# Green Chemistry

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## Journal Name

## ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x www.rsc.org/



Prince N. Amaniampong, <sup>a,#</sup> Quang Thang Trinh,<sup>b,#</sup> Jithin John Varghese,<sup>b</sup> Ronan Behling,<sup>c</sup> Sabine Valange,<sup>c</sup> Samir H. Mushrif,<sup>d,e\*</sup> Francois Jerome<sup>a,c\*</sup>

Correspondence to: FJ email: francois.jerome@univ-poitiers.fr; SHM email: SHMushrif@ntu.edu.sg

The utilization of low frequency ultrasound (US) offers a straightforward and powerful tool for the production of nanostructured materials, in particular for structurally stable, highly crystalline, and shape-controlled catalytic materials. Herein, we report an unconventional strategy for the synthesis CuO nanoleaves within 5 min of US irradiation time. The asobtained CuO nanoleaves were found to be selective in the base-free aqueous oxidation of glycerol to dicarboxylic acids (78% yield in tartronic and oxalic acids), in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and under mild reaction conditions. Density Functional Theory (DFT) investigations revealed a synergy between the CuO catalyst and H<sub>2</sub>O<sub>2</sub> in maintaining the structural integrity of the catalyst during the reaction, creating alternative efficient pathways for the selective formation of dicarboxylic acids. Isotope labeling experiments using H<sub>2</sub><sup>18</sup>O<sub>2</sub> further confirmed that oxygen from hydrogen peroxide, not from CuO, was preferentially incorporated into the dicarboxylic acid, significantly preserving the monoclinic structure of the CuO catalyst.

## INTRODUCTION

The utilization of biomass for the production of renewable platform chemicals and fuels has become an important topic aiming at accelerating the transition of our society into a more sustainable development.<sup>1-5</sup> Among bio-based chemicals, glycerol, the main co-product of the vegetable oil industry, has attracted growing interest from the catalysis community.<sup>6-14</sup> A number of homogeneous and heterogeneous catalysts have been investigated to convert glycerol to value-added chemicals such as glyceric acid, lactic acid, propanediols, dihydroxyacetone, acrolein, among others.<sup>15-20</sup> In some investigations, high yields of methanol from crude glycerol to value solver also reported.<sup>21</sup> However, the conversion of glycerol to

valuable dicarboxylic acids, particularly oxalic (OXA) and tartronic acids (TAR), has been less thoroughly investigated. Beside their promising utilization in the synthesis of renewable polymers,<sup>22, 23</sup> these two dicarboxylic acids are also employed for the extraction of rare earths from monazite, celluloid production, leather manufacturing<sup>24</sup> and for the synthesis of pharmaceutical intermediates.<sup>25-27</sup> World market for OXA rose steadily at an annual rate of 3.15% from the year 2001 and the consumption reached 278 thousand tons by the year 2010, as stated in a report published by Global Industry Analysts, Inc.<sup>28</sup> Particularly, the largest market for OXA is in Asia with an annual growth rate of ~10% from 2012 to 2016. On the other hand, applications of TAR as a high value-added chemical in pharmaceutical disorder treatments such as osteoporosis and obesity or in food industry as an anticorrosive and protective agent are currently hindered due to the high cost of this chemical (1564 US\$/g),<sup>29</sup> and therefore the development of less expensive and greener methods to produce TAR is desired (see SI, section 16).

Oxidation of glycerol has been shown achievable over several noble metals, with Pt, Pd and Au being the most investigated catalysts.<sup>19, 30-32</sup> Particularly, these noble metals supported on graphite, MgO,<sup>33</sup> TiO<sub>2</sub><sup>30, 34</sup> and carbon nanotube (CNT)<sup>35</sup> have been documented to display high catalytic activity in the presence of molecular oxygen (T: 30-80°C, 0.1-0.8 MPa O<sub>2</sub>, 2-4 pH), either under mild acidic or basic reaction conditions, with glyceric acid often obtained as the prime product (Selectivity:

<sup>&</sup>lt;sup>a.</sup> INCREASE (FR CNRS 3707), Université de Poitiers, ENSIP, 1 rue Marcel Doré, TSA41105, 86073 Poitiers Cedex 9, France

<sup>&</sup>lt;sup>b.</sup> Cambridge Centre for Advanced Research and Education in Singapore (CARES), Campus for Research Excellence and Technological Enterprise (CREATE), 1 Create Way, Singapore 138602, Singapore.

<sup>&</sup>lt;sup>c</sup> Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Université de Poitiers,

<sup>&</sup>lt;sup>d</sup> School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore.

Department of Chemical and Materials Engineering, University of Alberta, 9211-116 St NW, Edmonton, Alberta T6G1H9, Canada.

