Bull. Mater. Sci. (2018) 41:128
https://doi.org/10.1007/s12034-018-1642-y

$CuBO_2$ nanonetwork: a novel and significant candidate for photocatalytic dye degradation

S SANTRA[1,4], A DAS[1], N S DAS[2] and K K CHATTOPADHYAY[1,3,*]
[1]Thin Film and Nanoscience Laboratory, Department of Physics, Jadavpur University, Kolkata 700032, India
[2]Department of Basic Science and Humanities, Techno India – Batanagar, Kolkata 700141, India
[3]School of Materials Science and Nanotechnology, Jadavpur University, Kolkata 700032, India
[4]*Present address*: Materials Research Centre, Indian Institute of Science, Bengaluru 560012, India
*Author for correspondence (kalyan_chattopadhyay@yahoo.com)

MS received 12 April 2018; accepted 6 June 2018; published online 11 September 2018

Abstract. $CuBO_2$ is a novel material in the research field of transparent conducting oxide. In this study, $CuBO_2$ nanostructures have been synthesized via sol–gel method. The phase formation is confirmed using an X-ray diffractometer. Detailed morphological analysis is performed by field emission scanning electron microscopy and transmission electron microscopy. A novel uniform nanonetwork-like structure is obtained and its band gap is found to be 4.24 eV. In ultraviolet light irradiation, this as-synthesized sample shows efficient photocatalytic activity for degradation of organic dye Rhodamine B. The degradation efficiency and the rate constant were calculated as ∼70% and 1.32×10^{-3} min^{-1}, respectively. This nanonetwork-like structure can be a potential candidate as the base material to attach various metals and metal oxide nanostructures to get highly efficient future photocatalysts. As a result, this study opens up a new gateway to fabricate novel environment-friendly nanocatalysts with high performance.

Keywords. $CuBO_2$; nanocatalyst; photocatalysis; microscopy.

1. Introduction

Transparent conducting oxide (TCO) with controlled morphology has attracted much attention in the recent field of scientific research [1–4]. These materials often show multi-functional activities, like photocatalysis [5,6], field emission [7–9], photoluminescence [10,11], thermoelectric power [12, 13], etc. They can be used in practical applications such as flat panel display, solar cells, flat panel display, etc. Most of the commercially used TCOs are n-type in nature and p-type TCO formation is proved to be very challenging. If a p-type TCO with the optoelectronic properties comparable to those of the n-type TCOs can be synthesized, then it will greatly enrich the research field of 'invisible electronics'.

The concept of TCO was primarily reported by Kawazoe *et al* [14] in 1997. In their work, fabrication of $CuAlO_2$ thin film with p-type conductivity and transparency of $CuAlO_2$ thin films was performed and a new idea, commonly known as 'chemical modulation of the valence band,' was proposed. This path-breaking study opened up the field of transparent electronics. Later on a group of Cu [I]-based delafossite TCOs was invented, such as $CuInO_2$, $CuCrO_2$, $CuGaO_2$, $CuYO_2$, etc. [1], and very recently $CuBO_2$ [15,16], which has already showed multifunctional activities [3,9,17–19]. In this present paper, a novel nanonetwork-like structure of $CuBO_2$ has been reported for the first time. Detailed morphological analysis and optical studies are carried out for the as-synthesized sample. This material showed wide-band-gap nature with band gap value ∼4.24 eV. Under ultraviolet (UV) light irradiation, $CuBO_2$ nanonetwork showed moderate degradation efficiency of Rhodamine B (RhB). In this paper, a possible mechanism of photocatalytic activity of this material is also described. In our previous paper, highly efficient dye degradation property of $CuBO_2$ nanoparticle has already been reported [20]. In that case, the nanoparticles having very high surface area showed excellent photocatalytic performance. However, in this present work, nanonetwork-like structures having less surface area in comparison with the nanoparticle system showed moderate performance. However, in comparison with nanoparticles, for nanonetwork-like systems, it is easier to attach various metal (e.g., Ag, Au, Pt, etc.) [21–23] nanostructures for better photocatalytic functionality. Hence, our present work to study the photocatalytic activity of $CuBO_2$ nanonetwork-like system can be a pioneering work to create a new opening for future composite photocatalytic nanocatalysts.

