

Synthesis of copper oxide by reactive magnetron sputtering for photoelectrochemical water splitting

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Abstract. Copper oxide contains of bivalent copper and monovalent copper, which is widely distributed in earth resources. In this article, the copper oxide films were deposited on transparent conducting glasses (FTO) by magnetron reactive sputtering under different sputtering conditions of power and oxygen flow. The use of reactive magnetron sputtering can deposit a uniform copper oxide film with large scale rapidly. An analysis in detail on composition, morphology, optical and electrochemical properties of the sputtered copper oxide film was carried out. It is found that, the copper oxide with sputtering power of 30 W and O₂ flow of 7 sccm provide a photoinduced current of -3.0 mA cm⁻² under a bias potential of -0.5 V (vs. Ag/AgCl), which was found to be near 1.5 times higher than that with O₂ flow of 5 sccm (30 W), and 3 times higher than O₂ flow of 7 sccm (60 W), respectively.

Introduction

In this century, we are facing the problems of environment pollution and energy shortage. Development of clean energy is an urgency strategy to solve these problems. Photoelectrochemical (PEC) water splitting for hydrogen production is a promising method to solve this crisis. Copper oxide is considered as one of the most potential photocatalytic semiconductor materials for PEC hydrogen production, due to its economical and abundant [1]. Recently, J. Han [2] prepared a Cu₂O/CuO electrode, which achieved a highly improved stability for PEC water reduction. An optimized Cu₂O/CuO/CuS was reported by Dubale [3], which provided an enhanced photocurrent of -5.4 mA cm⁻² at 0 V (vs. RHE). Commonly, copper oxides contain of monovalent copper (Cu⁺) and divalent copper (Cu²⁺). Cu₂O is p-type semiconductor with a bandgap of 2.0 eV [4], which has a highly theoretical light-to-hydrogen conversion efficiency [5]. Compare with other photocatalytic semiconductor materials, such as WO₃ [6-8], BiVO₄ [9-11], Fe₂O₃ [12, 13], Ta₂N₃ [14], Cu₂O shows a better cost-performance and a relatively higher light-to-hydrogen conversion efficiency. And its conduction band potential is much more suitable for the PEC water reduction process. However, its valence band potential is just near the water oxidation potential, which limited its PEC water oxidation process. And its instability is also a big problem for Cu₂O. In order to solve these problems, consider of compositing Cu₂O with other stable semiconductors, such as CuO [15-17], WO₃ [18, 19]. CuO can provide a much positive valence potential for improving the water oxidation process, and its much stable than Cu₂O. CuO is a p-type semiconductor with a direct bandgap of 1.4 eV [20], it has a larger light response range than Cu₂O. In general, copper oxide can be deposited by several methods, such as electrochemical deposition [21], reactive magnetron sputtering [22], metal organic chemical vapor deposition [23], and sol-gel [24]. Among these deposition methods, reactive magnetron sputtering is a simple method for uniform film deposition, which can scaled up to mass-produced [25]. Furthermore, the properties of the sputtered film can be reproducible, and the sputtered products are easily to control by adjusting the sputtering gas flow.

In our previous study, we have reported on the influence of the sputtering gas ratio on the PEC performance of the CuO_x thin-film [26]. In this study, we reported on the preparation of $\text{Cu}_2\text{O}/\text{CuO}$ film prepared by reactive magnetron sputtering and the effect of different sputtering conditions on its PEC performance. The PEC performance of the $\text{Cu}_2\text{O}/\text{CuO}$ film was characterized by photoinduced potential-current, photoinduced time-current test and electrochemical impedance spectroscopy (EIS). X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-Vis diffuse reflectance spectrum were utilized to characterize the composition, morphology and optical property of the sputtered copper oxide film.

