PHOTOCATALYTIC ACTIVITY OF NANOSTRUCTURED COPPER (II) OXIDE PARTICLES

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ABSTRACT

Copper (II) Oxide nanostructured particles have been successfully synthesized by a simple wet chemistry method. The materials obtained were characterized and applied in photodegradation of methylene blue. The XRD pattern obtained reveals crystallinity with major peaks at 2 values 35.53°, 38.71° and 48.75° exhibiting cupric phase of the material with monoclinic lattice system. The average grain size of the particle was estimated using Scherrer formular to be 25.79 nm. The morphology of the materialas revealed by the SEM image shows coaleascence of grains as large island. Photocatalytic activity of the black coloured Copper (II) oxide was demonstrated on Methylene blue with photodegradation efficiency obtained to be 45.12 %.

Keywords: Semiconductor, Nanostructured, Photocatalytic, Morphology, Synthesis, XRD

INTRODUCTION

Copper oxides are semiconductors that have been studied for several reasons such as the natural abundance of starting material copper (Cu); the easiness of production by Cu oxidation; their non-toxic nature and the reasonably good electrical and optical properties. Copper forms two well-known oxides: tenorite (CuO) and cuprite (Cu_2O). Both the tenorite and cuprite were p-type semiconductors having band gap energy of 1.21 to 1.51 eV and 2.10 to 2.60 eV repectively. As a p-type semiconductor, conduction arises from the presence of holes in the valence band (VB). CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal emittance (Johan *et al.,*2011).

The p-type semiconductor of copper oxide (CuO) is an important functional material used for gas sensors, magnetic storage media, solar energy transformation, electronics, semiconductors, varistors, and catalysis. It has therefore been studied together with other copper oxides, especially with respect to its applications as a photothermally active and photoconductive compound. Thus, great efforts have been made to study the preparation of nanosized CuO in the past two decades. Conventional methods for the preparation of CuO powders include one-step solid-state reaction at room temperature, thermal decomposition of copper salts and mechanical milling of commercial powders. It is well known that the unique functions of semiconductor nanoparticles have led to the development of novel photovoltaic and light emitting devices. Thus, there is a renewed interest in understanding the fundamental physical properties of CuO, as well as for upgrading its performance in applications (Vidyasagar *et al.,* 2011).

Nanocrystalline semiconductor particles have drawn considerable interest in recent years because of their special properties such as a large surface to volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk materials. The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis. Among the oxides of transition metals, CuO has attracted much attention because it is the basis of several high-Temperature superconductors. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications. However, up till now, the reports on the preparation and characterization of nanocrystalline CuO are relatively few compared to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide (Wang *et al.*, 2002).

A challenging and strategic concern is actually the use of copper oxide based nanosystems for the direct photocatalytic splitting of water, an attractive solution to provide clean and recyclable H_2 energy in view of increased environmental concerns. Barreca *et al.* (2009) demonstrated for the first time that tailoring the system morphology by appropriate synthetic strategies is a key tool to achieve unprecedented performances of the CuO system in photo-activated H_2 generation even in the absence of TiO_2.

Vaseen *et al.* (2008) successfully synthesized nanostructured CuO by aqueous solution process, without the use of any complex apparatus and reagents, using copper nitrate, NaOH and ethylenetetramine. The detailed structural characterizations exhibited the nanocrystalline nature with monoclinic structure for the as-synthesized flower-shaped CuO nanostructures. Degradation of methylene blue was performed to investigate the photocatalytic activity of the as-grown flower-like nanostructures. The photocatalytic property in flower-shaped nanostructures was probably due to the recycling of Cu^{1+} ion under light on the CuO interface and large surface area of the flower-like moieties (Vaseen *et al.,* 2008).

Liu *et al.* (2012) have used different morphologies of CuO nanostructures for the photodecomposition of the pollutant rhodamine B (RhB) in water. The photocatalytic activity was correlated with the different nanostructures of CuO. The one dimensional (1D) CuO nanoribbons exhibit the best performance on the RhB photodecomposition because of the exposed high surface energy {_121} crystal plane. The photocatalytic results show that the high energy surface planes of the CuO nanostructures mostly affect the photocatalytic activity rather than the morphology of the CuO nanostructures. Their method of synthesis also shows that, it is possible to control the morphologies of nanostructures in a simple way.

Previous studies show that Cu_2O can act as photocatalyst to cause degradation of methylene blue. The mechanism was proposed to be due the formation of hydroxyl radical species (.OH) which resulted from the excited electrons being captured by the absorbed O_2 and the corresponding holes being trapped by the surface hydroxyl (Pan *et al.,* 2012).

In the present work, we present a very simple and effective method to synthesize good-quality particles of CuO nanostructures using simple aqueous solution method. The structural characterization and the photocatalytic activity of the CuO nanostructure particles was also evaluated by examining the degradation of methylene blue.

