Synthesis And Catalytic Properties of Single Facet Nano Cuo Prepared Via Soft Chemical Method

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ABSTRACT

Well faceted CuO nanocrystals, were fabricated by thermal-assisted green strategy at reflux temperature in a short period of time. A possible growth mechanism of such highly faceted nanostructures based on typical biomolecule-crystal interactions in aqueous solution is tentatively proposed. The large surface area and rich exposed active sites are expected to endow such nanostructures with excellent performances in catalysis as demonstrated here for the remarkable photocatalytic activity with respect to the oxidation organic dye (Methylene blue). This interesting result highlights the advantage of such a CuO nanostructure over the bulk counterpart, i.e. the high density of active sites and large surface area, which places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in photocatalysis. The synthesized material is characterized by XRD, IR, SEM, TEM, and DRS techniques. Their photocatalytic activities were determined by oxidative decomposition of Methylene blue in aqueous solution under visible light irradiation.

I. Introduction

Manipulation of size, shape, morphology and composition of technologically important photocatalytic materials, within the dimension of nanometers to micrometers, has been a great challenge for material scientists for the last few decades. Cu-based nanomaterials have been extensively studied due to their many potential applications. As a well-known p-type semiconductor with a narrow bandgap of 1.2 eV, CuO has been extensively studied because it is an important component of copper oxide superconductors.[1,2] With regard to its commercial value and interesting properties, CuO has also been widely exploited in a versatile range of applications such as catalysts,[3] magnetic storage media,[4] field emission devices,[5] gas sensors,[6] lithium batteries,[7] and solar cells. In particular, CuO was evaluated at one time as a possible alternative to precious metal catalysts such as platinum, palladium and rhodium for reactions involving H_2, such as the oxidation of CO and hydrocarbons, and the reduction of NOx in automobile exhaust systems. Other groups have reported the preparation of high purity, monodisperse nanocrystalline CuO using sonochemical preparation, microwave irradiation and precipitation-pyrolysis. Although great progresses have been made in the synthesis of CuO nanostructures, it remains a major challenge to develop a facile, one-step route for the synthesis of CuO architectures composed of nanoscale building blocks.[18]here we report, synthesis of CuO nanomaterial by the chemical decomposition under highly reducing condition using suitable reducing agent in the presence of starch as a stabilizing agent to prepare uniform nanomaterial. The photocatalytic efficiency of the prepared CuO nanomaterial was determined by oxidative decomposition ofMethylene blue in aqueous solution under visible light irradiation.

II. Experimental

A. Materials and measurements

All chemicals used in our experiments were reagent grade and used without further purification. The morphology and structure of products were determined by transmission electron microscopy(TEM) (Philips-CM200 TEM), X-ray diffraction (XRD) (XPERT-PRO) with Cu K radiation, Fourier transform infra-red spectrophotometer (BRUKER Model-Alpha) and UV-Visible diffuse reflectance spectrophotometer (ShimadzuUV-1800).

B. Synthesis of CuO Nanomaterial

CuO nanomaterial was prepared by decomposition of copper ammonia complex. The detailed experimental procedure was as follows. The copper ammonia complex solution prepared by adding 1 gm copper metal in10 ml of (27%) ammonia solution which forms the blue copper ammonia complex by consuming all the copper metal. This blue solution of copper ammonia complex was added in 100 ml of 0.25M $NaBH_4$ solution having 4 gm starch as a stabilizing agent. The above solution refluxed for 1 hour, during the reflux color of the solution changes from blue to colorless and then it turns slowly to brick red which indicates the formation of CuO

nanomaterial. The nanoparticle is then separate out by centrifuge at 3000 rpm and washing properly with plenty of water for the removal of unreacted chemicals.

C. Evaluation of photocatalytic activity

The photocatalytic activity of CuO Nano Material was evaluated by photodegradation of Methylene blue as a model pollutant. The selected nanomaterial was dispersed in the Methylene blue solution (2×10^{-5}M) to achieve a concentration of 20 mg/100 ml(the amount of the overall photocatalyst is same in every photo-degradation experiment). The mixed suspension was first stirred in dark for 1 h to reach the adsorption-desorption equilibrium of Methylene blue dye. A Philips lamp (40W/230V) was placed 10 cm away from the reaction vessel, which was used to provide a full-spectrum emission without any filter to simulate the sunlight source. The photocatalytic reaction was started by turning on the Philips lamp. 4ml of the aliquot was extracted at various irradiation times and centrifugated to remove the photocatalyst. The concentration of residual Methylene blue in the upper clear layer was determined by recording the maximum absorbance of Methylene blue at 663 nm with the UV-vis spectrophotometer.

III. Results and discussion

The X-ray diffraction analysis of products was carried out to identify the components of the products (Fig. 1). All diffraction peaks are indexed with the corresponding planes of CuO. No other peak due to possible impurities can be detected, which indicates that the products are of high purity. The XRD spectra showing the intense peak at 36.4 is having plane (111) which is the crystal plane of CuO. The low intensity peaks at 29.6 and 61.7 which match well with the plane (110), and (113). These are similar to those in the JCPDS File No.5-0661.