2. Experimental

2.1 *Synthesis*

A modified sol–gel method [9,16] has been used for synthesizing the $CuBO_2$ nanonetwork. In this typical synthesis, commercially available CuO and B_2O_3 were used without any further purification. These oxides were dissolved in concentrated nitric acid (69%) separately, followed by mixing at 75°C. As the chelating agent, adequate amount of citric acid solution was added dropwise. Later on ethylenediamine was added slowly for gelification and the final pH of the solution was maintained at 6.2. The as-prepared gel was baked in an oven at 110°C for 20 h and followed by annealing in a furnace at 550°C for 4 h. A fluffy ash-like material was obtained and finally it was grinded and collected to get the $CuBO_2$ nanopowders.

2.2 *Characterizations*

To check the phase, the as-synthesized $CuBO_2$ sample was characterized using an X-ray diffractometer (XRD, Bruker, D-8 Advance). Field emission scanning electron microscopy (FESEM, Hitachi, S-4800) was used for morphological analysis; lattice spacing and nanocrystallinity were studied by high-resolution transmission electron microscopy (JEOL 200 kV HRTEM). A UV–vis–NIR spectrophotometer (Shimadzu UV-3101PC) was used to record the transmission spectrum for further band gap calculation of the as-prepared sample. The photocatalytic activities of this sample were studied using a standard photocatalytic set-up in UV light irradiation.

3. Results and discussion

3.1 *Structural analysis*

XRD study has been carried out for the $CuBO_2$ sample using Cu Kα_1 radiation. Figure 1 shows the XRD pattern of as-prepared material. In these spectra, a few sharp peaks were found that assure good crystallinity. The peaks by XRD were assigned as (006), (100), (012), (106), (107), (018) and (00$\underline{11}$) planes of the $CuBO_2$ (Joint Committee for Powder Diffraction Standards-28 1256). This observation confirms the proper phase formation of $CuBO_2$ [9].

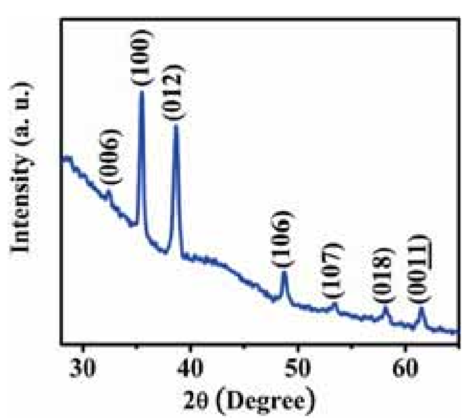


Figure 1. XRD pattern of $CuBO_2$ nanocrystals.

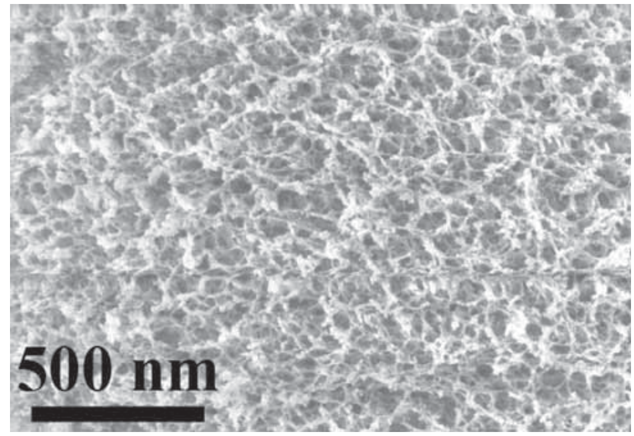


Figure 2. FESEM image of $CuBO_2$ nanonetwork.

3.2 *Morphological analysis*

To observe the morphology of the as-prepared $CuBO_2$ nanopowder, FESEM studies were carried out. The FESEM image (figure 2) clearly revealed the formation of uniform network-like structures.

The HRTEM image (figure 3) also supports the previous analysis by FESEM. In figure 3a, the nanonetwork-like morphology of the as-prepared sample is depicted. Figure 3b reveals the occurrence of lattice spacings ∼0.23, ∼0.25 and ∼0.27 nm, which define the presence of (012), (100) and (012) planes, respectively, of $CuBO_2$ nanocrystal. The SAED pattern (figure 3c) also shows the (106) and (100) planes and assures the polycrystallinity of the material. These analyses also support the XRD results and hence again confirm the proper phase formation.