Experimental

The FTO glasses were cleaned with acetone and ethanol (1:1) by ultrasonic for 5 min firstly, then cleaned with deionized water for 5 min, and blow-dried by N_2 . The $\text{Cu}_2\text{O}/\text{CuO}$ film was prepared by reactive magnetron sputtering in Ar and O_2 atmosphere at room temperature, using a copper target with purity of 99.99%. During the sputtering process, the deposition chamber was pumped down to a pressure of 2×10^{-5} Pa. The copper target was cleaned by a pre-sputtering in Ar ambient for 5 min, followed by a second pre-sputtering with Ar and O_2 mixture ambient for 3 min. In order to analyze the influence of sputtering power on PEC performance of the sputtered film, in the first group of experiment, the Ar/ O_2 flow was fixed at 30/7 sccm, and the sputtering power was fixed at 15, 30 and 60 W. In the second group of experiment, the sputtering power was fixed at 30 W, the Ar/ O_2 flow was adjusted at 30/5, 30/7 and 30/9 sccm, to characterize the influence of oxygen flow on the PEC performance of the film. After deposition of sputtering, connect a copper wires with the conductive parts of the FTO substrate using conductive sliver tape, isolated the exposed conductive parts of FTO substrate with parafilm.

Characterization

The composition, microstructure and morphology of the sputtered film were characterized by XRD and SEM. UV-Vis diffuse reflectance spectrum was utilized to investigate the light absorption capabilities of the sputtered films. The PEC performance test was measured using a three electrode system by Electrochemical Workstation. The sputtered $\text{Cu}_2\text{O}/\text{CuO}$ film was worked as a working electrode, Pt sheet was worked as a counter electrode, and Ag/AgCl (saturated KCl) electrode was worked as a reference electrode. The PEC performance was tested in 0.1 mol/L Na_2SO_4 electrolytes. The photoinduced potential-current characteristic curve was measured from a bias potential of 0.5 V to -0.5 V (vs. Ag/AgCl), which was performed during light on and off in turns with one second respectively. The photoinduced potential-time curve was tested under a bias potential of 0 V (vs. Ag/AgCl). The EIS test was tested under an AC voltage of 5 mV, with a frequency range from 10^6 to 10^{-1} Hz, under a dark condition.

Results and discussion

Figure 1 shows the XRD patterns of the sputtered copper oxide films. The diffraction patterns for the $\text{Cu}_2\text{O}/\text{CuO}$ film under different gas ratios have two broad peaks at 30.4° and 46.3° corresponding to Cu_2O (110) and CuO (-112), respectively. With the increasing of oxygen flow, the Cu_2O (111), Cu_2O (222) and CuO (-202) crystal planes were developed on the sample with O_2 flow 7 sccm, indicating that Cu_2O was formed owing to the increasing of oxygen. And the CuO (110) and CuO (202) crystal planes were widely developed on the sample with O_2 flow 9 sccm, demonstrating that Cu_2O turn to CuO when oxygen flow exceeds to a percentage.

