Synthesis and Characterisation of Nanostructured Cupric Oxide for Photocatalytic Applications

Etchu E. Mbu, David Dodoo-Arhin, Seteno K. Ntwampe, E. Nyankson and B. Agyei-Tuffor

***Abstract*— Being energetically sustainable, eco-compatible and resulting in the partial or total decomposition of pollutants, photocatalysis can be regarded as an appropriate wastewater treatment strategy. Here-in, we explore a simple, surfactant-free, cost effective synthesis route for nanostructured cupric oxide (CuO) and their subsequent characterisation towards photocatalytic application. The synthesised nanoparticles have been characterised using XRD, SEM, FTIR, UV-Vis and BET techniques. The particle sizes were calculated using Scherer's equation and found to range from 12 nm to 14 nm. Classical tauc plots from UV-Vis spectroscopy revealed optical bandgaps ranging from 2.12 eV to 2.4 eV. BET analysis showed surface areas ranging from 26.8 to 49.3 m^2/g. The synthesised CuO nanoparticles from these properties showed potential for visible light range photocatalysis**.

***Keywords*—** CuO, Nanoparticles, Photocatalysis, Semiconductor.

I. INTRODUCTION

Photocatalysis can be defined in simple terms as a phenomenon whereby a light source, supplies a system with photons of energy which are meant to activate a catalyst in a catalysis reaction. Such a catalyst is meant to enhance the rate of the reaction without being itself consumed during the entire reaction. Photosynthesis is a naturally occurring example of photocatalysis whereby chlorophyll acts as the photocatalyst, absorbing light for the plant to be able to make food of its own[1]. Every such reaction therefore has a minimum energy threshold (activation energy), required to get the catalyst functional.

In recent years, this phenomenon (photocatalysis) has been widely applied to wastewater treatment whereby organic pollutants such as dyes are released into the environment in wastewater from effluent of industries. Some of the reasons for the increasing interest in this method for application in wastewater treatment include: Its low energy requirements compared to those of conventional methods (such as thermal degradation for example) which have high energy requirements. This method can therefore be described as energetically sustainable[2].

It can be used in all three phases, i.e solid, liquid and gaseous phases of matter, offering pollutant treatment at source; thereby, degrading pollutants partially or completely into harmless / less harmful substances and minimising secondary waste/pollutant production while offering the possibility of recovery and even reuse (recycling) of the photocatalyst[2]. In most cases, one of its (photocatalysis) target sources of energy is clean solar energy, making it cost efficient and relatively eco-compatible (environmentally benign)[3].

Semiconductor photocatalysts have been widely applied in the degradation of organic pollutants. One of the reasons would be the fact that their energy bandgaps (minimum photon activation energy) can be tailored to suit a given application through methods such as doping[4]. However, some can be synthesised with bandgaps which are suitable enough for a given application. Given that the ease of activation of a semiconductor catalyst depends on the size of the activation barrier (bandgap energy) which needs to be overcome for an electron to be displaced into the reaction system, the smaller the barrier, the more feasible the reaction.

Given that in solution, the pollutant would need to adsorb as much as possible on the surface of the semiconductor, in making a choice for a semiconductor, surface area of the semiconductor should also be taken into consideration. In other words, a small bandgap energy and large surface area semiconductor would be a good pick for photocatalysis.

Some of the most commonly used semiconductor photocatalysts include TiO_2 [5], [6], SnO[7], [8], ZnO and Cu_2O[9] with more and more of CuO[8], [10] with time. This study examines the properties of CuO nanomaterials

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synthesised from two precursor salts with neither a metal base nor a surfactant for suitability in photocatalysis.

II. MATERIALS AND METHODS

A. *Reagents*

The reagents used during the study were of analytical grade. They included, hydrated copper nitrate ($Cu(NO_3)_2.3H_2O$) (Sigma-Aldrich Co., Germany), hydrated copper sulphate ($CuSO_4$. $5H_2O$) (Breckland Sc. Supplies, UK), sodium hydroxide (NaOH) (Qualikems Fine Cem Pvt Ltd, India) and ethanol (Fisher Scientific, UK). Deionised water was used throughout this study.

