Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 517–521

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of single phase CuO nanowires and effect of electric field on their growth and investigation of their photocatalytic properties

Mansoor Farbod*, Narges Meamar Ghaffari, Iraj Kazeminezhad

Physics Department, Shahid Chamran University, Ahvaz, Iran

Received 9 February 2013; received in revised form 17 May 2013; accepted 10 June 2013
Available online 24 June 2013

Abstract

Single phase CuO nanowires were grown at a large scale via thermal oxidation of a Cu substrate in air at 500 °C for several times. Usually during the oxidation process, a layer of Cu_2O is grown on the surface of the substrate. Our results showed that by further annealing of the CuO (nanowires)/Cu_2O layer, isolated from the Cu substrate, it is possible to convert the Cu_2O to CuO nanowires. It was found that the Cu ion diffusion through the grain boundaries is the dominant growth mechanism in the thermal oxidation method. Also, effects of applying an electric field on the growth of nanowires have been investigated and it was found that the annealing in the electric field caused an increase in the concentration and uniformity of nanowires diameter. Also the adhesion of the CuO nanowires layer on the Cu substrate was observed. The photocatalytic activities of CuO nanowires were examined by photocatalytic degradation of Methyl Orange and Bromocresol Green dyes. The results showed that the nanowires grown at 500 °C had the best photocatalytic performance on both dyes.

Keywords: A. Sintering; B. Grain boundaries; E. Substrates; CuO nanowires

1. Introduction

In recent years, the one-dimensional nanostructures have been widely studied due to their high aspect ratio and potential applications in different areas. CuO nanowires as p-type semiconductors with narrow gaps and monoclinic structures have promising applications in electronic nanoscale devices [1]. There are many methods for synthesizing CuO nanowires [2–4]. Among them, the direct thermal oxidation of a Cu substrate is the simplest and most suitable for large scale production [5]. A challenge concerning the CuO nanowires is their fabrication in the single phase form. Usually during the oxidation process, a layer of Cu_2O phase grows on the surface of the substrate [6,7] which can alter the CuO nanowires properties. The growth mechanism of CuO nanowires through thermal oxidation is another issue which has been investigated by researchers [6,8] but not all the details are elucidated and need to be studied more. The VLS and VS growth mechanisms are the ones which are believed to be the dominant growth mechanisms of nanowires. Although this is true for most of the nanowires, but the growth mechanism of CuO nanowires seems to be more complicated. Therefore, different mechanisms based on grain boundary diffusion of Cu^{+2} ions and lattice diffusion have been suggested [8]. Another issue related to the CuO nanowires is finding a simple way to align the synthesized nanowires. Although some researchers have used silicon substrate in order to grow aligned nanowires and nanotubes [9,10], it seems applying an external electric field during sintering is another way to control the alignment of one dimensional nanostructures [11,12]. It is worth noting that the photocatalytic performance of CuO nanowires has not been studied enough. CuO nanowires have peculiar properties which make them suitable for photodegradation of some dyes which cannot be degraded by the other photocatalysts. Nowadays, the environmental pollutions have numerous negative effects on the human life. Therefore, decomposition of organic pollutants is one of the main subjects of the new researches. In this regard, the application of photocatalyst semiconductors in the decomposition of hazardous

*Corresponding author. Tel./fax: +986113331040.
E-mail address: farbod_m@scu.ac.ir (M. Farbod).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.06.032

pollutants has attracted more attention compared to the usual methods [13].

In our previous study, the growth of CuO nanowires by the direct oxidation method at different temperatures was investigated [7]. Here, we will report on the fabrication of single phase CuO nanowires and further studies of the growth mechanism of CuO nanowires. The effect of applying a DC electric field on the aligned growth of nanowires has also been examined. Moreover, the photocatalytic activity of synthesized nanowires is investigated by degradation of Bromocresol Green and Methyl Orange dyes, which are used as pH indicators and tracking dyes.

2. Experimental details

A pellet of Cu as the substrate was cleaned and prepared according to the Ref. [7]. The substrate was then transferred immediately into a furnace and annealed in air at 500 °C for several times ranging from 1 to 38 h. In order to investigate the effect of the electric field on the growth of nanowires, an electric field ranging from 13,000 to 130,000 V/m was applied to the samples during the growth by putting them between two 10×10 cm^2 flat metallic (iron) plates which were 0.3 cm apart and applying various DC voltages of 40, 60, 200, 300 and 400 V across the plates. The experimental setup is schematically shown in Fig. 1.

