Research Article

Morphology-Dependent Ullmann C-O Arylation Using Cu_2O Nanocrystals

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Five different copper-oxide nanocrystals were prepared by colloidal synthesis to form either cubic, octahedral, rhombic dodecahedral, truncated cubic, or fluffy sphere structures. These Cu-oxide nanocrystals were characterised using scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-vis. The SEM images show that the Cu_2O nanocrystals are relatively uniform and all the crystals have a particle mean diameter below 1000 nm. The smallest particle mean diameter is 411 nm for the rhombic dodecahedral crystals, while the octahedral crystal displays the largest particle mean diameter of 864 nm. The XPS results indicate that the copper is primarily Cu^{I} in Cu_2O , but some as Cu^{II} are also present. The apparent optical band gap energies could be determined from the optical properties of the five Cu-oxide nanocrystals, using the classical Tauc equation. The apparent optical band gap energies ranged between 2.04 and 2.14 eV. The Ullmann C-O coupling reaction was used to investigate the catalytic performance of the Cu-oxide nanocrystals. The fluffy sphere gave the highest % conversion, while the rhombic dodecahedral showed the lowest conversion.

1. Introduction

Aryl ethers are an important structural component since it is present in many pharmaceutical, polymers, dyes, pesticides, and fertilisers [1]. These aryl ethers can be prepared by catalytic arylation of phenols with aryl halides. Palladium is one of the possible metals used as a catalyst, but more commonly inexpensive copper(I) catalysts are used in the Ullmann coupling reaction. Organometallic Cu(I) catalysts are very active and selective to catalyse arylation reactions [2]; however the difficulty with homogeneous catalysts is separation and reusability. Therefore, heterogeneous copper-based catalysts are an appealing alternative. With the development of many new catalysts involving nanomaterials, the Ullmann coupling reactions have proven to be successful with supported and unsupported copper(I) nanoparticles [3–7]. The high catalytic activity towards the Ullmann coupling of N-H containing compounds with aryl halides and the stability of Cu_2O supported on graphene is attributed to the Cu_2O being highly dispersed on the graphene [8]. Cu_2O /graphene has also been

used to catalyse the Ullmann C-O crosscoupling of aryl halides and phenols under mild conditions [9]. Another stable Cu-containing catalyst successfully used for a variety of different crosscoupling reactions with broad functional group compatibility is chitosan@ Cu_2O [10], as well as Cu- $\text{Cu}_2\text{O}/\text{C}$ and CuO- $\text{Cu}_2\text{O}/\text{C}$ [11], prepared from the carbonisation of Cu-BTC-MOF under an N_2 atmosphere. There have also been some interesting reports on the environmentally friendly preparation of Cu-oxide nanoparticles for catalytic purposes, using *Euphorbia maculata* [12], *Convolvulus persicus* L. [13], and Gum Arabic [14].

However, due to structural complexity (variety of surface sites, with different crystal facets, steps, edge, planes, and corners) of nanoparticles, the investigation of morphological effects of the nanoparticles on their catalytic properties is impaired. Nanocrystals, on the contrary, have a uniform and well-defined morphology. In particular, Cu_2O (Cu^{I}) micro- and nanocrystals have a wide variety of different structures with well-defined morphologies like cubes, rhombic dodecahedral, octahedron, concave cube, sphere, stars,

etc. [15–18]. It has been reported that Cu_2O nanocubes were successfully employed in the crosscoupling reaction of aryl halides and phenols [19].

This inspired the investigation into the influence of well-defined morphology Cu-oxide nanocrystals on the Ullmann C-O coupling reaction. Herein, we report the preparation of five Cu-oxide nanocrystals with different morphologies. Their spectroscopic properties are investigated, and along with the morphology, it is related to their catalytic activity towards the Ullmann C-O arylation reaction.

2. Materials and Methods

2.1. Materials and General Procedures. Solid and liquid reagents used in preparations were purchased from Sigma-Aldrich (used without purification). UniLAB-grade solvents were purchased from Merck. Double-distilled water was used where necessary. XPS data was recorded on a PHI 5000 VersaProbe system, with a monochromatic Al $K\alpha$ X-ray source. The surface morphology and the elementary composition were investigated using a Shimadzu Superscan ZU SSX-550 electron microscope (SEM) coupled with an energy-dispersive X-ray spectroscope (EDS). UV-vis characterisation of the Cu-oxide nanocrystals in suspension was measured on an Olis CLARITY CCD UV-vis spectroscopic system.

