Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 8 (24): 4674-4678, 2008
ISSN 1812-5654
© 2008 Asian Network for Scientific Information

Preparation of Cu_2O from TiO_2 and CTAB using the Anode Support System

[1]A. Abdulkarem, [2]E.A. Ammar, [3]Y. Ying and [4]L.J. Lin
College of Physical Science and Technology, Central China Normal University,
Wuhan, 430079, People's Republic of China

Abstract: This study describes the application of an anode-support system to the electrolytic production of (Cu_2O) nanoparticle. Using TiO_2 particle and Acetyl trimethyl ammonium bromide (CTAB/TiO_2) particle with size of 10-20 and 10-30 nm, respectively, composites were obtained by an electrochemical method. The growth of the Cu_2O nanoparticle, it is found that the role of CTAB/TiO_2 is to interact with $Cu(OH)_2$, which can adsorb OH^- and become negative charged, to disperse the $Cu(OH)_2$ solid and to induce the growth of Cu_2O. Although CTAB/TiO_2 is significant for the preparation of the nanomaterials, the properties of the composites of this materials were evaluated by Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD).

Key words: Electrochemical method, nanoparticles, CTAB, Cu_2O

INTRODUCTION

The study of metal oxide nanoparticles has been an extremely active area in recent years because of their interesting properties different from those of bulk substances (Su-Yuan *et al*., 2004). Variation in crystal structure parameters, discretization of electron energy levels and increased surface to volume ratio makes nanocrystalline materials very interesting (Nikesh *et al*., 2005). The various composites formed by TiO_2 and different oxides have been reported by Fuerte *et al*. (2002), Li *et al*. (2001) and Bedja and Kamat (1995). To our best knowledge, the nano-size TiO_2-Cu_2O and (TiO_2-CTAB)/Cu_2O is a kind of new composite that has been studied. Cu_2O is a nonstoichoimetric p-type semiconductor; the component elements are inexpensive and abundantly available (Musa *et al*., 1998). Cuprous oxide is the subject of much current research interest; it has a band gap of about 2.17 eV and a highly optical absorption coefficient (Noguet *et al*., 1979). Therefore, preparing nanometer sized particles of Cu_2O is of special importance to improve the solar energy conversion efficiency (Jialin *et al*., 2004) Polycrystalline thin films of Cu_2O can be produced by thermal, anodic and chemical oxidation and reactive sputtering (Economou *et al*., 1977).

The electrochemical behaviour of copper is of considerable interest with respect to fundamental and applied research due to its wide application in industry. Hence, the oxidation behaviour of this metal has been extensively studied by electrochemical techniques, particularly in neutral and alkaline environments, which results on the formation of passivating layers (Cascalheira *et al*., 2004).

Acetyl trimethyl ammonium bromide (CTAB) is a cationic surfactant; induce the sphere-rod transition of micelles in aqueous solution when some salts such as NaCl, NaOH and so on are added. Therefore, CTAB can be employed to synthesize materials with special morphologies (Ying *et al*., 2004; Ryszard *et al*., 1988).

The preparation of Cu_2O nano powders by the anode dissolution of copper in an alkaline NaCl solution has been wildly used as the best suitable process on an industrial scale. The products meet the requirement for purity and colour, however, the powder has the size of several both micrometer and nanometer scale (Nikhil *et al*., 2001; Ji, 1990).

Recently, it has been studied without adding titanium dioxide nanoparticles (P-25) and cubic crystal was obtained with diameter of a bout (1 μm) but after adding (P-25) pure Cu_2O in the nanometer scale was obtained (Jialin *et al*., 2004).

However, in this study without adding (P-25) by the same method and reaction, pure cubic crystal with the diameter of about 80-150 nm was obtained.

Similarly, after adding (P-25) the same material was obtained but with smaller size (10-20 nm).

After adding CTAB to the solution (TiO_2-Cu_2O) using the same method and reaction, we obtained cubic crystal of Cu_2O

In this study, we have used a novel electrochemical method to prepare Cu_2O nanoparticle, by added Titanium dioxide (TiO_2) and changing the reaction conditions in the

Corresponding Author: A. Abdulkarem, College of Physical Science and Technology, Central China Normal University, Wuhan, 430079, People's Republic of China

anode bath, also by the same method Cu_2O nanoparticles were prepare. By adding (P-25) with capping agent acetyl trimethyl ammonium bromide (CTAB) to gather soft template in the anode bath, Cu_2O nanoparticles arrays on copper substrate was obtained on the anode plate. The product's properties of Cu_2O nanoparticle and characterizations are investigated by transmission electron microscopy (TEM), SEM, X-ray diffraction (XRD).