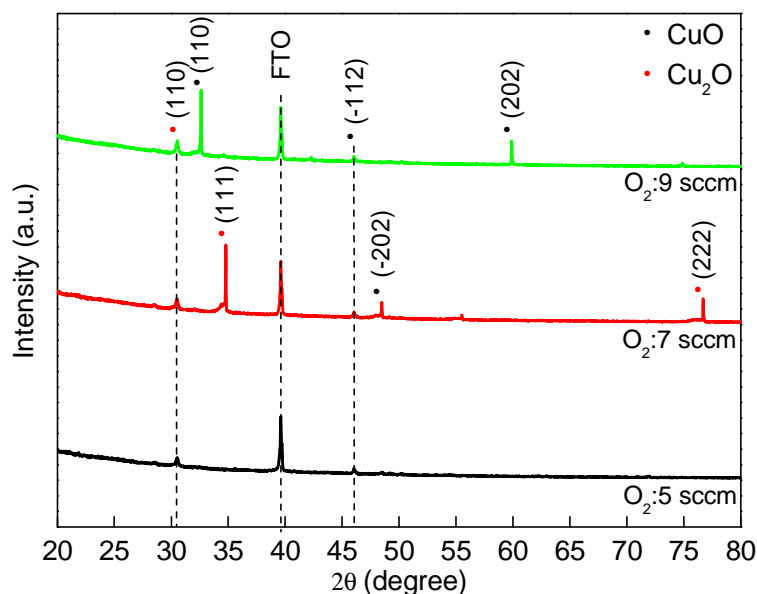
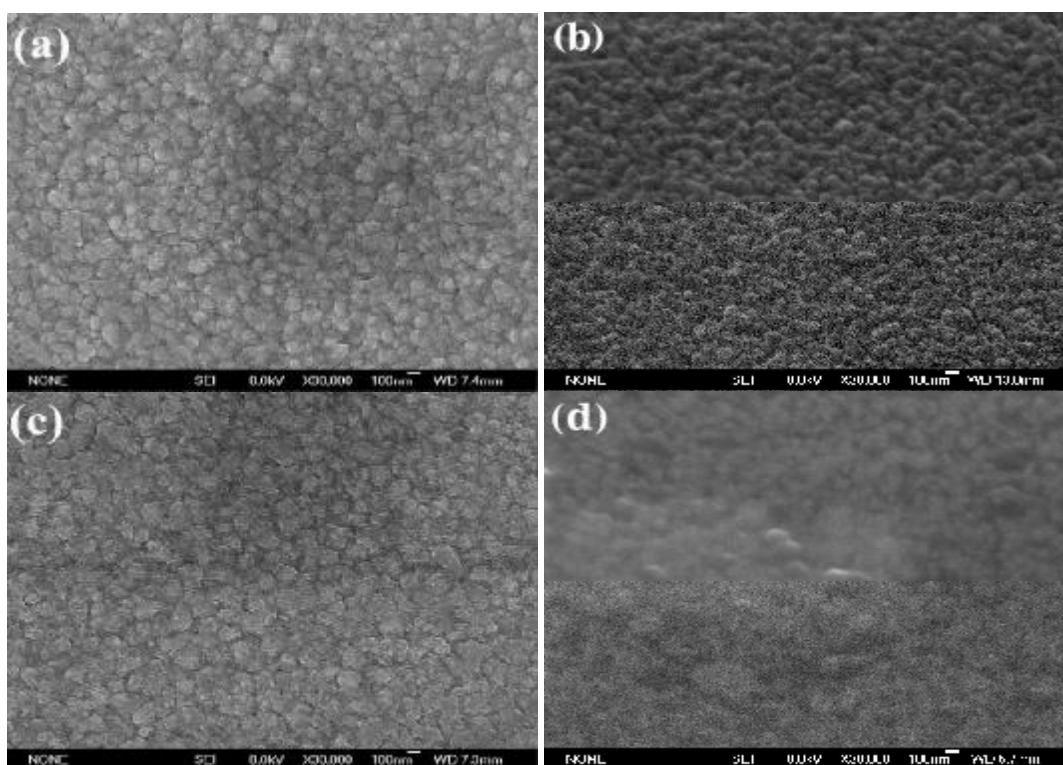


Fig. 1 XRD patterns of $\text{Cu}_2\text{O}/\text{CuO}$ films under different oxygen flows.

The SEM images of the surface of the $\text{Cu}_2\text{O}/\text{CuO}$ films were shown in figure 2. Fig. 2(a), (c) and (e) show the surface morphologies of the samples under different oxygen flows at a magnification of 30000. As we can see from Fig. 2(a), the $\text{Cu}_2\text{O}/\text{CuO}$ film consists of high crystallinity approximately 100 nm in diameter. The copper oxide particles grow to 150 nm in diameter under the oxygen flow of 7 and 9 sccm, as the increase of oxygen flow. Fig. 2(b), (c) and (d) show the SEM images of the samples under different sputtering power. As we can see that, the $\text{Cu}_2\text{O}/\text{CuO}$ film under 15 W consists of high crystallinity about 50 nm in diameter and the sample under 60 W shows a very low crystallinity.