In order to investigate the photocatalytic performance of CuO nanowires, the degradation of Bromocresol Green and Methyl Orange was examined. The dye solutions were prepared by dissolving the dye powders in de-ionized water with the concentration of 20 mg/l. For each experiment, after adding 0.1 g CuO nanowires to about 100 ml of dye solution, the sample was placed in a home-made photoreactor and stirred in darkness for 30 min. The mixture was then illuminated under a UV source while being stirred and the sampling was carried out in 30 min intervals. After separating the CuO nanowires from the dye solutions using a 3000 rpm centrifuge, the UV–visible absorption spectra of the clear solutions were taken.

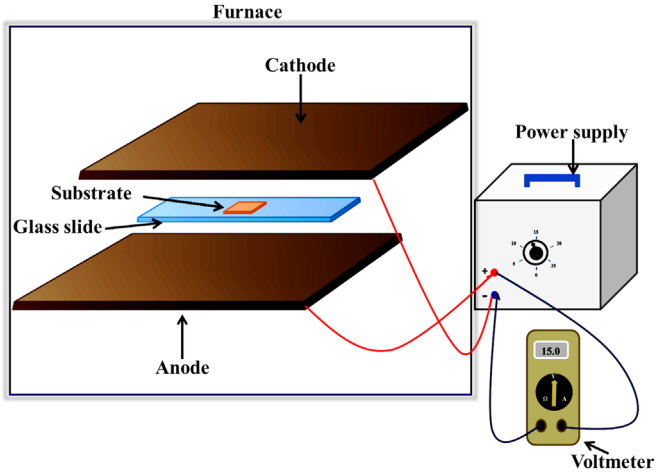

Fig. 1. Schematic drawing of the samples in the electric field.

The characterization of nanowires was performed by taking SEM images using a 1455 VP scanning electron microscope and XRD using a PW-1840 Philips diffractometer and UV–vis absorption measurement by use of a GBC, Cintra 100 spectrophotometer.

3. Results and discussion

In our previous study [7] we found that the annealing of a Cu substrate at 500 °C for 4 h was the best condition to synthesize CuO nanowires. Based on different studies, the growth of CuO nanowires is accompanied by the growth of a Cu_2O layer on the surface of the Cu substrate [6,7]. The growth of CuO nanowires occurs according to the following oxidation reactions:

$$4Cu + O_2 \rightarrow 2Cu_2O$$

$$2Cu_2O + O_2 \rightarrow 4CuO$$

It seems that the growth of a Cu_2O layer during the oxidation process is inevitable. Since the second reaction is a very slow one, we decided to examine a longer growing time to investigate whether is it possible to change the phase fraction of the two copper oxide phases in order to produce pure CuO nanowires or not. Fig. 2a, b, and c shows the XRD patterns of nanowires which were grown at 500 °C for 4, 24 and 36 h respectively. One can observe that by increasing the annealing time up to 24 h, the intensity of CuO peaks increases and that for Cu_2O phase decrease, but by further annealing, once again the Cu_2O phase fraction starts to increase (see Table 1) and cannot be removed. The pattern in Fig. 2d belongs to a black and fragile CuO/Cu_2O layer grown at 500 °C for 24 h (sample b), peeled off from the substrate and annealed again for another 14 h. All peaks except some very small Cu_2O peaks belong to the CuO phase. This means that as long as the Cu substrate exists, the Cu_2O phase continues to

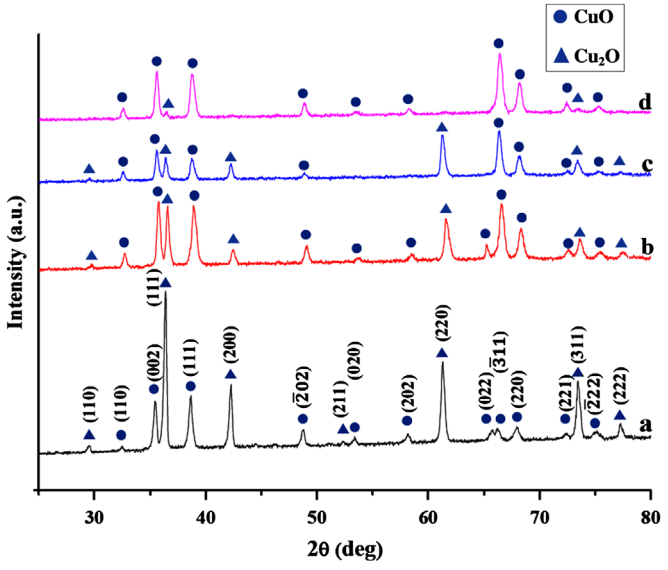

Fig. 2. XRD pattern of samples grown at 500 °C for (a) 4 h, (b) 24 h, (c) 36 h and (d) the sample b, peeled off from substrate and annealed for another 14 h.