2.2. Catalyst Preparation

2.2.1. Perfect Cubes (PC). CuCl_2 (1.365 g) was dissolved in 100 ml H_2O and heated to 60°C . A NaOH (4 g in 20 ml H_2O) solution was added dropwise to the CuCl_2 . After 20 min stirring, the solution turned black. A D-(+)-glucose (1.8 g in 30 ml H_2O) solution was slowly added, and the mixture was stirred for a further 30 min. The nanocrystals were isolated by centrifugation, followed by washing with water and again centrifuged. The crystals were dried overnight under vacuum at 60°C .

2.2.2. Octahedral (Oct) [20]. $\text{Cu}(\text{CH}_3\text{COO})_2$ (2 g) was dissolved in 80 ml H_2O and heated to 70°C . A NaOH (1.4 g in 10 ml H_2O) solution was added dropwise to the Cu solution (the solution turned black). A D-(+)-glucose (1.8 g in 10 ml H_2O) solution was slowly added, and the mixture was stirred for a further 60 min at 70°C (solution turned red-brown). The nanocrystals were isolated by centrifugation, followed by washing with water and again centrifuged. The crystals were dried overnight under vacuum at 60°C .

2.2.3. Rhombic Dodecahedral (RD) [21]. CuSO_4 (3 g) was dissolved in 150 ml H_2O and heated to 100°C . Oleic acid (48 ml) dissolved in 240 ml EtOH was added dropwise while stirring. A NaOH (3.2 g in 30 ml H_2O) solution was added dropwise to the Cu solution and stirred for 5 min. A D-(+)-glucose (141 g in 70 ml H_2O) solution was slowly added, and the mixture was stirred for a further 90 min at 100°C . The nanocrystals were isolated by centrifugation, followed by washing with water and again centrifuged. The crystals were dried overnight under vacuum at 60°C .

2.2.4. Truncated Cubic (TC). CuCl_2 (298 mg, 2.2 mmol) was dissolved in 175 ml water. This solution was heated to 55°C , and 17.5 ml of a 2 M NaOH solution was added dropwise. The solution was stirred for a further 30 min at 55°C , followed by the dropwise addition of 17.5 ml of 0.6 M ascorbic acid. The solution was stirred for a further 5 h at 55°C . The precipitate was filtered and washed with water.

2.2.5. Fluffy Spheres (FS). CuCl_2 (600 mg) was dissolved in 320 ml H_2O and heated to 40°C . A NaOH (2.8 g in 30 ml H_2O) solution was added dropwise to the CuCl_2 . After 30 min stirring, the solution turned black. A D-(+)-glucose (3.75 g in 50 ml H_2O) solution was slowly added, and the mixture was stirred for a further 5 h at 55°C . The nanocrystals were isolated by centrifugation, followed by washing with water and again centrifuged. The crystals were dried overnight under vacuum at 60°C .

2.3. Catalytic Reaction. All catalytic reactions were conducted in a PARR preparation vessel (sealed stainless-steel reaction vessel) lined with a Teflon cup. A mixture of iodobenzene (14 mmol; 1.6 ml), phenol (14 mmol; 1.3 g), Cs_2CO_3 (14 mmol; 9.1 g), THF (10 ml), and the Cu-oxide catalyst (5 mg) was loaded in the reaction vessel and degassed with N_2 for 1 min. The reaction vessel was placed in an oven at 150°C for 2 h. After cooling, the catalyst was removed by centrifugation, the reaction mixture was poured into a saturated solution of aqueous NaHCO_3 (20 ml), and the product was extracted with DCM. A ^1H NMR of the crude product was recorded, and the conversion was determined from the ratio between the starting materials and the product.

3. Results and Discussion

Five different nanocrystals/nanoparticles, namely, cubic (PC), octahedral (Oct), rhombic dodecahedral (RD), truncated cubic (TC), and fluffy spherical (FS) structures, were prepared by established colloidal synthesis using D-(+)-glucose, ascorbic acid, or oleic acid as the structure-directing agent. The hybrid morphological features of these Cu-oxide nanocrystals could be determined from the scanning electron microscopy (SEM) images (see Figure 1). The particle size distribution of each morphology Cu-oxide nanocrystal was shown by the histogram provided in the supplementary information, while the average particle size and statistics are presented in Table 1.

The optical properties of the five Cu-oxide nanocrystals were measured with a CLARITY UV-vis spectrophotometer (which is immune to light scattering). The UV-visible spectra of all the Cu-oxide nanocrystals suspended in water exhibited an increase in light absorption between 250 and 600 nm (see Figure 2). Similar broad absorption peaks have been reported for cubic Cu-oxide suspended in ethanol [22], other Cu-oxide nanoparticles [23], and Cu-oxide thin films [24].