3.3 *Optical studies*

The transmission spectrum of the as-synthesized sample was recorded within the wavelength range 300–800 nm. The material showed good transparency (>70%) in the visible region (figure 4a).

The value of energy band gap was determined using the following relation between absorption coefficient α and incident photon energy $h\nu$:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g). \qquad (1)$$

In equation (1), 'E_g' is the band gap and 'A' is a constant. Taking $n = 1/2$ (i.e., direct allowed transition), $(\alpha h\nu)^{1/n}$ *vs.* $h\nu$ is plotted (Tauc plot, figure 4b). The direct band gap of this material was determined by extrapolating the linear portion of the graph to $h\nu$-axis and was found to be ∼4.24 eV.

3.4 *Photocatalytic activity study*

As the energy band gap of the sample was found to be in the UV range, the photocatalysis property of the as-synthesized

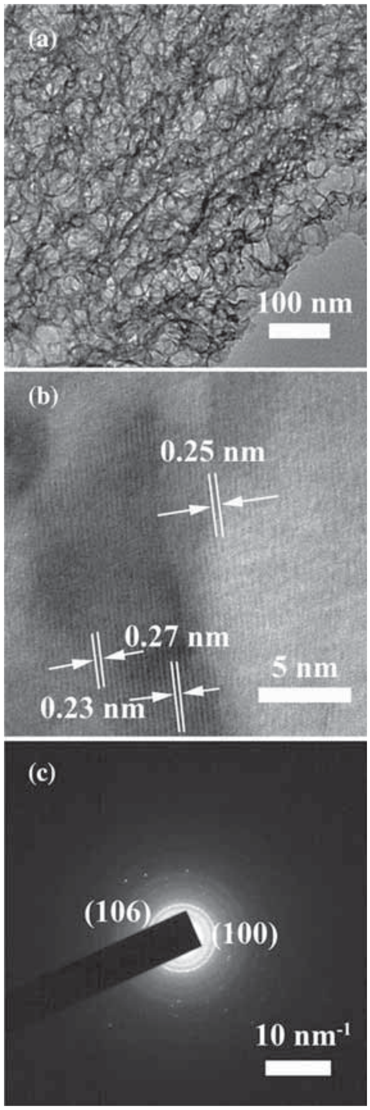


Figure 3. (**a**) TEM, (**b**) HRTEM images and (**c**) SAED pattern of $CuBO_2$ nanonetwork.

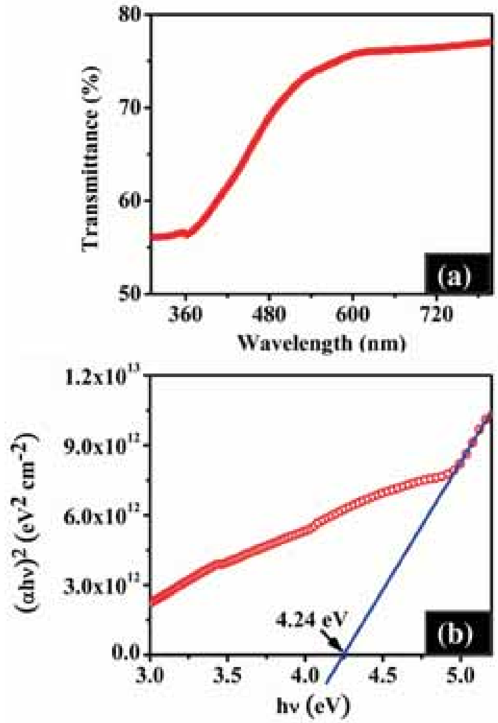


Figure 4. (**a**) Transmittance spectra, and (**b**) Tauc plot for band gap calculation of $CuBO_2$ nanocrystals.