MATERIALS AND METHODS

Materials and Synthesis

Copper (II) Oxide nanostructured particles was prepared by putting Copper (II) acetate in Isopropanol alcohol with diethanolamine (DEA) mixed continously. A small amount of diethylene glycol was added into the solution. The resulting solution was mixed using magnetic stirrer for about 45 mins. The solution was then filtered using cellulose nitrate membrane 0.45 μm.

The nanoparticles were prepared by taking a good volume of the precursor put in a glass container and dried gradually until a good dried quantity was obtained. This was then taken to the furnace and annealed at 600°C for 1hour in air.

The particles obtained were analysed using X-ray diffractometer (XRD) to reveal the phase of the oxide formed and crystallinity of the material. Scanning Electron Microscope (SEM) image was obtained to show the morphology. UV-Visible spectrophotometer absorption measurements were taken inorder to monitor the photodegradation of the organic dye which in this work is Methylene Blue.

RESULTS AND DISCUSSION

Structural Properties of the Copper (II) Oxide Particles

(a) X-ray diffraction pattern of Copper Oxide particles

The crystal phases and crystalinity were analysed using X-ray diffractometer (XRD) measured with Cu-k radiation (= 1.54178 Å). Figure 1 shows the XRD patterns of the CuO product prepared and annealed at 600°C for 1 hour. This resulted in the crystallinity of the sample, seen as increased distinctive peak intensity in the diffraction pattern. The 2 value of the XRD peaks matched with the JCPDS 2 values corresponding to Copper (II) Oxide , indicating a successful synthesis of CuO with high purity. These results also show that the crystals have monoclinic structure and the average grain size estimated by the Scherrer's equation as 25.79 nm confirming the nanostructured property of the material.

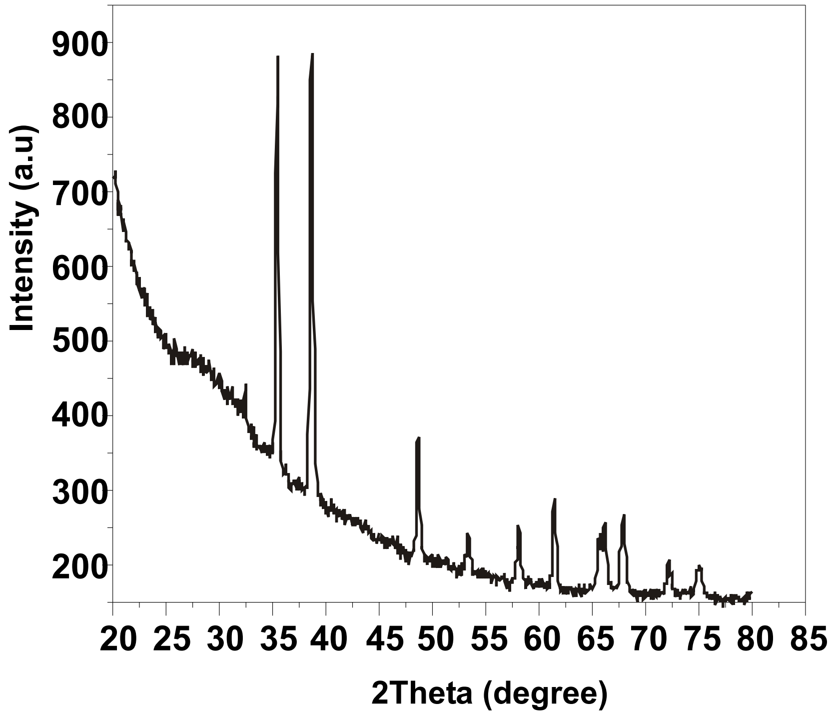

Figure 1: XRD Pattern of the Copper (II) Oxide Particle

The grain size was estimated from X-ray diffraction data using the Scherrer formula:

$$D \quad \frac{K}{FWHM \cos}$$

where K = Scherrer constant,
FWHM = full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern,
= wavelength of x-rays, and
= diffraction angle of x-rays

The Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.94. The size obtained from the Scherrer formula yields the apparent or average particle-size for a material. Powders of materials are generally aggregates of smaller particles, and thus consist of a distribution of particle sizes (Swaminathan and Iutzi, 2008).

(b) Morphology of the Copper (II) Oxide aggregated particles

Low magnification SEM images of CuO particles in figure 2 shows aggregates of granular grains. Morphology has special significance since it dictates physical and chemical properties. Unlike bulk materials, properties of nanomaterials are strongly correlated to shape. This shape is attained during growth through a self-assembling process dictated by the interplay of size and molecular interactions (Sanyal *et al.*, 2002). The heat treatment caused annealing and formation of larger grains by coalescence of the grains, thereby increasing the degree of crystalinity of the sample.