MATERIALS AND METHODS

The experiments were performed in an electrolytic cell; the electrolytic cell was divided into three parts. Anodic bath cathode, bath and a heat up bath. An anion exchange membrane is used for spacing out the anode and cathode bath.

The anodic electrolyte was the aqueous solution of 225 g L^{-1} sodium chloride and TiO_2 (P-25) as the template is 125 mg L^{-1} with a piece of copperplate as the anode, the cathodal electrolyte was the aqueous solution of sodium hydroxide (0.1 mol L^{-1}) NaOH with a piece of stainless steel as the cathode. For the preparation of (TiO_2-Cu_2O) particle composite 2 g TiO_2 (Dessuga, P-25) was added into the anodic bath at the beginning of the reaction. The temperature of the reaction was kept at about 80°C. During the reaction the necessary perpetual agitating was done. The electrolytic current was adjusted to 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 A, respectively and the time was controlled from 20 to 40 min, respectively.

The colour of the solution changed to orange and then to brick red. After deposition of the anodic solution, the anodic electrolyte was taken out and was centrifugated. Then, the deposition was washed immediately by distilled water till there was no chloride and then washed with ethanol for one time. Finally the products were dried in a vacuum oven at 60 C for 3 h. Also by the same method, for the preparation of (TiO_2, CTAB)/Cu_2O particle composite, added 0.5 g cetyl trimethyl ammonium bromide (CTAB) to the same solution. The electrolytic current was admitted to 0.4, 0.6 and 0.8 A, respectively. And the time was controlled 25-40 min, respectively. The products were dried in a vacuum oven at 60°C for 2 h and the products were dried in a vacuum at a temperature of 120°C for 2 h.

RESULTS AND DISCUSSION

Figure 1a shows the SEM image of pure Cu_2O particle composites prepared with the current 0.2A and the reaction time of 40 min and it is the cubic crystals with the diameter between 80-150 nm, which is reasonably to believe that the existence of nano-TiO_2 in the electrolyte can make the Cu_2O product in nano size particle.

Figure 1b shows the XRD pattern of the sample is composed of pure Cu_2O without any impurities as from the XRD pattern. The cubic crystals prepared by the same method but without TiO_2 and (TiO_2, CTAB), in the anodic bath which shows that there are five peaks with 2θ angle values of 26.6, 32.6, 37.9, 54.6, 65.1 corresponding to

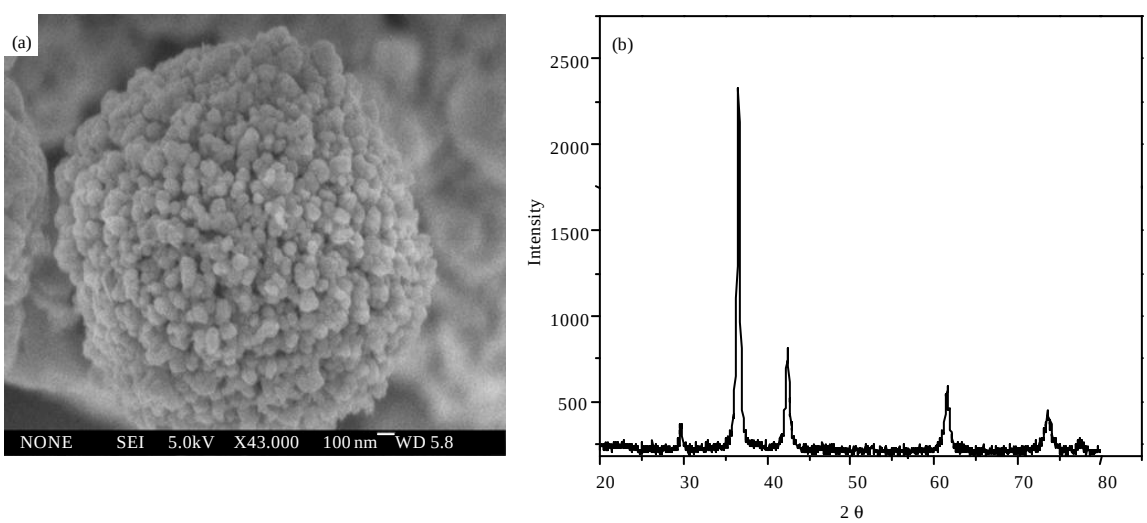

Fig. 1: (a) The SEM image of pure Cu_2O particle prepared without adding TiO_2 by applied current of 0.2A and a reaction time of 40 min and (b) the XRD pattern of the same sample