<sup>&</sup>lt;sup>#</sup>Authors contributed equally

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

#### ARTICLE

30- 100 %) along with glycolic acid, lactic acid, dihydroxyacetone as co-products.<sup>33, 35</sup> In some reports, bimetallic<sup>33, 34, 36, 37</sup> and trimetallic<sup>38</sup> noble metals were employed for glycerol oxidation reactions, with the aim of improving the catalyst activity, stability and product selectivity. Unfortunately, in most of the reported studies, dicarboxylic acids such as TAR and OXA are formed in relatively low yields (< 20 %). Very recently, Jin et al reported encouraging yields of TAR (64 %) and OXA (24%) from glycerol, in the presence of molecular oxygen, using cobalt-based catalyst with specific activity depending on the catalyst preparation method.<sup>39</sup> Improved yield to TAR has been achieved over Au/HY (yield: 72%)<sup>27</sup> and bismuth-promoted Pd/Carbon-support (yield: 79%)<sup>40</sup> The use of non-precious supported-copper based catalysts has also been attempted in the one-pot transformation of glycerol, albeit with lower selectivity towards TAR and OXA (total dicarboxylic acids yield < 10 %).<sup>41,</sup> <sup>42</sup> Interestingly, layered double hydroxides (LDH) hosted transition metal complexes (LDH-[MnSO3-salphen]) have been shown to exhibit preferential selectivity towards OXA (50.8 %), although at low glycerol conversion (29.4 %), within 4 h at 60 °C.<sup>42</sup> Conversely, the use of LDH-hosted sulphonato-salen Cr(III) complexes resulted in the selective formation of 1,3dihydroxyceton (59.3 % selectivity), at a glycerol conversion of 85.5 % at 60 °C, within 6 h.43

To date, the best yields of TAR and OXA were obtained over noble metals (Pd, Au), which poses significant problems as regards availability and cost. Replacing precious metals by cheap and accessible non-noble metals, while keeping high activity, selectivity and stability, is one of the biggest challenges faced by modern catalysis.<sup>44, 45</sup> In this context, metal oxides appear as an attractive alternative to noble metal catalysts.<sup>46</sup> Particularly, tailoring the morphologies and sizes of these metal oxides contributes significantly to improve their catalytic properties. Among these metal oxides, copper oxide (CuO) has been extensively investigated and multiple synthesis routes have been explored in the literature.<sup>47-51</sup> Due to its versatile properties and wide applications, hitherto, different morphological structures such as ribbons, spheres, platelets, dandelion and hollow structures have also been synthesized.<sup>52,</sup> <sup>53</sup> Although several synthetic methods have been explored, the synthesis of highly pure and crystalline nanostructured CuO in a fast and efficient one-pot method still remains a challenge; particularly for aqueous phase reactions. Traditionally, the synthesis of CuO involves surfactants, energy-consuming synthesis time and high calcination temperatures (> 400°C) to finally transform the synthesized  $\text{Cu}_2\text{O}$  to  $\text{CuO.}^{54,\ 55}$  Recently, sonochemistry has emerged as an attractive approach for preparing nanostructured materials.56-59 The physical and chemical effects induced by the implosion of cavitation bubbles lead to an important improvement of reaction rates and often allow nanostructured materials to be synthesized at ambient temperatures, apace with in-situ pseudo-calcinations of catalytic materials.

Here, we report a fast and efficient synthesis route for the production of highly crystalline, highly pure and uniform 2D CuO nanoleaves (NLs) at 25  $^\circ$ C and under low frequency

ultrasound irradiation. This method involves short sonication synthesis time (5 min), the use of environmentally benign reactants and does not require any surfactant, template or calcination step as usual, thus simplifying the downstream procedure. The as-synthesized 2D CuO NLs were then characterized and tested as a catalyst in the oxidation of glycerol with H<sub>2</sub>O<sub>2</sub>, instead of molecular oxygen as usual which raises safety issue at an industrial scale. Particularly, 2D CuO NLs not only produced OXA and TAR in an overall yield of 78% but were also found more stable in water than CuO synthesized by a conventional route. A comparison of collected results with those from the state of the art is provided in the supporting information and shows the interest of CuO, in particular in terms of yields in TAR and OXA (Table S1) Using DFT calculations we reveal the detailed mechanism of glycerol activation and conversion to TAR and OXA on CuO NLs. We also provide explanation for the role of hydrogen peroxide  $(H_2O_2)$  in keeping the CuO structure intact during the reaction. In agreement with DFT prediction, isotope labelling  $(H_2^{18}O_2)$ hydrogen peroxide-<sup>18</sup>O<sub>2</sub> experiments with demonstrated that oxygen from hydrogen peroxide, and not from CuO, was preferentially utilized for the oxidation reaction.

