reduced recombination has also been reported for the TiO_2/CuO systems.[4,6] In general, a common point of these mechanisms is that the improved photocatalytic activity is resulted from an enhanced charge separation due to the charge transfer at the interface between TiO_2 and

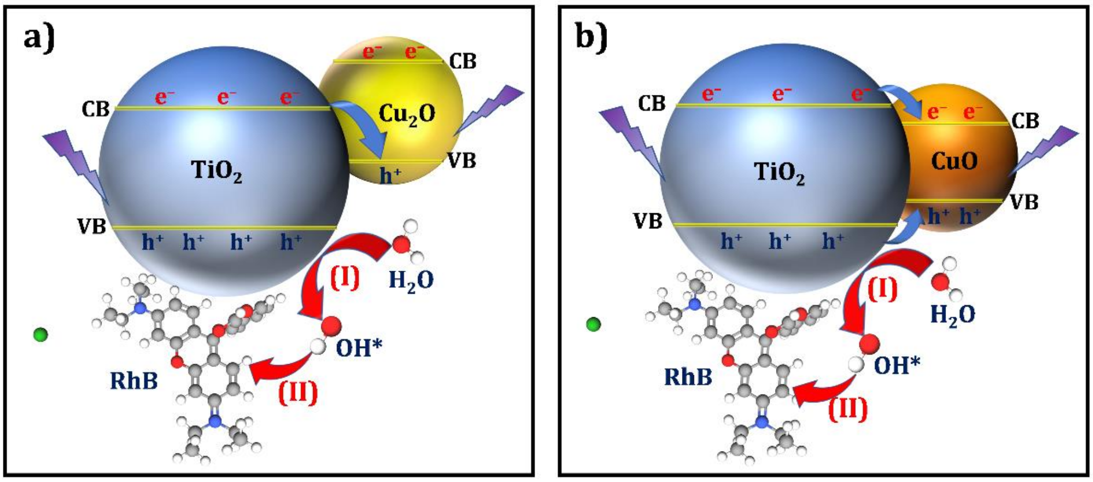

Figure 4. *Band alignment and charge transfers between* TiO_2 *and* Cu_2O *(a) and between* TiO_2 *and CuO (b) and the proposed degradation mechanism of RhB by the two photocatalysts. In this mechanism, RhB is decomposed by the OH* radicals (reaction II), which are supplied from the oxidation of* H_2O *by holes in the valance band of* TiO_2 *(reaction I).*

copper oxides. This can decrease the recombination of the photogenerated electron-hole pairs, which can be proved by comparing the photoluminescence spectra acquired for P25 TiO_2 and TiO_2/Cu_2O photocatalysts as demonstrated in the previous study.[16]

The lower photocatalytic activity of TiO_2/CuO compared to TiO_2/Cu_2O could be due to the difference in the charge transfer mechanism and the recombination process of the photogenerated electron-hole pairs. Accordingly, for Cu_2O, since the top of the valence band of Cu_2O is located near the bottom of the conduction band of TiO_2, the recombination takes place mainly between the electrons of TiO_2 and the holes of Cu_2O (Fig. 4a).[23] This prevents the transition of holes from TiO_2 to Cu_2O and increases the lifetime of holes in TiO_2. For TiO_2/CuO, while electrons are easily transferred from TiO_2 to CuO, the top of the valence band of CuO located closer to the valence band of TiO_2 can facilitate the hole transfer from the TiO_2 towards CuO (Fig. 4b).[4,5] This causes the accumulation of both electrons and holes in the CuO nanoclusters that can lead to a decrease in hole concentration in TiO_2. As the degradation of RhB is mainly caused by holes either via the direct oxidation or via the formation of OH* radicals,[16] a decrease in hole concentration can lower the photocatalytic activity. In addition, in the thermal oxidation of Cu_2O to form CuO, at the same Cu concentration, the size of CuO particles is likely larger due to the addition of oxygen atoms. This change in the particle size could cause an additional effect on the catalytic performance of TiO_2/CuO. However, this effect has not been investigated in this work.

4. CONCLUSIONS

In summary, we have demonstrated the fabrication of TiO_2/Cu_2O and TiO_2/CuO photocatalysts and investigated their photocatalytic activity in the degradation of RhB solutions under UV irradiation. TiO_2/Cu_2O photocatalysts were realized by depositing nanoclusters of Cu_2O on TiO_2 nanoparticles using ALD technique. This approach enabled the deposition of ultrasmall clusters with an average diameter in the range of 1.3 - 2.0 nm and with a Cu atomic concentration in the range of 0.4 - 4.6%. The thermal annealing of TiO_2/Cu_2O photocatalysts in the air at 400 °C for 4 h converted Cu_2O into CuO, resulting in the TiO_2/CuO photocatalysts. The results show that the surface modification by Cu_2O and CuO nanoclusters could improve the photocatalytic activity of TiO_2. This was achieved for the TiO_2/Cu_2O photocatalysts with a Cu concentration of below 1.2%, whereas TiO_2/CuO only exhibited an improvement for the Cu concentration of below 0.7%. The activity of the TiO_2/CuO photocatalysts was significantly lower than that of the TiO_2/Cu_2O having the same Cu atomic concentration. Our work provides a new method for the synthesis of high-efficiency CuO_x-based photocatalysts that can be useful in many other applications.

Acknowledgement: *We sincerely acknowledge Prof. Dr. J. Ruud van Ommen (Delft University of Technology) for providing the conditions to perform experiments on ALD of Cu_2O. Mehmet Sarilar and Baukje Terpstra (Reactor Institute of Delft University of Technology) for the ICP-OES measurements and analyses. This work is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2017.373.*

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TÓM TẮT

Tính chất quang xúc tác của vật liệu TiO_2 biến tính bằng các đám nano đồng ôxít được chế tạo bằng công nghệ lắng đọng lớp nguyên tử

Trong công trình này, chúng tôi sử dụng công nghệ lắng đọng lớp nguyên tử để lắng đọng các đám nano Cu_2O trên các hạt nano TiO_2, tạo ra các chất xúc tác quang TiO_2/Cu_2O với nồng độ Cu trong khoảng 0,4-4,6%. Bằng cách xử lý nhiệt chất xúc tác TiO_2/Cu_2O trong không khí ở 400 ℃ trong 4 giờ, quá trình ôxi hóa Cu_2O dẫn đến sự hình thành chất xúc tác TiO_2/CuO có cùng nồng độ Cu. Các kết quả thu được đã chứng minh sự lắng đọng thành công của các đám nano Cu_2O có đường kính trung bình trong khoảng 1,3-2,0 nm với cấu trúc tinh thể lập phương tâm mặt. Trong khi đó, cấu trúc đơn tà của CuO cũng được quan sát với cường độ yếu. Tính chất quang xúc tác của các vật liệu TiO_2/Cu_2O và TiO_2/CuO được khảo sát thông qua sự phân hủy của dung dịch RhB dưới tác dụng của bức xạ UV. Kết quả cho thấy sự có mặt của các đám nano Cu_2O và CuO với nồng độ Cu thấp có thể cải thiện hoạt tính quang xúc tác của TiO_2. Với cùng nồng độ Cu, chất xúc tác TiO_2/Cu_2O có hoạt tính xúc tác cao hơn so với TiO_2/CuO.

Từ khóa: Lắng đọng lớp nguyên tử; Biến tính bề mặt, TiO_2/Cu_2O; TiO_2/CuO; Xúc tác quang.