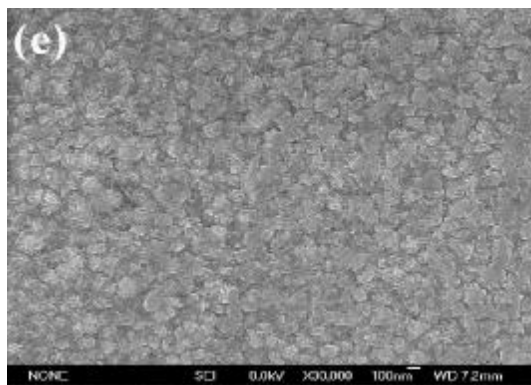


Fig. 2 Typical SEM images of the Cu₂O/CuO films under different sputtering conditions, (a) 30 W, O₂ flow 5 sccm; (b) 15 W, O₂ flow 7 sccm; (c) 30W, O₂ flow 7 sccm; (d) 60 W, O₂ flow 7 sccm; (e) 30 W, O₂ flow 9 sccm.

Figure 3 shows the UV-Vis absorption spectrum of the samples. It can be found that the Cu₂O/CuO films have strong light absorption capability in ultraviolet light region and visible light region. As Fig. 3(A) shows, the sample under oxygen flow 7 sccm provides a better light absorption capacity in different oxygen flows. As we can see from Fig. 3(B), the light absorption capacity of the sample tends to stronger, as the increasing of sputtering power.

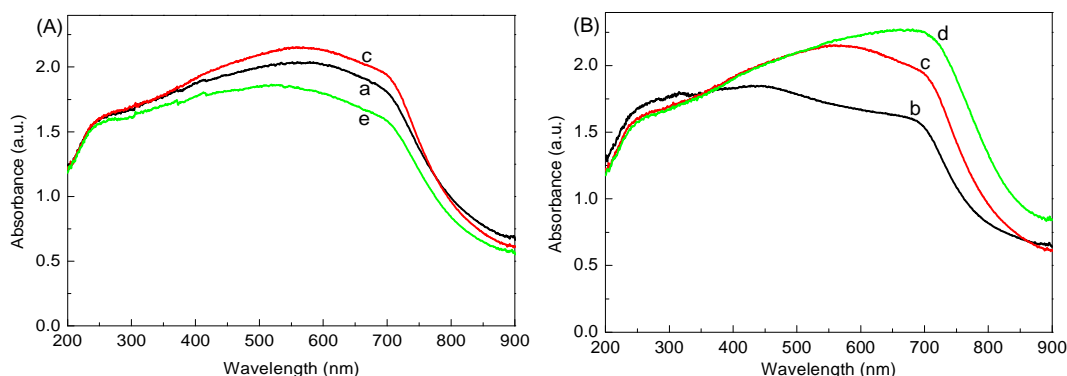


Fig. 3 UV-Vis absorption spectra of the samples under different sputtering conditions, (a) 30 W, O₂ flow 5 sccm; (b) 15 W, O₂ flow 7 sccm; (c) 30 W, O₂ flow 7 sccm; (d) 60 W, O₂ flow 7 sccm; (e) 30 W, O₂ flow 9 sccm.

Figure 4 shows the EIS spectra of the Cu₂O/CuO films under different oxygen flows. EIS can be used to analyze the degree of interfacial electron reaction and the interface transfer rate, which related to the electrochemical property of a semiconductor material. According to the EIS result, the impedance arc of the Cu₂O/CuO film under O₂ flow 7 sccm increased dramatically, demonstrating that it has strong semiconductor property. Furthermore, the impedance arc of the Cu₂O/CuO film under O₂ flow 5 sccm is very small. It can be declared that it has metalloid property, indicating that there is a small amount of copper in the sputtered film under 5 sccm.