Table 1
CuO/Cu_2O phase fraction of samples with different annealing times.

Sample		a	b	c	d
Phase fractions	CuO	0.34	0.67	0.59	0.96
	Cu_2O	0.66	0.33	0.41	0.04

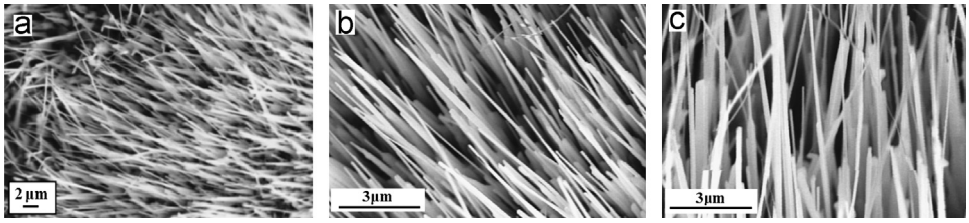

Fig. 3. FE-SEM image of samples annealed at 500 °C for (a) 4 h, (b) 24 h and (c) is the sample b, peeled off from the substrate and annealed for another 14 h.

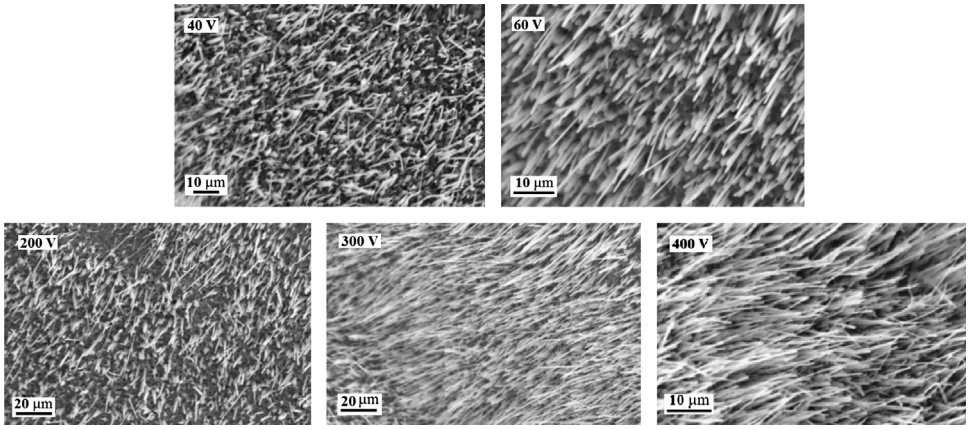

Fig. 4. FE-SEM images of nanowires annealed in air for 4 h at different electric field ranging from 13,000 V/m (40 V) to 130,000 V/m (400 V).

grow. Table 1 lists the phase fraction of CuO/Cu_2O for different samples. Fig. 3 shows the SEM images of samples a, b and d. The analysis of SEM images showed that the nanowires grew uniformly and by increasing the annealing time, the average nanowire's length increased. This means that the Cu_2O is converting into CuO but at the same time (samples a–c) the Cu_2O phase is produced continuously due to the oxidation of Cu substrate. For sample d, since the substrate is not present, the whole Cu_2O converts into the CuO phase.

Gonçalves et al. [8] have proposed a growth mechanism which says that during oxidation, at first a highly porous Cu_2O layer is formed. Then, due to the formation of Cu_2O at the oxide/air interface, for further oxidation, Cu atoms have two routes of lattice and grain-boundary diffusion to reach the growing interface. The migration through the lattice diffusion results in continuous growth of the Cu_2O layer, whereas the grain boundary diffusion gives rise to the formation of the CuO nanowires. Our results confirm such a model because by annealing the peeled off Cu_2O/CuO layer, the migration of Cu atoms through the lattice diffusion is stopped and the whole Cu_2O phase converts to the pure CuO nanowires.