B. *Synthesis*

The CuO nanomaterials (N60, S60 and S25) [1] were precipitated using 1.6g/L of NaOH from 0.02M copper precursor solutions at 60 °C and 25 °C as represented in (1), (2) and (3).

$$Cu(NO_3)_2.3H_2O_{(aq)} + 2NaOH_{(s)} \xrightarrow[\blacktriangle]{60\ ^{\circ}C} CuO_{(s)} + 2NaNO_{3(aq)} + 4H_2O_{(l)} \quad (1)$$

$$CuSO_4.5H_2O_{(aq)} + 2NaOH_{(s)} \xrightarrow[\blacktriangle]{60\ ^{\circ}C} CuO_{(s)} + Na_2SO_{4(aq)} + 6H_2O_{(l)} \quad (2)$$

$$CuSO_4.5H_2O_{(aq)} + 2NaOH_{(s)} \xrightarrow[\blacktriangle]{25\ ^{\circ}C} CuO_{(s)} + Na_2SO_{4(aq)} + 6H_2O_{(l)} \quad (3)$$

The different precipitates were then centrifuged and washed with 50 % ethanol: 50 % deionised water. They were then oven dried at 70 °C, and a black CuO powder was recovered for characterisation.

C. *Characterisation*

X-Ray Diffraction (XRD) (X'Pert PRO X-Ray Diffractometer (PanAnalytical, the Netherlands), operating with Cu K-α radiation (wavelength of 1.544 Å) at 45 kV and 40 mA with a 20° - 70° 2θ range, a 0.2° step width scanning 1.2 deg/min on a 2 g sample), were employed to study CuO crystal properties. UV-Vis spectrophotometer with (Thermo Fisher Scientific, China) operating within a scanning range of 200 to 900 nm with a 5 nm scan step was used for absorbance on 3 ml samples. A Scanning Electron Microscope (SEM) – TESCAN with EDX analysis software (Performance in Nanospace, Czech Republic) operating at within 0.2 to 30 kV and $2x10^{-5}$ ms to 10 ms per pixel scanning speed on a 0.5 g sample, was used to study surface morphology. Fourier Transform Infra-Red Spectroscopy (FTIR) was performed using a PerkinElmer Spectrum Two spectrometer (PerkinElmer Inc., UK) with a 4000 to 400 cm^{-1} scanning range and 4 cm^{-1} resolution on a 0.1 g sample. Brunauer–Emmett–Teller (BET) surface area and porosity analysis were carried out using an ASAP 2020 V4.01 for CO_2 adsorptive analysis (Micrometrics, USA).

III. RESULTS AND DISCUSSION

A. *XRD*

The X-Ray Diffraction patterns recorded for all three samples were characteristic of CuO and are shown in Fig. 1 together with the preferred particle growth planes.

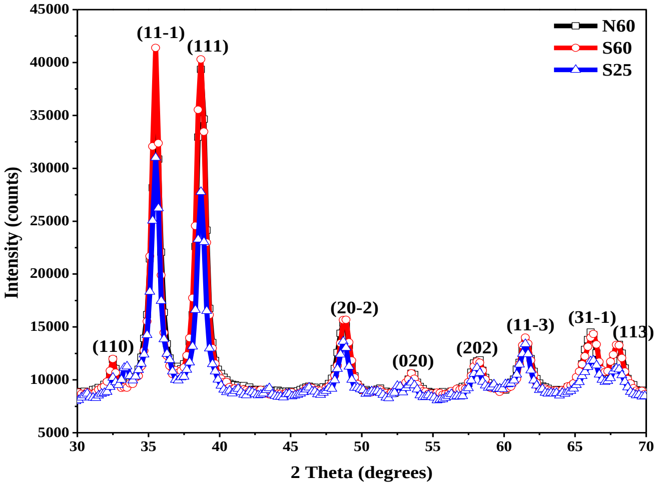

Fig. 1. XRD patterns of the synthesised CuO nanomaterials

These results confirmed that CuO nanoparticles were indeed synthesised. Scherrer's equation was us used to calculate crystal sizes for the various samples which were found to be 13.5 nm, 13 nm and 12 nm respectively, for S60, S25 and N60.

B. *Absorbance*

The absorbance values from the UV-Vis spectrophotometry are represented in Fig. 2. Using tauc plot calculations, the bandgap energies were calculated and found to range from 2.11 eV to 2.4 eV, increasing in the order S60 ~ S25 < N60. The trend followed the principle of the quantum size effect whereby bandgap increases with decreasing crystal size and vice versa[11], [12]. The bandgaps of the nanomaterials also suggested that the samples would likely absorb photons in the visible range of the EM Spectrum (EMS) (1.8 eV to 3.2 eV)

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[1] The letter N and S denote the precursor salt (nitrate or sulphate) from which the nanoparticles were synthesised while the numbers 60 and 25 denote the temperatures in degrees Celsius at which the nanoparticles were precipitated from solution.