The broad absorption peaks observed for the five Cu-oxide nanocrystals, in the short wavelength area, are related to the intrinsic band gap energy of Cu-oxide. The apparent band gap energy, E_g' , of the Cu-oxide nanocrystals was

FIGURE 1: The SEM images of the (a) cubic, (b) octahedral, (c) rhombic dodecahedral, (d) truncated cubic, and (e) fluffy spherical structures.

TABLE 1: Mean, minimum, and maximum diameter (in nm) as well as the standard deviation of the particles as measured from the TEM images of the five Cu-oxide nanocrystals.

Morphology	Mean (nm)	Minimum (nm)	Maximum (nm)	Standard deviation (nm)
PC	701	599	867	72
Oct	864	665	1067	107
RD	411	222	783	147
TC	834	398	1333	230
FS	427	166	786	103

determined using the classical Tauc equation (the term apparent is used since this is not a thin film but nanocrystals):

$$\alpha E_p = K(E_p - E_g)^{1/2}, \quad (1)$$

where α is the absorption coefficient ($\alpha = \ln(T/d)$, where T is the transmission and d is the thickness; average edge length was used in this case), K is a constant, E_p is the photon energy

($E_p = hc/\lambda$, where h is Planck's constant and c is the speed of light), and E_g is the band gap energy. The extrapolate value (E_p at $\alpha = 0$) of the straight line to the x -axis of the graph of $(\alpha E_p)^2$ versus E_p represents the apparent band gap energy. The Tauc plots of all Cu-oxide nanocrystals are shown in the Supplementary Information, and the apparent band gap energy, E_g' , of all five Cu-oxide nanocrystals is presented in Figure 2.

X-ray photoelectron spectroscopy (XPS) was used to determine the atomic composition and oxidation state of the copper as well as the ratio of the different atomic species present on the surface of the nanocrystals. The wide scan spectra showing all the elements present (C, O, and Cu) of the truncated cube Cu-oxide nanocrystal (as an example) is given in the Supplementary Information (Figure S6). All these photoelectron lines were charge corrected by shifting the spectra so the lowest binding energy of the simulated adventitious carbon C 1s photoelectron line is set at 284.8 eV. The O 1s oxygen peak of the Cu-oxide nanocrystals was located at ca. 531.6 eV, which is in good correlation with what is reported in the literature (531.57 eV) [26].

FIGURE 2: The UV-visible spectra of the Cu-oxide (2.5 mg/9 ml water) of (a) perfect cubic (PC), (b) octahedral (Oct), (c) rhombic dodecahedral (RD), (d) truncated cubic (TC), and (e) fluffy spherical (FS), structures, as well as a table indicating the apparent band gap energy E_g' .

The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ photoelectron envelope of the Cu-oxide nanocrystals gave sharp well-defined peaks. These photoelectron envelopes were simulated with two Gaussian peaks with a full width at half-maximum (fwhm) of ~ 2.0 eV (see Figure 3). The spin-orbit splitting between the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ photoelectron lines were ca. 19.9 eV, with small shake-up features at ca. 10–12 eV higher than the main photoelectron lines. These shake-up features typically correspond to the presence of Cu^{II}.

The simulated Cu $2p_{3/2}$ and Cu $2p_{1/2}$ photoelectron lines at ca. 932.8 and 952.7 eV are assigned to Cu^I in Cu₂O. This is in correlation to published values of 932.5 eV [25–28], while the main Cu $2p_{3/2}$ and Cu $2p_{1/2}$ photoelectron lines at ca. 934.8 and 954.8 eV, as well as the satellite structures at 941.8, 944.0, and 962.9 eV, are attributed to the presence of Cu^{II}, which can be either CuO or Cu(OH)₂. According to literature, CuO is usually present at 933.6 eV while Cu(OH)₂ is at 934.8 eV [25, 26, 29]. Thus, in our case, it would seem that the Cu^{II} is present as Cu(OH)₂, but will only be referred to as Cu^{II}. The ratio between the Cu^I in Cu₂O and Cu^{II} could be determined from the atomic % (see Table 2). In all cases, the Cu^I content is more than 70%.

Even though the Cu-oxide nanocrystals are more than 70% present in the Cu^I state, there are marked differences between the binding energies of the Cu^I $2p_{3/2}$ photoelectron lines of the Cu-oxide nanocrystals. This is probably due to a combination of the included difference in the chemical environment interaction of the different crystal facets present on the surface of the Cu-oxide nanocrystals and the % Cu^{II} present in the sample.