nanonetwork was studied by exciting the same by UV radiation. The well-known hazardous dye RhB was used to test the degradation properties of as-synthesized sample. To study the photocatalytic activity of this material, $CuBO_2$ nanopowder (0.03 g) was taken in 40 ml of 10^{-5} M RhB solution and stirred continuously in UV light. At regular intervals of time (2 h), 3 ml photocatalytic solution was taken out and after centrifugation for 4 min at 1200 rpm the absorbance spectra were recorded within the range of 480–600 nm. In figure 5a the time-resolved UV absorption spectra of RhB have been depicted and it can be seen that the absorption peak of RhB decreases with increasing UV irradiation time. The photodegradation efficiency (η) is calculated from equation (2) [24]:

$$\eta = ((A_0 - A)/A_0) \times 100. \quad (2)$$

Here, A_0 and A are the absorbance peak intensities of RhB before and after UV light irradiation, respectively.

After calculation using this equation it was found that in the presence of $CuBO_2$ nanonetwork as the catalyst, after 12 h of UV light irradiation, RhB was degraded ∼70%. The inset image shows pictorial representation of the RhB solution collected at different times of UV irradiation.

Apart from the absorbance test, the rate constant for RhB degradation in UV light was determined using the well-known Langmuir–Hinshelwood model for photocatalytic reaction. According to this model,

$$-\,dC/dt = k_r k_a C/(1 + k_a C) \quad (3)$$

where k_r and k_a are rate constant and adsorption constant, respectively. After simplification, this equation can be written as,

$$\ln(C/C_0) = k_r k_a t = kt \quad (4)$$

Here, C and C_0 are the concentrations of the dye at any time 't' and initial time, respectively, and 'k' is the rate constant. From the linear plot of $\ln(C/C_0)$ *vs.* time (figure 5b) the rate constant of RhB degradation by this $CuBO_2$ nanonetwork was calculated and it was found to be 1.32×10^{-3} min^{-1}. In table 1 the rate constants of some other photocatalyst for RhB degradation are compared with that of $CuBO_2$ nanonetwork and it is found that our sample shows

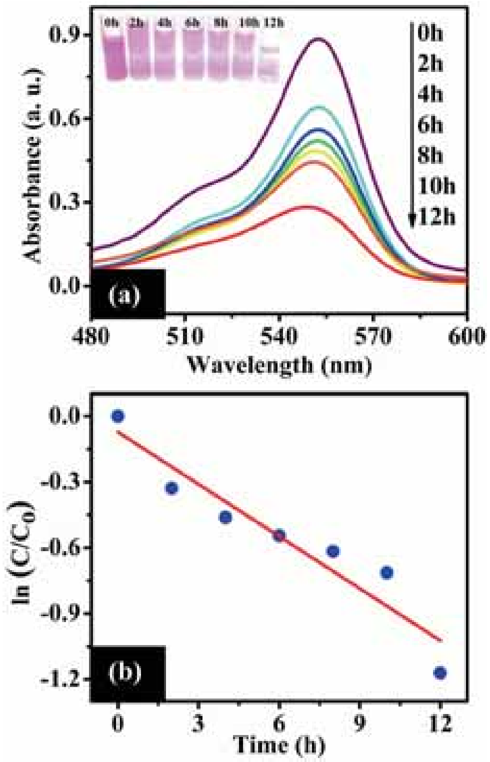


Figure 5. **(a)** Effect of UV irradiation time on the absorption curve intensity of RhB, and **(b)** plot of ln C/C_0 *vs.* UV irradiation time.

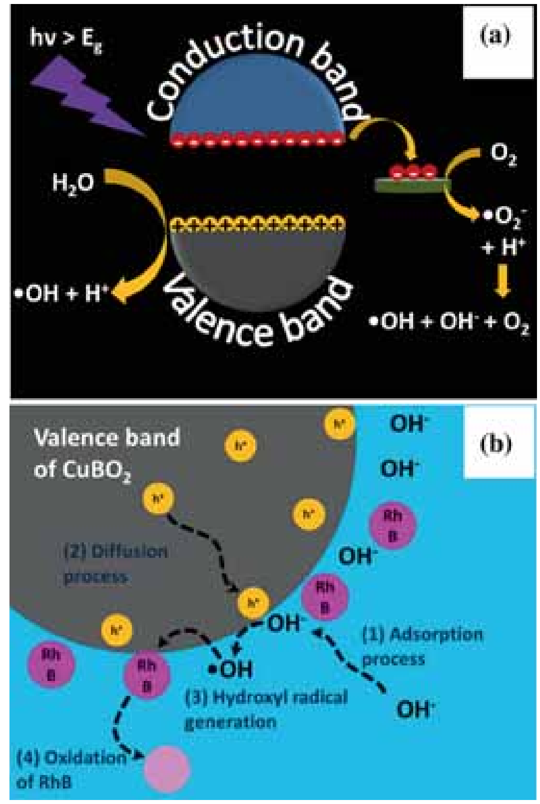
Table 1. Comparison of 'k' for different photocatalysts.