Fig. 4 shows the FE-SEM images of nanowires grown at 500 °C for 4 h in air at different electric fields (voltages). As it can be observed, the growth of nanowires increased by increasing the voltage from 40 to 400 V (13,000–130,000 V/m), except at the 200 V where the growth is poor and diluted. At 300 and 400 V the growth is strong and all the Cu substrate is covered by concentrated nanowires. The growth at 60 V was good and some sort of alignment of nanowires was observed. Compared to the nanowires grown without applying the electric field which had a cone shaped form, the nanowires were thinner and uniform in diameter. Li et al. [11] have grown CuO nanoneedles using oxidation of a layer of Cu films in electric field (2000–5000 V/m) and at high temperatures of 600–730 °C. They argue that during the nanowires growth, there are two different electric fields, the local field which sets up by the ionization of the Cu and O atoms at the interface and the external applied field. When these two fields are in the same direction, the diffusion rate of Cu ions will be enhanced and the CuO nanowires grow along the direction of applied field, resulting in the increase of nanowires length. At high voltages, due to oxygen ions obstruction, the growth of the

nanowires will be limited. As mentioned in Section 2, we have grown the samples at lower temperature (500 °C) and higher electric filed (13,000-130,000 V/m). So it seems the obstruction of oxygen ions at lower temperature (500 °C) occurs at higher electric fields (the voltage of 200 V across the plates) and the growth of the nanowires will be restricted. At higher electric fields, possibly due to air ionization and producing oxygen ions, the growth of nanowires will be promoted.

The adhesion of Cu_2O/CuO layer to the substrate was the most interesting phenomenon which was observed for samples annealed in the electric field. It is to be noticed that the grown copper oxide layer is usually peeled off from the substrate during the oxidation process which can restrict their applications. Based on these observations, it seems that by applying the electric field, the diffusion of Cu^{2+} ions from substrate to the Cu/Cu_2O interface, accelerates and causes an increase in the concentration of CuO nanowires. Also, some sorts of local defects are created on the surface of Cu substrate and the CuO layer adheres to them locally on which the adhesion of the whole oxide layer to the substrate occurs. Fig. 5 shows the cross section of a sample which is fabricated in the electric field.

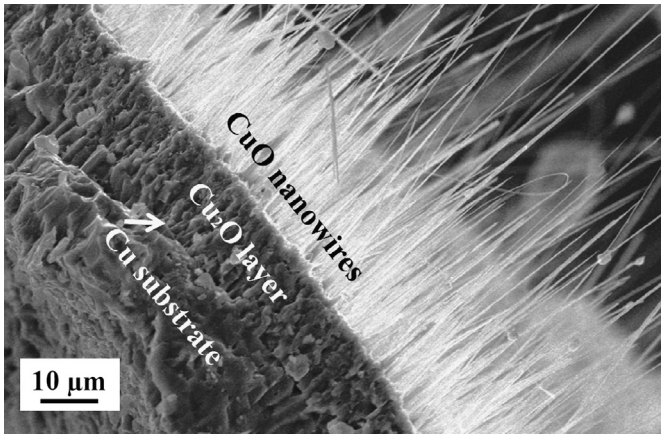

Fig. 5. Cross section image of a sample annealed in electric field which shows different layers. The arrow indicates the interface between the Cu_2O layer and the Cu substrate.

In order to investigate the ability of CuO nanowires in water purification, their photocatalytic performance was studied. Fig. 5 shows the absorption spectra of Bromocresol Green at 30 min intervals in the presence of the CuO nanowires which were produced at 400, 500 and 600 °C in air [7]. Based on our knowledge, the photodegradation of Bromocresol Green dye by CuO nanowires has not been reported.

As it can be seen from Fig. 6a, b and c, although the maximum absorption wavelength does not change for different nanowires, the dye decomposition rates are not the same for the nanowires with different aspect ratios. For the prepared nanowires at 500 °C, the decomposition rate is higher than the others. The same trend happens in decomposition of Methyl Orange (Fig. 7). Fig. 6 shows the photocatalytic degradation (C/C_0) of Bromocresol Green and Methyl Orange dyes by nanowires which were grown at different temperatures.