## **METHODS**

# Preparation of Copper (II) Oxide Nanoleaves (CuO NLs) under ultrasound irradiation

All chemical reagents were used without further purification. In a typical synthesis method, 40 mL of 0.25 M NaOH aqueous solution was added to 10 mL of 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution and a sky-blue suspension was obtained. This suspension was subsequently exposed a low frequency ultrasound irradiation. Ultrasound was generated by a Digital Sonifier S-250D from Branson (power of standby  $P_0 = 27.0 \text{ W}$ , nominal electric power of the generator  $P_{elec}$  = 8.2 W). A 3.2 mm diameter tapered microtip probe operating at a frequency of 19.95 kHz was used. The volume acoustic power of this system was P acous.vol = 0.25 W.mL-1 in water (determined by calorimetry measurements)<sup>60</sup>. The ultrasound probe was immersed directly in the reaction medium and a Minichiller cooler (Huber) was used to control the reaction temperature at 25 °C. On completion of sonication at the desired time, the dark blue or black precipitates were washed thoroughly with distilled water and dried in an oven at 60 °C overnight.

# Preparation of Copper (II) Oxide Nanoleaves (CuO NLs) under Mechanical stirring

Copper (II) oxide nanoleaves synthesis procedure was adapted following the procedure previously described by Amaniampong *et al.*<sup>48</sup> Briefly, 20 mL of 0.25 M NaOH aqueous solution was added to 5 mL of 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution under stirring at room temperature and the mixture was continuously stirred overnight. The solid sample was then washed with deionized water several times and dried in an oven at 60 °C.

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## **Catalyst Characterization**

Crystallographic analysis of the CuO NLs were performed by means of XRD measurements in  $2\theta$  mode on a Bruker AXS D8 diffractometer with Cu<sub>ka</sub> ( $\lambda$  = 0.154056 Å) radiation at 40 kV and 20 mA. XPS was performed on a Thermo Escalab 250 spectrometer. The binding energy was calibrated using C1s (284.6 eV) as a reference. The as-synthesized CuO nanoleaves morphology was also studied by SEM (JEOL JSM 6700F field emission), TEM and HR-TEM (JEOL JEM-2100F). Surface area analysis was determined by nitrogen physisorption on a Micromeritics TrisStar apparatus. The specific area was calculated using the Brunauer-Emmett-Teller (BET) equation.

#### Activity test and analytical methods

The general procedure for testing the catalytic oxidation of glycerol over CuO NLs catalyst in the presence of H<sub>2</sub>O<sub>2</sub> is briefly described here. Typically, about 0.100 g of glycerol was charged into a 25 mL capacity round-bottom flask and an appropriate amount of CuO NLs catalyst (unless otherwise stated) added. To this, 2 equivalent H<sub>2</sub>O<sub>2</sub> and 2 mL of DI water were added sequentially. The reaction mixture was heated in a temperature controlled oil bath and heated to desired reaction temperatures. Once the pre-set temperature of the oil bath is attained, stirring rate was set at 250 rpm and reaction proceeds until the desired reaction time. After the reaction, approximately 05 mL of the reaction liquid sample was taken and diluted and filtered before HPLC analysis. Oxalic acid, tartronic acid, glycolic acid, formic acid and glyceraldehyde were all confirmed using a Varian Pro Star HPLC equipped with an ICE-COREGEL 107H column 300 x 7.8 mm from Transgenomic, a UV/Vis detector (Varian Pro Star, 210 nm) and a refractive index detector (Varian 356-LC). A H<sub>2</sub>SO<sub>4</sub> aqueous solution (7 mM) was used as the eluent with a 0.4 mL min<sup>-1</sup> flow rate. External calibration of the liquid chromatography was performed using standards of oxalic acid, glycolic acid, glycerol, tartronic acid, glyceraldehyde and formic acid was quantified by the difference between the two HPLC analyses. Noteworthy, the detected amount of formic acid reported in our study is the solubilized fraction of it, although the volatized amount of formic acid at the analyze condition is small according to its corresponding Henry's law coefficient.<sup>50</sup> After each set of reaction, the catalyst is filtered off, by washing thoroughly with DI water, it is then dried in an oven at 60 °C overnight. The recovered dried samples are weighed to estimate the exact amount of recovered catalyst after recycling. Typically, 90-85 % of the catalyst amounts are recovered. All other reactant amounts are adjusted to the amount of recovered catalyst in order to obtain uniform reaction parameters throughout the experiment.