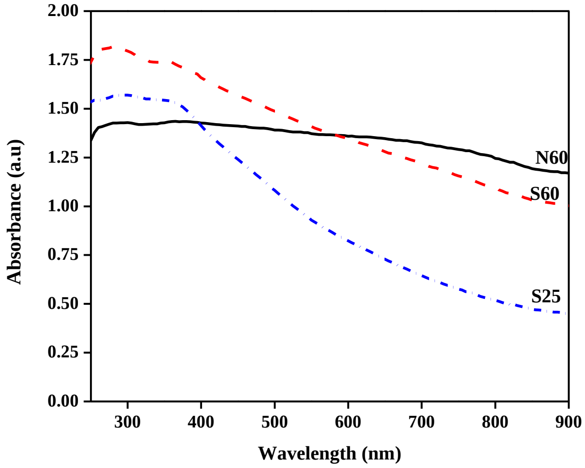

Fig. 2. Absorbance curves of the synthesized CuO nanomaterials

C. FTIR

FTIR was used to further to confirm the synthesis of CuO nanomaterials. Fig. 3 shows some of the characteristic peaks for CuO confirming the presence of the desired molecules.

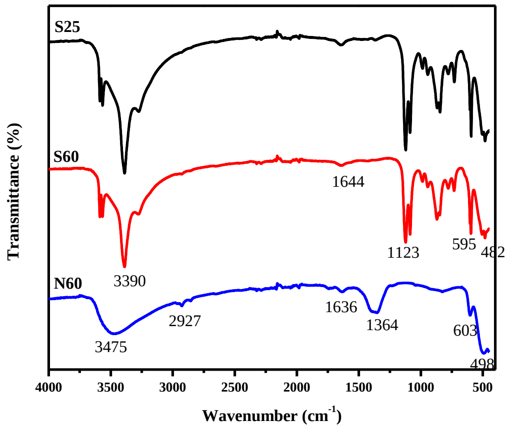

Fig. 3. Infra-Red absorbance peaks of synthesised CuO nanomaterials

D. SEM

Microscopy images were taken to observe the surface features of the synthesised CuO nanoparticles. Fig. 4 shows surface images of the three CuO nano samples. Mostly rough, the images reveal the presence of smaller hair-like features on the bold particle masses observed. This could imply enhancement of reaction surface area.

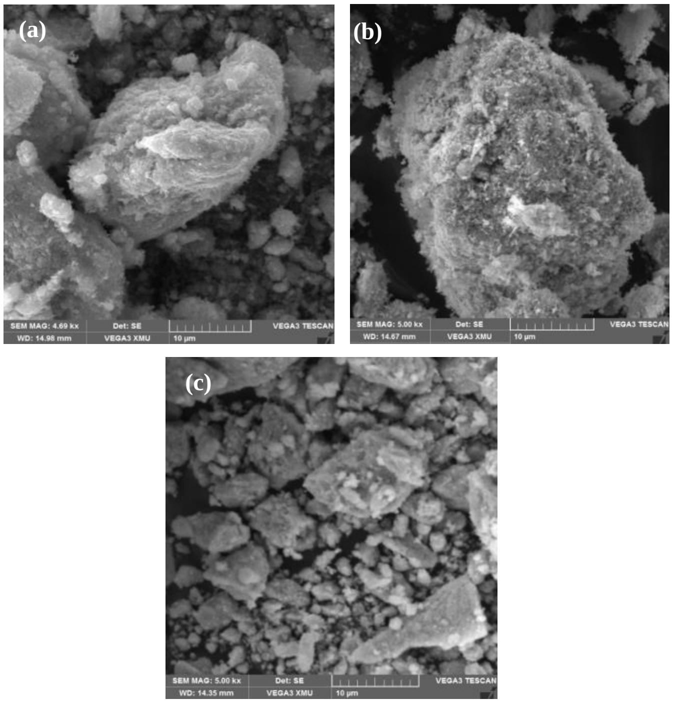

Fig. 4. SEM images of (a) S60, (b) S25 and (c) N60

E. BET

Surface area studies were carried out using a carbon dioxide (CO_2) adsorption isotherm system. Fig. 5 Shows the various profiles for the respective samples at low partial pressure values. According to the IUPAC classification scheme for adsorption isotherms, all samples show a characteristic Type I adsorption profile which is usually observed for adsorbents with micropores[13].