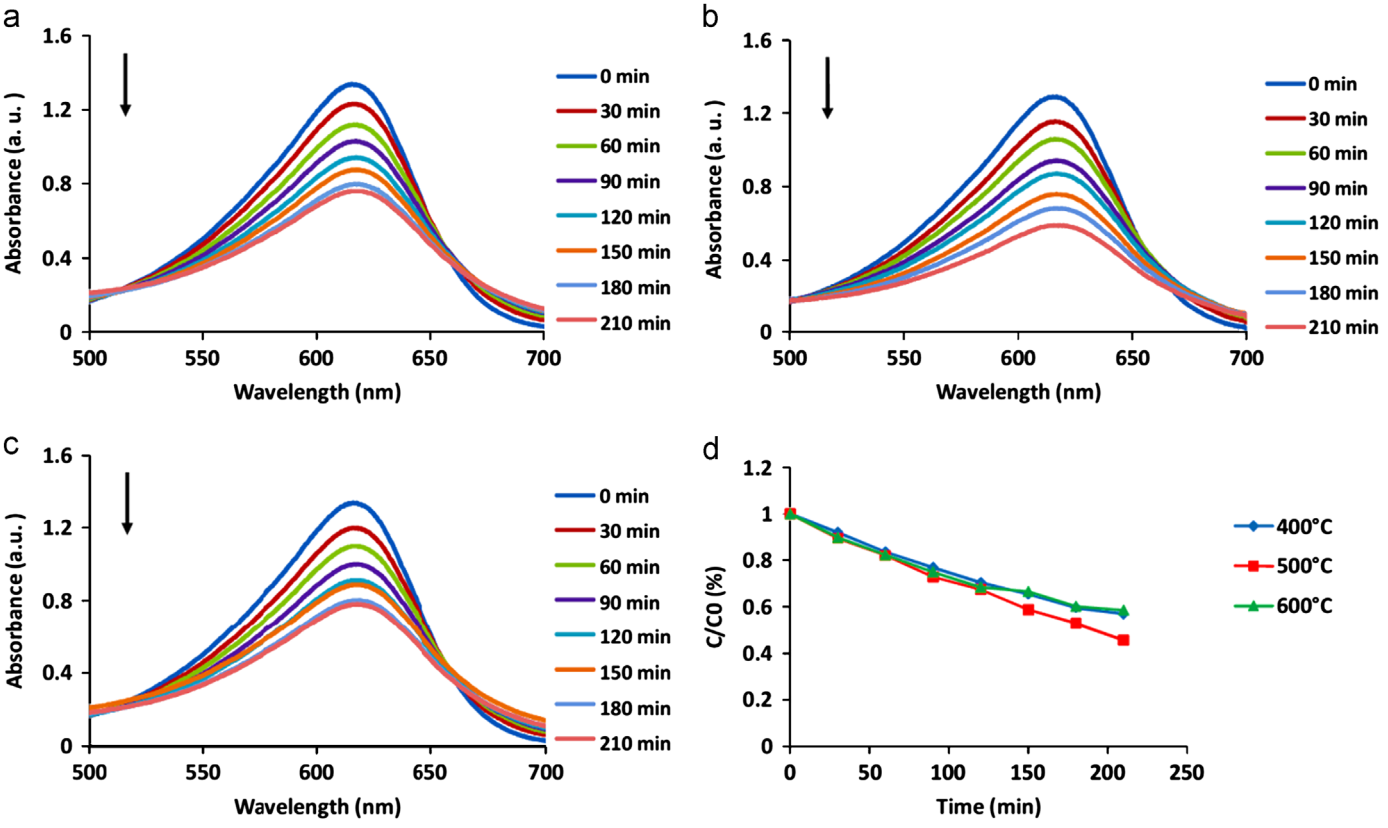

Fig. 6. UV–vis spectra of Bromocresol Green dye solutions in 30 min intervals. The decomposition was performed by prepared nanowires at (a) 400 °C, (b) 500 °C and (c) 600 °C for 4 h and (d) photocatalytic degradation of Bromocresol Green versus reaction time for different nanowires.

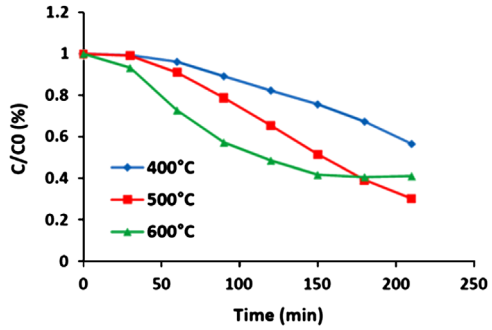

Fig. 7. Photocatalytic degradation of Methyl Orange versus reaction time for nanowires produced at different temperatures.

C_0 indicates the initial concentration of dye after 30 min stirring in darkness and C is the dye concentration after UV irradiation. As it is clear from Fig. 7, the prepared CuO nanowires at 600 °C have a better performance in decomposition of Methyl Orange at the first 150 min and decompose about 60% of primary dye, but after that the produced nanowires at 500 °C show better performance.