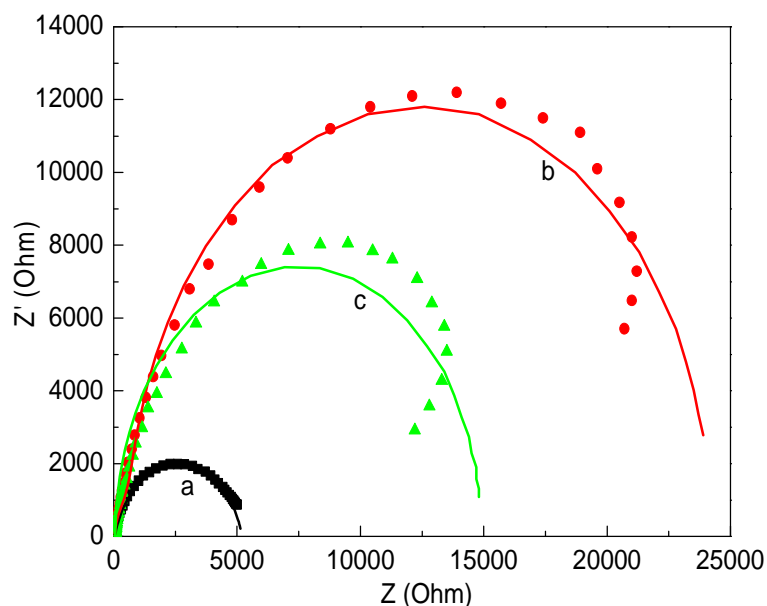
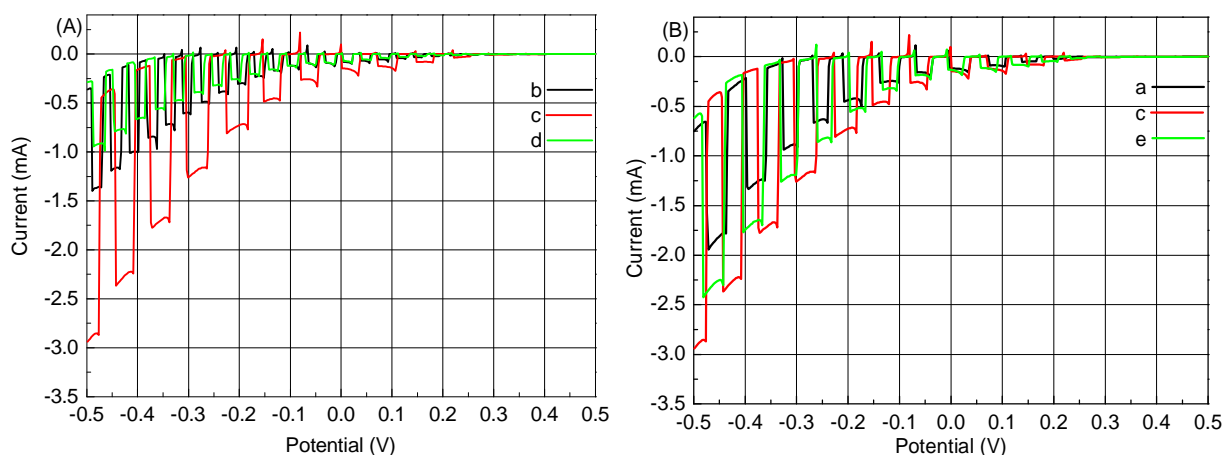


Fig. 4 EIS spectra of the $\text{Cu}_2\text{O}/\text{CuO}$ films under different oxygen flows, (a) O_2 flow 5 sccm, (b) 7 sccm, (c) 9 sccm.