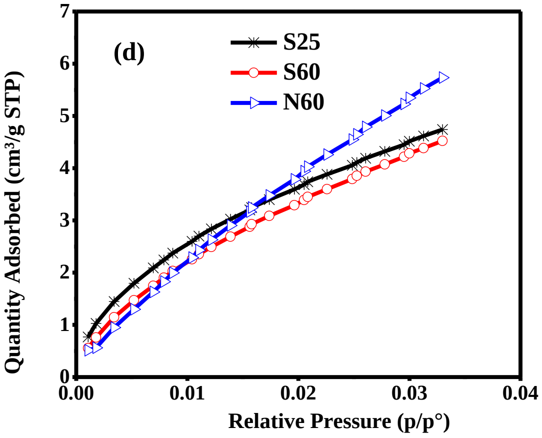

Fig. 5. Adsorption isotherms of the synthesized CuO nanomaterials

The BET analysis revealed that the samples had surface area values of 26.8 m^2/g, 28.4 m^2/g and 49.3 m^2/g respectively for S25, S60 and N60 with N60 having the highest surface area value as suggested by the adsorption isotherms in Fig 5. These values are relatively high compared to some of those observed

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in literature for CuO samples used in photocatalytic reactions. Zaman et al [14] recorded a maximum surface area of 8.4 m^2/g while Sasikala et al [7] recorded 1.82 m^2/g (for bare CuO) and 5.54 m^2/g (for cerium loaded CuO). Both cited results for surface area of CuO nanomaterials were several times lower than those recorded in this study, yet the authors were able to attain over 90 % organic material photodegradation after 5 hrs. The statistics would suggest that the CuO nanomaterials synthesised in this study could perform even better, both percentage and time wise. Therefore, the synthesised nanomaterials could be suitable for photocatalytic applications.

Fig. 6 shows another BET surface analysis plot for the synthesised CuO nanomaterials. A summary of the characterisation results is also shown in Table I.

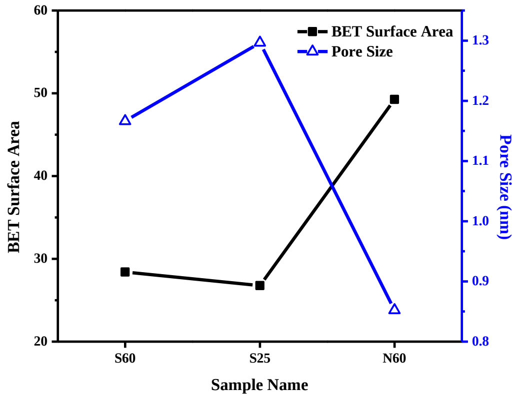

Fig. 6. Relationship between BET surface area and micro pore size for the synthesised CuO nanomaterials

TABLE I: SUMMARY OF CHARACTERIZATION RESULTS

Sample Name	Particle Size (nm)	Band Gap (eV)	BET Surface Area (m^2/g)	Micropore Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)
S60	13.5	2.12	28.4	110.9	1.2	0.0083
S25	13	2.11	26.8	91.7	1.3	0.0087
N60	12	2.4	49.3	206.9	0.9	0.0105

IV. CONCLUSION

CuO nanomaterials of different sizes were successfully synthesised from $Cu(NO_3)_2.3H_2O$ and $CuSO_4.5H_2O$ using a cost-efficient, eco-compatible method. The synthesised nanomaterials were characterised using XRD, FTIR, UV-Vis spectrophotometry, BET and SEM analysis. XRD, FTIR and UV-Vis spectrophotometry confirmed the presence of CuO nanomaterials while the UV-Vis spectrophotometric studies also revealed band gaps ranging from 2.11 eV to 2.14 eV. BET surface area analysis revealed that the nanomaterials had surface areas of 26.8 m^2/g, 28.4 m^2/g and 49.3 m^2/g which were relatively high compared to those observed in cited literature. The results above therefore strongly suggest that the synthesised nanomaterials could be suitable for photocatalytic applications.

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