It is to be noticed that the photodegradation of Methyl Orange by CuO nanowires is higher compared to that of Bromocresol Green. Also, the decomposition of Methyl Orange which is difficult to be decomposed was carried out by CuO nanowires, a good candidate for replacing TiO_2 which has been known to be the best photocatalyst [14].

4. Conclusion

CuO nanowires were grown by direct oxidation process. The results confirmed that the Cu lattice diffusion results in the continuous growth of the Cu_2O layer, whereas the grain boundary diffusion gives rise to the formation of the CuO nanowires. It was found that by annealing the peeled off CuO/Cu_2O layer isolated from the substrate for a longer time, it is possible to produce single phase CuO nanowires. By applying an electric field during the growth, some sort of alignment was observed at 60 V. Also the uniformity in diameters of nanowires and adhesion of oxide layer to the substrate were increased. Furthermore photocatalytic degradation of Bromocresol Green and Methyl Orange were carried out by CuO nanowires. The results showed that the nanowires which were prepared at 500 °C had better photocatalytic performance.

Acknowledgments

The authors acknowledge Shahid-Chamran University of Ahvaz for financial support of this work.

References

[1] G.A. Ozin, Nanochemistry: synthesis in diminishing dimensions, Advanced Materials 4 (1992) 612–649.
[2] L.S. Huang, S.G. Yang, T. Lia, B. Gu, Y.W. Du, Y.N. Lu, S.Z. Shi, Preparation of large-scale cupric oxide nanowires by thermal evaporation method, Journal of Crystal Growth 260 (2004) 130–135.
[3] S.Y. Kun, S.C. Min, Y.H. Tao, L.H. Lin, G.H. Jun, Controlled synthesis of highly ordered CuO nanowire arrays by template-based sol–gel route, Transactions of Nonferrous Metals Society of China 17 (2007) 783–786.
[4] Z. Jiang, Q. Niu, W. Deng, Hydrothermal synthesis of CuO nanostructures with novel shape, Nanoscience 12 (2007) 40–44.
[5] J.T. Chen, F. Zhang, J. Wang, G.A. Zhang, B.B. Miao, X.Y. Fan, D. Yan, P.X. Yan, CuO nanowires synthesized by thermal oxidation route, Journal of Alloys and Compounds 454 (2008) 268–273.
[6] M.L. Zhong, D.C. Zeng, Z.W. Liu, H.Y. Yu, X.C. Zhong, W.Q. Qiu, Synthesis, growth mechanism and gas-sensing properties of large-scale CuO nanowires, Acta Materialia 58 (2010) 5926–5932.
[7] M. Farbod, N. Meamar Ghaffari, I. Kazeminezhad, Effect of growth parameters on photocatalytic properties of CuO nanowires fabricated by direct oxidation, Materials Letters 81 (2012) 258–260.
[8] A.M.B. Gonçalves, L.C. Campos, A.S. Ferlauto, R.G. Lacerda, On the growth and electrical characterization of CuO nanowires by thermal oxidation, Journal of Applied Physics 106 (2009) 034303–034307.
[9] Y.T. Yin, Y.Z. Chen, C.H. Chen, L.Y. Chen, The growth mechanism of vertically aligned ZnO nanowire arrays on non-epitaxial Si(100) substrates, Journal of Chinese Chemical Society 58 (2011) 817–821.
[10] A. Ural, Y. Li, H. Dai, Electric-field-aligned growth of single-walled carbon nanotubes on surfaces, Applied Physics Letters 81 (2002) 3464–3466.
[11] X. Li, J. Zhang, Y. Yuan, L. Liao, C. Pan, Effect of electric field on CuO nanoneedle growth during thermal oxidation and its growth mechanism, Journal of Applied Physics 108 (2010) 024308–024313.
[12] O. Englander, D. Christensen, J. Kim, L. Lin, S.J.S. Morris, Electric-field assisted growth and self-assembly of Intrinsic Silicon nanowires, Nano Letters 5 (2005) 705–708.
[13] D. Chatterjee, Sh. Dasgupta, Visible light induced photocatalytic degradation of organic pollutants, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 6 (2005) 186–205.
[14] R. Thapa, S. Maiti, T.H. Rana, U.N. Maiti, K.K. Chattopadhyay, Anatase TiO_2 nanoparticles synthesis via simple hydrothermal route: degradation of orange II, methyl orange and rhodamine B, Journal of Molecular Catalysis A: Chemical 363–364 (2012) 223–229.