Sample	k (min^{-1})	Reference
Bi_2MoO_6	1.80×10^{-3}	[25]
C_{60}–C_3N_4	0.41×10^{-3}	[26]
RGO–SnO_2	3.60×10^{-3}	[27]
SiO_2@TiO_2 nanospheres	4.73×10^{-3}	[28]
Ag_2Se-G-TiO_2	0.35×10^{-3}	[29]
Titania-loaded siliceous mesoporous material	4.55×10^{-3}	[30]
Co_3O_4 nanoparticles	1.95×10^{-3}	[31]
$CuBO_2$ nanonetwork	1.32×10^{-3}	This work

comparable and sometimes better performance than the other reported results.

3.5 *Probable explanation for catalytic activity*

The $CuBO_2$ nanonetwork showed efficient UV-driven catalytic properties to degrade the harmful dye RhB. It is well known that catalytic activity of nanomaterials always depends upon their effective surface area. Also, nanostructures having higher aspect ratio tend to exhibit better photocatalytic properties. The nanonetwork of $CuBO_2$ synthesized in this work was highly porous as observed from FESEM and HRTEM studies and therefore it has high effective surface area. This may account for the good photocatalytic property of the sample.



Scheme 1. Schematic representation of **(a)** hydroxyl radical formation and **(b)** overall photocatalytic activity of $CuBO_2$ nanocrystal.

In electromagnetic irradiation, when the frequency of incident wave is greater that the band gap value of $CuBO_2$, it generates electron–hole pairs (e^-–h^+). As $CuBO_2$ is a p-type semiconductor, h^+s play a major role in the photocatalytic process. In this case, due to highly dispersed valence band, h^+s show higher mobility and therefore it makes e^- and h^+ separation easier. These h^+s reach the surface and facilitate the photocatalysis process. During photocatalysis, h^+s react with water and produce a very strong and nonselective oxidizing agent, hydroxyl radicals ($^\bullet OH$), which oxidizes the RhB. As a result, in UV light irradiation, RhB is decomposed in the presence of $CuBO_2$ nanocatalyst. The following equations show the consecutive steps of the proposed degradation mechanism [20,32]:

$$CuBO_2 \xrightarrow{h\nu} h^+ + e^-$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+$$

$$e^- + O_2 \rightarrow {}^\bullet O_2^-$$

$${}^\bullet O_2^- + H^+ \rightarrow {}^\bullet OOH$$

$$e^- + {}^\bullet OOH + H^+ \rightarrow H_2O_2$$

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^-$$

$${}^\bullet OH + \text{RhB} \rightarrow \text{intermediates} \rightarrow \text{degradation products}$$

The photocatalytic mechanism is depicted in scheme 1.

4. Conclusions

A novel $CuBO_2$ nanonetwork was synthesized by sol–gel method and its detailed structural, morphological and photocatalysis properties were studied subsequently. In UV irradiation, the as-synthesized material showed moderate photocatalytic activity for 10^{-5} M of hazardous and environment pollutant dye RhB. The degradation efficiency and the rate constant were found to be, ∼70% and 1.32×10^{-3} min^{-1} accordingly. The significant UV photocatalysis property of this new delafossite nanostructure may be of great importance for potential application as a cleaning reagent. Due to the highly porous structure, this novel nanonetwork-like structure of $CuBO_2$ can be a possible candidate for easy fabrication of future $CuBO_2$–metal/metal oxide nanocomposites for highly efficient photocatalysis.

Acknowledgements

SS thanks the Department of Science and Technology (DST), the Government of India, for awarding her INSPIRE fellowship during the execution of this work. The authors also wish to acknowledge the financial assistance by the University Grants Commission (UGC) and DST, the Government of India.