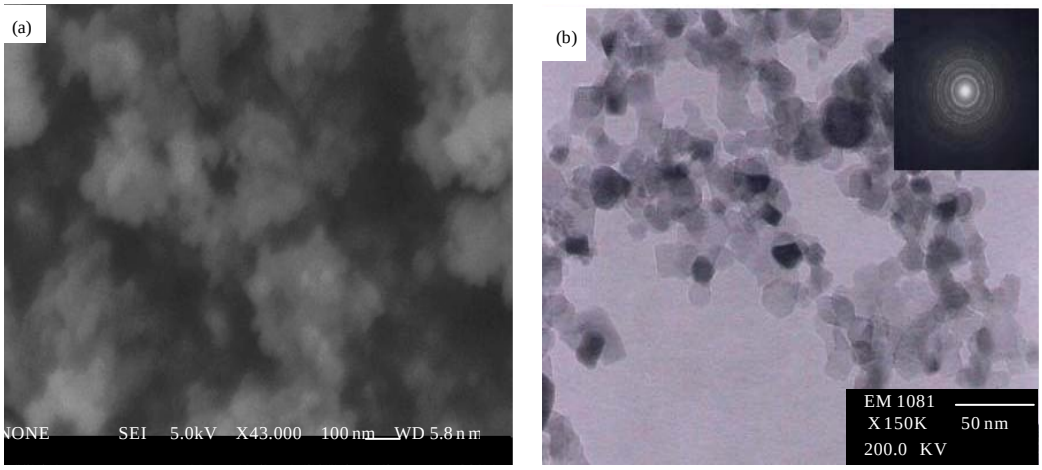

Fig. 2: (a) Shows the SEM images of the Cu_2O nanoparticle prepared by adding TiO_2 and with applied current of 0.4A and a reaction time of 40 min (b) the TEM image of the same sample (inset: the SAED pattern)

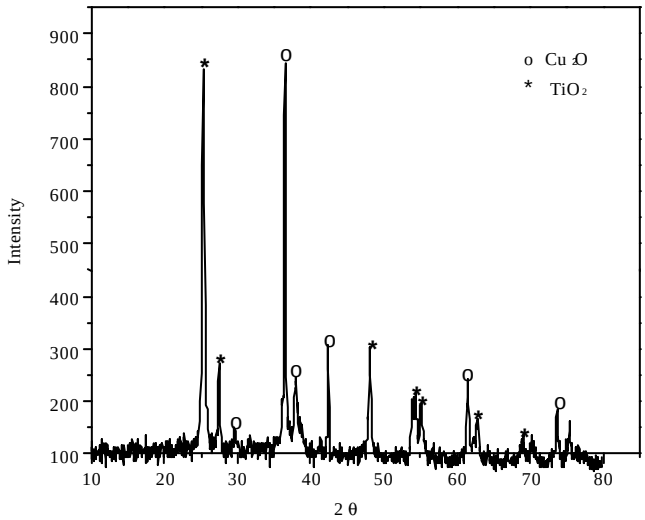

Fig. 3: The XRD pattern of the Cu_2O nanoparticle prepared by adding TiO_2 and with applied current of 0.4A and a reaction time of 40 min

the lattice planes [110], [111], [200], [220], [311], respectively, of crystalline Cu_2O. This results match well with standard data of pure Cu_2O powders. Analysis with XRD showed that the sample is composed of pure Cu_2O without any impurities as from the XRD pattern.

Figure 2a shows the SEM images of the Cu_2O nanoparticle composites and Fig. 2b shows the TEM nanoparticle composites prepared, when the perpetual current of 0.4A and the reaction time 40 min. The particle size was between 10-20 nm in diameter. The cubic crystals are Cu_2O particles. It shows that Cu_2O is closely adjoined to TiO_2.