The catalytic performance of the five Cu-oxide nanocrystals was tested for the Ullmann coupling of phenol and an aryl halide to form an aryl ether (see Figure 4). The

FIGURE 3: Comparative XPS spectra showing simulated peak fittings for the main and satellite peaks of the Cu $2p_{3/2}$ and $2p_{1/2}$ photoelectron lines of all the Cu-oxide nanocrystals: (a) perfect cubic (PC), (b) octahedral (Oct), (c) rhombic dodecahedral (RD), (d) truncated cubic (TC), and (e) fluffy spherical (FS) structures.

octahedral-shaped Cu-oxide nanocrystal was used to investigate the effect of different reaction conditions such as the base, atmosphere, and aryl halide to be used, and the results can be seen in Table 3. A small but notable increase in % conversion from 48% to 54% was observed when using Cs₂CO₃ as a base during the Ullmann coupling instead of *t*-BuOK when the reaction was conducted in air (entries 1 and 2). However, when the atmosphere of the reaction was changed from normal air to Ar, the % conversion increased to 69%

TABLE 2: The binding energies of the O 1s, Cu^I 2p_{3/2}, Cu^{II} 2p_{3/2}, Cu^{II} sat₁, Cu^{II} sat₂, Cu^{II} sat₃, photoelectron lines, and Cu LMM Auger lines as well as the % ratio presence of Cu^I:Cu^{II} and the modified Auger parameter (Auger_{para}).

	O 1s (eV)	Cu ^I 2p _{3/2} (eV)	Cu ^{II} 2p _{3/2} (eV)	Ratio % Cu ^I :Cu ^{II}	Cu ^{II} sat ₁ (eV)	Cu ^{II} sat ₂ (eV)	Cu ^{II} sat ₃ (eV)	Cu LMM (eV)	Auger _{para} (eV)
PC	532.0	932.9	935.1	85.7	943.6	945.7	963.7	570.0	1849.60
Oct	531.9	933.0	935.1	70.1	942.1	944.6	963.0	570.2	1849.51
RD	531.0	933.0	934.1	82.7	943.2	945.0	964.4	570.0	1849.78
TC	531.7	932.7	934.9	77.3	941.2	944.3	963.6	569.9	1849.46
FS	531.7	932.6	934.8	79.4	942.4	944.4	963.2	569.8	1849.53

FIGURE 4: Reaction conditions used for the Ullmann coupling reaction.

(entries 1 and 5). The type of aryl halide used is a significant factor for the % conversion obtained for the Ullmann coupling. Under the same reaction conditions, the % conversion increased from 8.4 to 16 to 69% when changing the aryl halide from X=Cl to Br to I, respectively (entries 3, 4, and 5). Thus, electrons withdrawn by the halides have a negative influence on the % conversion.

The main purpose of this study is to investigate the effect of the different morphologies and their other physical properties of Cu-oxide nanocrystals on the % conversion of phenol and aryl halide to form aryl ethers during the Ullmann coupling. From entries 5 to 9 in Table 3, it is clear that the different morphologies have a remarkable influence on the catalytic performance of the Cu-oxide, with the % conversion ranging between 63 and 91%. The catalytic performance in the order of % conversion is as follows: FS > TC > PC > Oct > RD.

The fluffy sphere Cu-oxide nanocatalyst does not have a defined facet exposed to the surface; thus, it seems that the more defects the particle has, the higher the catalytic conversion. As for the other four Cu-oxide nanocrystals, they all have well-defined morphologies with defined facets exposed to the surface. The truncated cubic Cu-oxide nanocrystals, which gave the second-best conversion, are enclosed by {100} facets on the basal planes, {110} facets on the edges, and {111} facets located on the corners. This again shows that the more facets and edges connecting the different facets, which could potentially have many defects, the higher the conversion. Comparing PC, Oct, and RD, they are all enclosed by a single facet, namely, {100} for PC, {111} for Oct, and {110} for RD. From this, it can be deduced that the order of reactivity for facets of Cu-oxide for the Ullmann reaction is {100} > {111} > {110}.

No trend could be established when comparing the % conversion with the particle mean diameter. In this investigation, it would seem that the size of the particles does influence the catalytic performance of the different Cu-oxide nanocrystals.

An inversely proportional relationship exists between the % conversion of the Ullmann coupling and the binding energy of the Cu^I 2p_{3/2} photoelectron line of the different Cu-oxide nanocrystals (Figure 5(a)). Increased binding energy (of an element with the same oxidation state) is associated with an increase in an electron-withdrawing environment that the element experiences. Increased binding energy implies that the element (in this case, Cu^I) binds more tightly to its electrons, making it more difficult for an electron to be emitted. It can be assumed that the more difficult it is to emit an electron, the more difficult it would also be to “free” an electron to take part in the catalytic reaction, hence the decrease in % conversion associated with the increased binding energy.