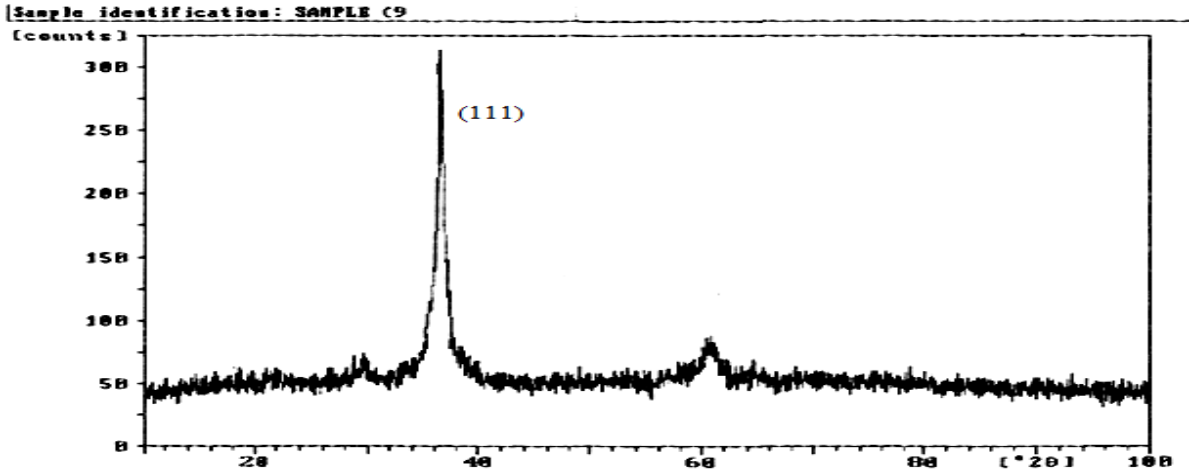

Fig. 1: XRD spectra of Prepared CuO nanoparticle.

The SEM [2a] and TEM [2b] images of the CuO nanoparticle were taken. The SEM images confirm the spherical morphology of CuO nanoparticles. High magnification images show that the small spherical structures are grown on the surface of the big spherical structures.

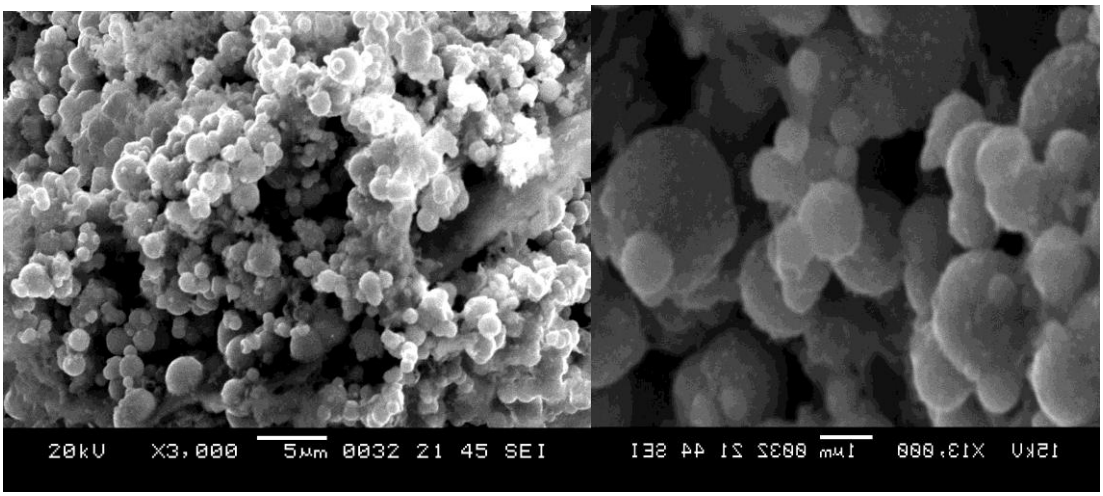

Fig.2 (a) SEM images of CuO nanoparticles Showing small spherical structures on the surface of bigeer one.

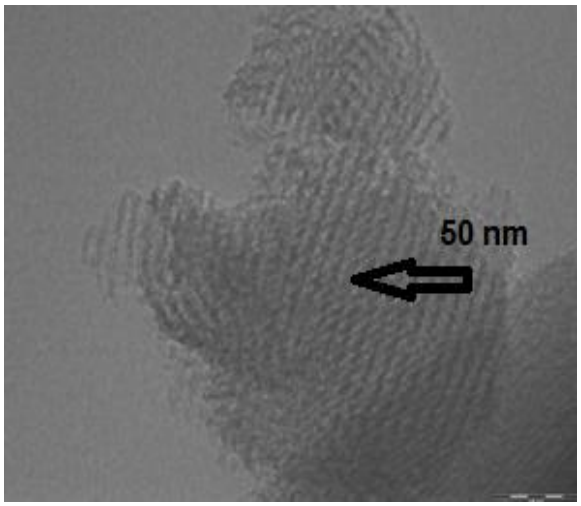

Fig.2(b): TEM images of CuO nanoparticles showing particles are well arrange with specific size.