Figure 3 shows the XRD pattern of the prepared Cu_2O nanoparticles harvested in the anode electrolyte, which shows that there are some impurities from the titanium dioxide. This results match well with standard data of pure Cu_2O powders. The results from the Fig. 1-3, it is evidence for that we have obtained pure Cu_2O which is consistence with earlier finding of Jialin *et al.* (2004) but we found smaller size nanoparticles than those obtained from previous experiment results by

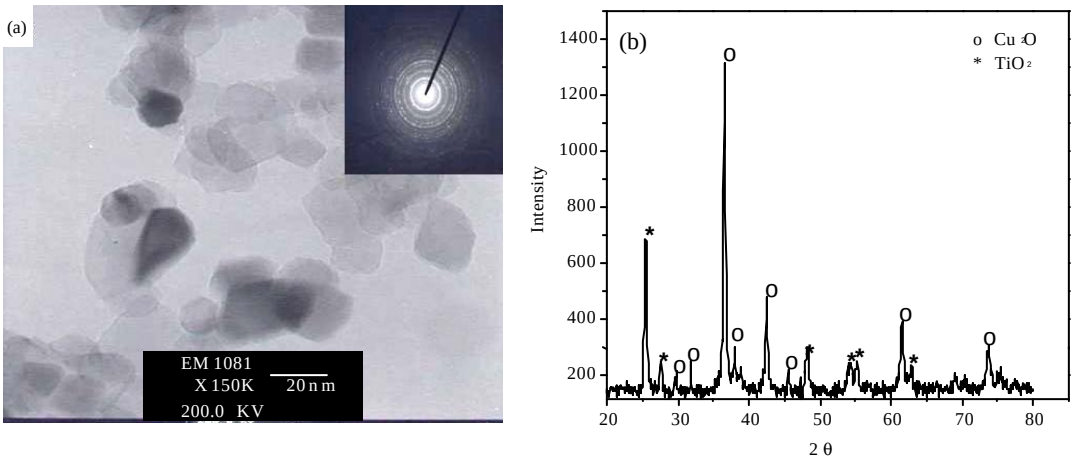

Fig. 4: (a) TEM image of the sample prepared by adding TiO_2 and CTAB with a current of 0.8A and a reaction time of 40 min (inset is the SAED pattern) (b) The XRD pattern of the same sample

Jialin *et al.* (2004). This new finding of smaller size of Cu_2O particle will contribute to the improvement the solar energy conversion efficiency (Musa *et al.*, 1998; Jialin *et al.*, 2004).

For the nanoparticles crystal growing on the copper anode there are two mechanisms, which may be used for explanation.

The first one is diffusion direct mechanism. The principle reactions in the anodic solution processes are the following:

When there is no (TiO_2, CTAB) in the electrolyte the CuCl ion can diffuse from copper electrode surface region to bulk solution in every direction, so the generated Cu_2O is in the crab or sphere form (TiO_2, CTAB) can form lamellar micelles in the solution. The micelles are positive charged and should be arrayed parallel to the electrical cell in the electrolyte cell. CuCl ion's diffusion is limited by the micelles; that is the ion's diffuses in a divest vertical to the electrode along the narrow pores constructed by the micelles.

The stage of hydrolysis, nucleation and the aggregation of uniform single crystalline subunits into the final large polycrystalline assemblies are all developed within the resulting in the growth of Cu_2O. The electric globular direction and the Cu_2O is formed.

The second mechanism is ion exchange where the formation of Cu_2O needs OH. The Br ion of TiO or (TiO_2,CTAB) may exchanges with OH in an alkaline and it can provide OH and take the Cl ion away the ion exchanges groups on the inside of anode owing to the electrostatic repulsion, this leads to the growth of Cu_2O and the cubic is formed.

Figure 4a shows the images of the Cu_2O nanoparticle composites prepared, For the preparation of (TiO_2, CTAB)/Cu_2O particle composite 2 g TiO_2 (Dessuga, P-25) and 0.5 g (CTAB) with the current of 0.8A and the reaction time of 40 min. The particles size was between 10-30 nm in diameter

Figure 4b analysis with XRD showed that the sample is composed of pure Cu_2O as from the XRD pattern. XRD pattern of the prepared Cu_2O nanoparticles harvested in the anode electrolyte.