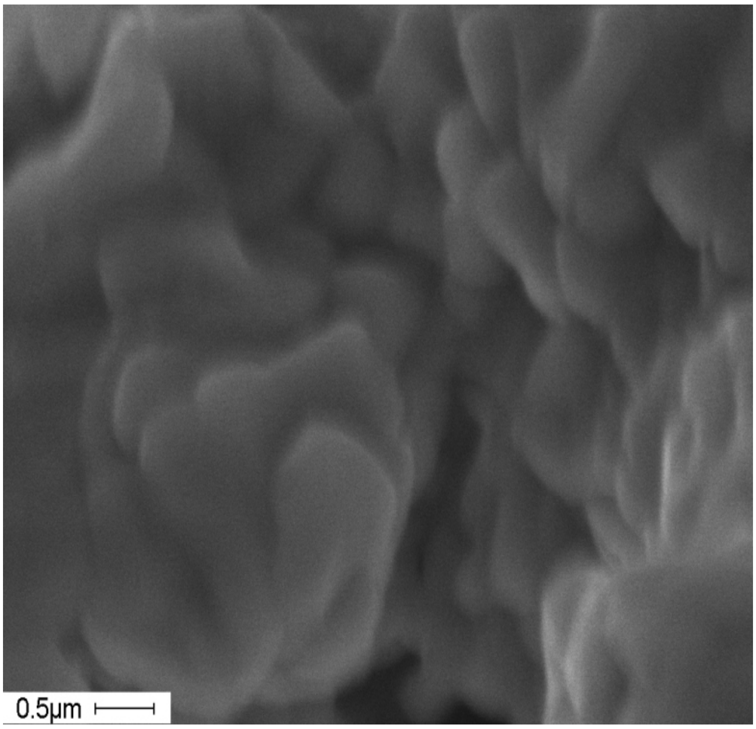

Figure 2: Low Magnification SEM Image of the CuO Particles Annealed at 600°C

(c) Photocatalytic Activity of Copper (II) Oxide Nanoparticles

Photocatalytic activity of Copper oxide was evaluated by monitoring the degradation of Methylene blue (MB) by UV-Visible spectrophotometer measuring the maximum absorption of MB as shown in figure 3 under visible light illumination, due to generated electrons/holes inducing a reaction to produce radicals, which reduce and decompose the organic dye.

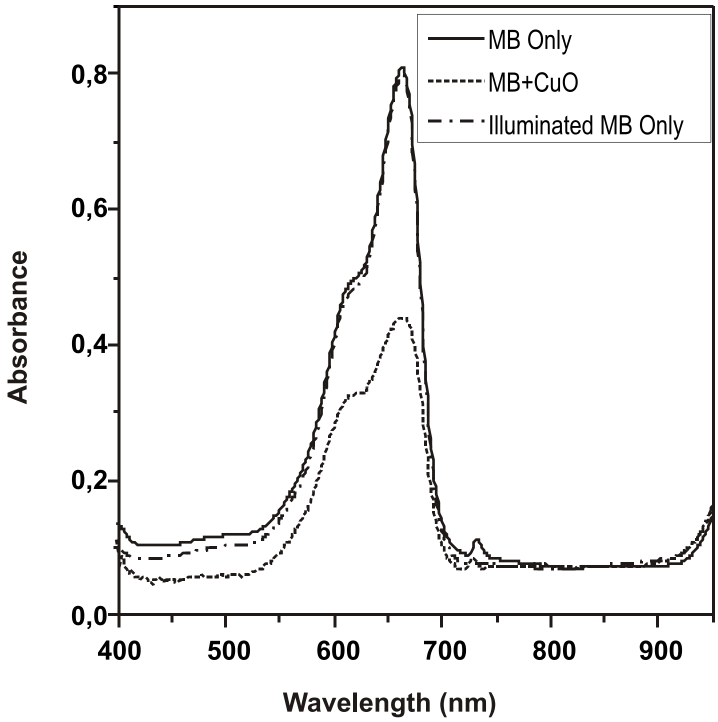

Figure 3: UV-Vis Spectra of Photodegraded Methylene Blue by photocatalyst CuO Nanoparticles after Illumination for 5mins

The photodegradation efficiency was calculated by the following formula:

$$\eta = \frac{A_0 - A_i}{A_0} X\ 100\%$$

Here A_0 was the initial absorbance of MB before reaction and A_i was the absorbance of the undegraded MB solution (Xiang *et al.*, 2010).

CONCLUSION

CuO nanostructured particles was successfully synthesized by aqueous solution process, (without the use of any complex apparatus and reagents), using Copper (II) acetate in Isopropanol alcohol with diethanolamine (DEA) and a small amount of diethylene glycol. Black Coloured Copper (II) Oxide Nanostructured particles were synthesized in cupric phase with monoclinic system. Diffraction peaks corresponding to CuO were observed for the particles at 35.53°, 38.71° and 48.75°. The detailed structural characterizations exhibited the nanocrystalline nature with monoclinic structure for the nanostructures. The average grain size of the particles is 25.79 nm.

Degradation of methylene blue was performed to investigate the photocatalytic activity of the nanostructured particles, which was observed to be very efficient. Photocatalytic degradation of MB was exhibited by CuO nanoparticles with photodegradation efficiency of 45.12 %.

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