References

[1] Banerjee A and Chattopadhyay K 2005 *Prog. Cryst. Growth Charact. Mater.* **50** 52
[2] Hosono H 2007 *Thin Solid Films* **515** 6000
[3] Santra S, Das N S, Maiti S and Chattopadhyay K K 2014 *Chem. Phys. Lett.* **604** 97
[4] Das N S, Santra S, Banerjee D, Das G C and Chattopadhyay K K 2014 *Mater. Res. Express* **1** 025902
[5] Georgaki I, Vasilaki E and Katsarakis N 2014 *Am. J. Anal. Chem.* **5** 518
[6] Méndez-Medrano M, Kowalska E, Lehoux A, Herissan A, Ohtani B, Bahena D *et al* 2016 *J. Phys. Chem. C* **120** 5143
[7] Arghya Narayan B and Sang W J 2011 *Nanotechnology* **22** 365705
[8] Santra S, Das N S, Das B, Banerjee D and Chattopadhyay K K 2015 *Cryst. Growth Des.* **15** 1518
[9] Saswati S, Nirmalya Sankar D, Dipayan S and Kalyan Kumar C 2014 *J. Phys. D: Appl. Phys.* **47** 505301
[10] Arockiasamy J S K and Irudayaraj J 2016 *Ceram. Int.* **42** 6198
[11] Santra S, Das N S and Chattopadhyay K K 2012 *Proceedings of the 16th International Workshop on Physics of Semiconductor Devices* SPIE p 6
[12] Miller S A, Gorai P, Aydemir U, Mason T O, Stevanovic V, Toberer E S *et al* 2017 *J. Mater. Chem. C* **5** 8854
[13] Van Nong N, Pryds N, Linderoth S and Ohtaki M 2011 *Adv. Mater.* **23** 2484
[14] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H and Hosono H 1997 *Nature* **389** 939
[15] Snure M and Tiwari A 2007 *Appl. Phys. Lett.* **91** 092123
[16] Santra S, Das N S and Chattopadhyay K K 2013 *Mater. Lett.* **92** 198
[17] Ruttanapun C 2013 *J. Appl. Phys.* **114** 113108
[18] Santra S, Das N S and Chattopadhyay K K 2013 *AIP Conf. Proc.* **1536** 723
[19] Soylu M, Al-Ghamdi A A, Omran S B and Yakuphanoglu F 2014 *J. Alloys Compd.* **617** 602
[20] Santra S, Das N and Chattopadhyay K 2013 *Mater. Res. Bull.* **48** 2669
[21] Yu C, Yang K, Zhou W, Fan Q, Wei L and Yu J C 2013 *J. Phys. Chem. Solids* **74** 1714
[22] Yu D H, Yu X, Wang C, Liu X C and Xing Y 2012 *ACS Appl. Mater. Interfaces* **4** 2781
[23] Tran V V, Nguyen O T, Le C H, Phan T A, Hoang B V, Dao T D *et al* 2017 *Jpn. J. Appl. Phys.* **56** 095001
[24] Byrappa K, Subramani A K, Ananda S, Rai K M L, Dinesh R and Yoshimura M 2006 *Bull. Mater. Sci.* **29** 2006 433
[25] Belver C, Adán C and Fernández-García M 2009 *Catal. Today* **143** 274
[26] Chai B, Liao X, Song F and Zhou H 2014 *Dalton Trans.* **43** 982
[27] Zhang J, Xiong Z and Zhao X S 2011 *J. Mater. Chem.* **21** 3634
[28] Wilhelm P and Stephan D 2007 *J. Photochem. Photobiol. A: Chem.* **185** 19
[29] Ali A and Oh W C 2017 *J. Korean Ceram. Soc.* **54** 388
[30] Rasalingam S, Peng R and Koodali R T 2015 *Appl. Catal. B: Environ.* **174–175** 49
[31] Ravi Dhas C, Venkatesh R, Jothivenkatachalam K, Nithya A, Suji Benjamin B, Moses Ezhil Raj A *et al* 2015 *Ceram. Int.* **41** 9301
[32] Tan H L, Amal R and Ng Y H 2017 *J. Mater. Chem. A* **5** 16498