An inversely proportional relationship was also established between the % conversion of the Ullmann coupling and the apparent band gap energy of the different Cu-oxide nanocrystals. Band gap is the energy difference between the valence band of electrons and the conduction band, and it also represents the minimum amount of energy required to excite an electron to a state in the conduction band. This means that a smaller band gap is associated with electrons that can be excited to a state where they are freer to either be conducting or take place in a catalytic reaction. Thus, explaining the increase % conversion seen with Cu-oxide nanocrystals with smaller band gap energies.

A plot of the binding energy of the Cu^I 2p_{3/2} photoelectron line and the apparent band gap energy of the different Cu-oxide nanocrystals is presented as a directly proportional relationship. This affirms that as the band gap energy increases, the more difficult it becomes to emit an electron. An increase in both entities implies an enhanced degree of difficulty for an electron to be “released” or become available for another purpose.

4. Conclusion

Cu-oxide nanocrystals with different morphologies (cubic, octahedral, rhombic dodecahedral, truncated cubic, and fluffy spheres) were prepared by colloidal synthesis. SEM images confirmed the morphologies, and the mean particle size and size distribution could be determined. From XPS studies, it was concluded that >70% of the Cu is present in the I oxidation state, while the remainder is Cu^{II}, most probably as Cu(OH)₂. A broad absorption peak in the short wavelength region was observed in the UV-vis spectra for the five Cu-oxide nanocrystals, which is related to the intrinsic band

TABLE 3: Catalytic performance of the five different Cu-oxide nanocrystals as catalysts for the Ullmann C-O crosscoupling of phenol with aryl halides.

	Cu-oxide nanocrystal	Atmosphere	Base	Aryl halide	% conversion	Cu ^I 2p _{3/2} (eV)	E _g ['] (eV)	Mean (nm)
1	Oct	Air	<i>t</i> -BuOK	I-Ph	48	933.0	2.11	864
2	Oct	Air	Cs ₂ CO ₃	I-Ph	54	933.0	2.11	864
3	Oct	Ar	Cs ₂ CO ₃	Cl-Ph	8	933.0	2.11	864
4	Oct	Ar	Cs ₂ CO ₃	Br-Ph	16	933.0	2.11	864
5	Oct	Ar	Cs ₂ CO ₃	I-Ph	69	933.0	2.11	864
6	PC	Ar	Cs ₂ CO ₃	I-Ph	79	932.9	2.13	701
7	RD	Ar	Cs ₂ CO ₃	I-Ph	63	933.0	2.14	411
8	TC	Ar	Cs ₂ CO ₃	I-Ph	85	932.7	2.07	834
9	FS	Ar	Cs ₂ CO ₃	I-Ph	91	932.2	2.04	427

FIGURE 5: Relationship between the % conversion of the Ullmann coupling and (a) the binding energy of the Cu^I 2p_{3/2} photoelectron line, (b) the apparent band gap energy of the different Cu-oxide nanocrystals, and (c) the correlation between the binding energy of the Cu^I 2p_{3/2} photoelectron line and the apparent band gap energy of the different Cu-oxide nanocrystals.

gap energy of Cu-oxide. The apparent band gap energy was determined from the Tauc plots, using the average edge length of the particles instead of film thickness (which is normally used). The band gap energies ranged between 2.04 and 2.14 eV, which is lower than the direct band gap of 2.17 eV. During the catalytic performance investigation of the Ullmann C-O arylation, it was found that fluffy spheres gave the highest % conversion, while the rhombic dodecahedral showed the lowest conversion. It was found that the mean particle size diameter does not show any correlation to the catalytic performance, thus implying that the morphology/facet and defects are important during catalysis. There was, however, a positive correlation between the catalytic performance and the ease with which valence and core electrons can be released.

Data Availability

The supplementary information data used to support the findings of this study have been submitted to Data in Brief.

Conflicts of Interest

The author declares that there is no conflict of interest.

Acknowledgments

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Supplementary Materials

Figure S1: the particle diameter (ϕ) histograms of the (A) cubic, (B) octahedral, (C) rhombic dodecahedral, (D) truncated cubic, and (E) fluffy spherical structures. Figure S2: the Tauc plot of the Cu-oxide nanocrystals used to determine the apparent band gap energy, E_g['] of cubic (TC), octahedral (Oct), rhombic dodecahedral (RD), truncated cubic (TC), and fluffy spherical (FS) structures. Figure S3: XPS wide scan of the truncated cube Cu-oxide nanocrystal. Graphical abstract of the manuscript. (*Supplementary Materials*)

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