The morphology of the prepared CuO is very interesting looking like pollen grain. The formation of small structures on bigger one may increase its surface area and indirectly the photocatalytic activity. From TEM image it is confirmed that the particle having size in between 50 to 80 nanometer agrees well with the XRD Analysis. TEM image confirmed the connectivity between the spheres which observed in SEM pictures. The morphological pictures observed in TEM and SEM analysis shows that the growth of particles is very well organized. The nuclei formation and growth of particles are simultaneously occur and hence it is observed that over the bigger particles the small particles are grown as like a secondary growth occur in biological system of flora. The control growth of particles may be due to the presence of starch molecules. In this study FT-IR spectrophotometric technique is used for understanding the role of the organic molecules. Figure 3 shows the IR spectra of pure starch and CuO nanoparticles coated with starch in the range of 400–4000 cm^{-1}. For pure starch (Fig. 3 [a]), the peaks in the range of 670–1000 cm^{-1} are attributed to the C–H bending vibration of –HC—CH– links. The two absorption peaks that appear at 1660 and 1163 cm^{-1} are due to the O–H bending and C–O stretching. The band observed between 3434 $cm^{-1}$is characteristic of O–H stretching vibrations. The peaks in the range 1300–1420 cm^{-1} are attributed to the C–H bending vibration of the –HC—CH– links of starch molecules. Comparing Figure 3[a] and [b], all the peaks in Figure 3[b] which is the IR spectra of CuO nanoparticle coated with starch as a stabilizer are weaker, the stretching vibration of O–H bands at 3434cm^{-1} gets weaker and the stretching band at 2926 cm^{-1} is discriminate in the spectrum of CuO coated with starch.

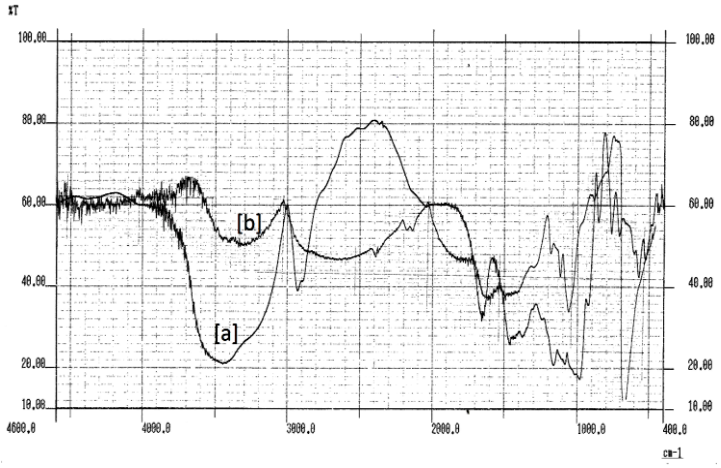

Fig. 3: [a] IR Spectra of pure starch [b] IR Spectra of CuO nanoparticle

The peaks in the range of 670-1000 cm^{-1} are attributed to C–H bending vibration of –HC—CH– links are shifted to higher wave numbers and some peaks disappeared in the spectrum of CuO coated with the surfactant. TheC-O stretching at 983.8 cm^{-1} which is characteristic of ether functional moiety is shifted to higher wave number at 1020.5cm^{-1}.There is sharp peak observed at 610 cm^{-1} in the spectrum CuO nanoparticles which is the characteristics of Cu-O bond formation. These dramatic differences indicate that there is chemical bonding could have been formed between starch and CuO nanoparticles.

The photoactivity of CuO nanomaterial was evaluated using methylene blue dye under visible light irradiation and the results are shown in Fig. 4. It can be seen that methylene blue was very stable under visible light irradiation without thecatalyst or over CuO nanomaterial in the dark. However, in the presence of CuO nanomaterial and light, the methylene blue degradation was enhanced. A control experiment showed that the absorption intensity of methylene blue gradually decreased withincreasing irradiation time without any shift of the absorption wavelength, suggesting a completecleavage of methylene bluechromophores. The total organic carbon(TOC) decreased 18.4% after 180 min visible light irradiation.

IV. Conclusion

Here we report the faceted CuO nanocrystals, were fabricated by thermal-assisted green strategy at reflux temperature and its photocatalytic performance is investigated. The experimental results indicate that faceted CuO nanocrystals exhibit a good photocatalytic performance. The photocatalytic performance is ascribed to the light absorption intensity and photoelectron-hole pair recombination. CuO nanocrystalscan be efficiently used for photocatalytic degradation of organic pollutant like methylene blue dye in aqueous medium under visible light source.

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