Figure 5(A) and 5(B) show the photoinduced potential-current characteristic curves (i-v curve) of the $\text{Cu}_2\text{O}/\text{CuO}$ films under different sputtering power and different oxygen flows, respectively. The photoinduced i-v test was measured in 0.1 M Na_2SO_4 electrolytes to analyze the PEC response of the sputtered samples. The photoinduced i-v curve was tested under a bias potential scanning from 0.5 V to -0.5 V (vs. Ag/AgCl). The photoinduced current feature confirmed that the $\text{Cu}_2\text{O}/\text{CuO}$ films tend to be p-type semiconductors. The photoinduced current of the samples started at approximately 0.2 V and increased with the negative shift of the bias potential. It can be found in Fig. 5(A), the $\text{Cu}_2\text{O}/\text{CuO}$ film under sputtering power 30 W provided a photoinduced current of -3.0 mA cm^{-2} at the bias potential of -0.5 V, which was approximately 2 times higher than that of 15 W, and 3 times higher than 60 W. As Fig. 5(B) shows, the $\text{Cu}_2\text{O}/\text{CuO}$ film under O_2 flow 7 sccm generated a photoinduced current of -3.0 mA cm^{-2} , which was about 1.5 times higher than 5 sccm, and 1.2 times higher than 9 sccm. The photoinduced time-current curve (i-t curve) of the better performed $\text{Cu}_2\text{O}/\text{CuO}$ film is shown in Fig. 5(C). The photoinduced i-t test was measured under a bias potential of 0 V. According to the Fig. 5(C), the $\text{Cu}_2\text{O}/\text{CuO}$ film is stable under the bias potential of 0 V. After turning on the light, a negative current peak appeared, indicating that some defects formed in the sputtered film. The charging process of instantaneous photoelectrons causes the formation of this strong negative current peak.



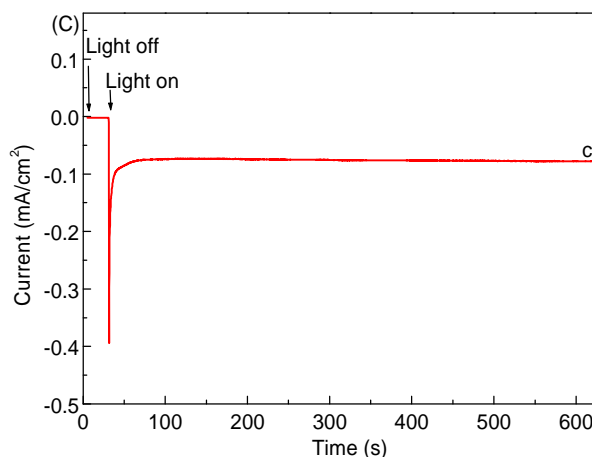


Fig. 5 The photoinduced potential-current characteristic curve of the $\text{Cu}_2\text{O}/\text{CuO}$ films, (A) under different sputtering power, (b) 15 W, (c) 30 W, (d) 60 W; (B) under different oxygen flows, (a) 5 sccm, (c) 7 sccm, (e) 9 sccm; (C) the photoinduced time-current curve of the sample under sputtering power 30 W, O_2 flow 7 sccm.

Conclusions

In summary, the $\text{Cu}_2\text{O}/\text{CuO}$ films under different sputtering power and oxygen flows were successfully prepared by a simple deposition method, reactive magnetron sputtering on FTO substrates. The sputtered products have been confirmed to be the mixture of CuO and Cu_2O , and the main component of the sample is CuO . With the increasing of sputtering power, the sputtered films tend to be lower crystallinity, resulting in the non-uniform of the sputtered films. Compare with different oxygen flows, the well-defined $\text{Cu}_2\text{O}/\text{CuO}$ film under 7 sccm is demonstrated to produce a better PEC performance. Simultaneously, UV-Vis diffuse reflectance spectrum and EIS test were carried out. It can be found that the sputtered films have strong light absorption capability in visible and ultraviolet light region. The well-defined $\text{Cu}_2\text{O}/\text{CuO}$ film under sputtering power 30 W, O_2 flow 7 sccm has the biggest impedance value, indicating that it has strong semiconductor property, resulting in a better PEC performance.

Conflict of interest

There is no conflict of interest.