CONCLUSION

(TiO_2-Cu_2O) and (TiO_2-CTAB)/Cu_2O composites were prepared by the novel electrochemical method. This method arises from an industrial procedure with minor modification, so it is simple, reliable and easy to carry out in the large scale.

With the cationic surfactant CTAB as a template, Cu_2O nano-structure can be obtained. The nano-particle are highly porous, which will be beneficial for the photocatalytic activity under visible light. According to the TEM images of the morphology of the compounds at the different growth stages and the comparison of the result obtained with and without NaOH, it can be confirmed that there is electrostatic interaction between the precursor $Cu(OH)_2 \bullet OH^-$ suspension and CTAB.

REFERENCES

Bedja, I. and P.V. Kamat, 1995. Capped semiconductor colloids, synthesis and photoelectrochemical behavior of TiO_2-capped SnO_2 nanocrystallites. J. Phys. Chem., 99: 9182-9188.

Cascalheira, A.C. and L.M. Abrantes, 2004. The electrochemical behaviour of copper in sodium salicylate aqueous solutions. Electrochimica Acta, 49: 5023-5028.

Economou, N.A., R.S. Toth and R.J.D. Komp, 1977. Trivich, solar energy Conference. Proceedings of the European Community of Photovoltaics, Reidel, Dordrecht, Luxembourg, pp: 1180-1185.

Fuerte, A. Hern'andez-Alonso, M.D. Maira, A.J. Mart'inez-Arias and A.M. Fern'andez-Garc'ia *et al*., 2002. Nanosize Ti-W mixed oxides: Effect of doping level in the photocatalytic degradation of toluene using sunlight-type excitation. J. Catal., 212: 1063-9.

Ji, J.W.C.C., 1990. Electrochemical preparation of cuprous oxide powder: Part II. Process conditions. J. Applied Electrochemistry, 20: 826-834.

Jialin Li, L. Liu, Y. Yua, Y. Tang and H. Li *et al*., 2004. Preparation of highly photocatalytic active nano-size TiO_2–Cu_2O particle composites with a novel electrochemical method. J. Electrochemistry Commun., 6: 940-943.

Li, X.Z. F.B., C.L. Yang and W.K. Ge, 2001. Photocatalytic activity of WOx-TiO_2 under visible light irradiation. J. Photochem. Photobiol. A Chem., 141: 209-217.

Musa, A.O., T. Akomolafe and M.J. Carter, 1998. Production of cuprous oxide, A solar cell material, by thermal oxidation and a study of its physical and electrical properties. Solar Energy Mater. Solar Cells, 51: 305-316.

Nikesh, V.V., A.B. Mandale, K.R. Patil and S. Mahamuni, 2005. X-ray photoelectron spectroscopic investigations of Cu_2O nanoparticles. Mater. Res. Bull., 40: 694-700.

Nikhil R.J., L. Gearheart and C.J. Murphy, 2001. Wet chemical synthesis of high aspect ratio cylindrical gold nanorods. Chem. Commun., pp: 617.

Noguet, C.M., Tapiero, C. Schwab, J.P. Zielinger and D. Trivich *et al*., 1979. Conversion photovoltaïque dans Cu_2O. Rev. Phys. Applied, 14: 231-236.

Ryszard Z., S. Ikeda, H. Nomura and S. Kato, 1988. Temperature dependence of adiabatic compressibility of aqueous solutions of alkyltrimethylammonium bromides. J. Chem. Soc. Faraday Trans., 1: 151-163.

Su-Yuan X., M. Zhi-Jie, W. Chun-Fang, L. Shui-Chao and J. Zhi-Yuan *et al*., 2004. Preparation and self-assembly of copper nanoparticles via discharge of copper rod electrodes in a surfactant solution: A combination of physical and chemical processes. J. Solid State Chemistry, 177: 3743-3747.

Ying, Y., D. Fei-Peng, C.Y. Jimmy, Z. Yuan-Yi and W. Po-Keung, 2004. One-dimensional shape-controlled preparation of porous Cu_2O nano-whiskers by using CTAB as a template. J. Solid State Chemistry, 177: 4640-4647.