References

- [1] Y.F. Lim, C.S. Chua, C.J.J. Lee and D. Chi: *Phys. Chem. Chem. Phys.* Vol. 16 (2014), p. 25928
- [2] J. Han, X. Zong, X. Zhou and C. Li: *RSC Adv.* 5 (2015), p.10790
- [3] A. A. Dubale, A. G. Tamirat, H. M. Chen, T. A. Berhe, C. J. Pan, W. N. Su and B. J. Hwang: *J. Mater. Chem. A*. Vol. 4 (2016), p. 2205
- [4] C. Li, T. Hisatomi, O. Watanabe, M. Nakabayashi, N. Shibata, K. Domen and J. J. Delaunay: *Energy Environ. Sci.* Vol. 8 (2015), p. 1493
- [5] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel and E. Thimsen: *Nat. Mater.* Vol. 10 (2011), 456
- [6] M. Higashi, R. Abe, T. Takata and K. Domen: *Chem. Mater.* Vol. 21 (2009), p. 1543
- [7] V. Cristino, S. Caramori, R. Argazzi, L. Meda, G.L. Marra and C.A. Bignozzi: *Langmuir*, Vol. 27 (2011), p. 7276
- [8] P. M. Rao, I. S. Cho and X. Zheng: *Proc. Combust. Inst.* Vol. 34 (2013), p. 2187

- [9] T.W. Kim and K.S. Choi: Science, Vol. 343 (2014), p. 990
- [10] Y.H. Ng, A. Iwase, A. Kudo and R. Amal: J. Phys. Chem. Lett. Vol. 1 (2010), p. 2607
- [11] X. Zhang, S. Chen, X. Quan and H. Zhao: Sep. Purif. Technol. Vol. 64 (2009), p. 309
- [12] A. Kay, I. Cesar and M. Grätzel: J. Am. Chem. Soc. Vol. 128 (2006), p. 15714
- [13] K. Sivula, F. Le Formal and M. Grätzel: ChemSusChem, Vol. 4 (2011), p. 432
- [14] G. Liu, S. Ye, P. Yan, F. Xiong, P. Fu, Z. Wang, Z. Chen, J. Shi and C. Li: Energy Environ. Sci. Vol. 9 (2016), p. 1327
- [15] Q. Huang, F. Kang, H. Liu, Q. Li and X. Xiao: J. Mater. Chem. A Vol. 1 (2013), p. 2418
- [16] Z. Zhang and P. Wang: J. Mater. Chem. Vol. 22 (2012), p. 2456
- [17] P. Wang, X. Wen, R. Amal and Y. H. Ng: RSC Adv. 5 (2015), p. 5231
- [18] L. J. Minggu, K. H. Ng, H. A. Kadir and M. B. Kassim: Ceram. Int. Vol. 40 (2014), p. 16015
- [19] J. Zhang, H. Ma and Z. Liu: Appl. Catal. B Environ. Vol. 201 (2017), p. 84
- [20] K. Nakaoka, J. Ueyama and K. Ogura: J. Electrochem. Soc. Vol. 151 (2004), p. C661
- [21] Y. Yang, Y. Li and M. Pritzker: Electrochim. Acta Vol. 213 (2016), p. 225
- [22] S. Masudy-Panah, R.S. Moakhar, C.S. Chua, H.R. Tan, T.I. Wong, D. Chi and G.K. Dalapati: ACS Appl. Mater. Interfaces Vol. 8 (2016), p. 1206
- [23] G. Malandrino, S.T. Finocchiaro, R.L. Nigro, C. Bongiorno and C. Spinella: Chem. Mater. Vol. 16 (2004), p. 5559
- [24] Y.F. Lim, C.S. Chua, C.J.J. Lee and D. Chi: Phys. Chem. Chem. Phys. Vol. 16 (2014), p. 25928
- [25] G.K. Dalapati, S. Masudy-Panah, A. Kumar, C.C. Tan, H.R. Tan and D. Chi: Sci. Rep. Vol. 5 (2015), p. 17810
- [26] T. Xie, T. Zheng, R. Wang, Y. Bu and J. P. Ao: Green Energy & Environment, (2018)