## **Computational Methods**

All the spin-polarized DFT calculations were done using the Vienna ab-initio simulation program (VASP).<sup>61, 62</sup> Plane-wave basis set with a cut-off kinetic energy of 450 eV, the projector-augmented wave (PAW)<sup>63</sup> and the Perdew-Burke-Ernzerhof

(PBE) functional<sup>64</sup> were utilized for those simulations. To correct the strong correlation and localization of 3d electrons of Cu in CuO structure, the Hubbard term in the form of GGA+U with  $U_{eff}$  = 7.0 ev was applied within the Dudarev's approach.<sup>65</sup> This correction described well the bulk properties (lattice parameters, band gap value and magnetic moment) of CuO and was successfully applied to simulate the activation of glucose and methane on CuO surfaces.<sup>48, 51, 52</sup> In this study, CuO was modeled as periodic four-layer (4×2) slabs and a 20 Å vacuum thickness above the top layer was used to prevent interaction between repeated unit cells. Two top layers and the adsorbates were allowed to fully relax while the bottom two layers were fixed at the optimized bulk lattice parameters to reduce the computational cost without influencing the accuracy of simulations. Magnetic moment in the bulkordering is applied for CuO(111) surface since it was found to result in the most stable structure as reported by Mishra et al.<sup>66</sup> The 3×3×1 Monkhorst-Pack grid was used to sample the Brillouin zone, and the tetrahedron method with Blöchl corrections was employed for all calculations. Transition states were searched using the Nudged Elastic Band (NEB) method, and subsequently confirmed with the frequency calculations. To get the free energies of the process, the entropy, zero-point energy and enthalpy correction were computed from statistical thermodynamics for all adsorbed structures, while those values for gas-phase molecules were taken from the standard thermodynamics NIST-JANAF table.<sup>44, 45, 67</sup>

## **RESULTS AND DISCUSSION**

#### Synthesis and Growth Mechanism of 2D CuO NLs

CuO NLs were prepared by sonication of an aqueous solution of copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) and sodium hydroxide (NaOH) at 19.95 kHz and at a controlled temperature of 25 °C. The mechanism of the formation of CuO NLs was investigated by XRD (Fig. 1).

Interestingly, it was observed that the initial sonication (1 to 3 min) of the reactant mixture ( $Cu(NO_3)_2$  and NaOH) rapidly formed a layered inorganic hybrid, herein identified as copper (II) hydroxynitrate, (Cu<sub>2</sub>(OH)<sub>3</sub>NO<sub>3</sub>), also known as gerhardtite (Fig. 1). The synthesis of gerhadtite on its own deserves crucial attention since its synthetic analog is being used in vehicle airbags due to its intrinsic mechanical and thermal properties. Besides particle dispersions, ultrasound irradiation played a crucial role in the further transformation of the formed gerhardtite to CuO. The color of the reactant solution changed from bright blue (after 1 min of sonication) to pale green (after 3 min of sonication) and finally to brown (from 5-30 min sonication), in line with the formation of CuO (Fig. 1). We postulate that in-situ generation of high temperatures, pressures, shockwaves, microjets and hydroxide radicals locally formed by the implosion of cavitation bubbles during ultrasound irradiation, contributed to a rapid hydrolysis and dehydration of intermediate copper (II) hydroxynitrate to CuO nuclei, and to its subsequent crystal growth by Ostwald ripening.<sup>56, 68</sup> The CuO nuclei subsequently undergo self-

ed (SEM)

As Prepared (SEM)

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Fig. 1 XRD patterns showing CuO evolution at irradiation times 1, 3, 5, 10, 20 and 30 min. Images of reaction products recovered after each ultrasound irradiation time are inserted in the XRD.

assembly along the same crystallographic orientation (like a single crystal). The XRD patterns (Fig. 1) revealed that defects and surface energy constraints of CuO nuclei drove the assembly along [-1 1 1] and [1 1 1] direction with excellent crystallographic orientation. This oriented attachment growth mechanism goes through the entire reaction time (from 5 to30 min), as further confirmed in the XRD analysis (Fig. 1). The major peaks centered at  $2\Theta = 35.5 \,^{\circ}$  and  $38.8 \,^{\circ}$  are indexed as CuO [-1 1 1] and CuO [1 1 1], respectively, and are characteristics of the pure phase monoclinic CuO crystallites. Furthermore, no side products such as Cu(OH)<sub>2</sub> and Cu<sub>2</sub>O were detected from the XRD pattern, further indicating the synthesis of highly pure leaf-like CuO nanostructures.

A stepwise reaction scheme for the formation of CuO, as observed from XRD characterization analysis is as follows:

1

(1)

$$2Cu(NO_3)_{2(aq)} + 2NaOH_{(aq)} + 2H_2O \longrightarrow$$

$$Cu_2(OH)_3NO_{3(s)}+2NaNO_{3(aq)}+H_3O_{(aq)}^++NO_{(aq)}^-$$

## **Morphological Characterization of CuO NLs**

The as-synthesized CuO was first analyzed by SEM (Fig. 2). The low magnification image illustrated that the leaf-shaped nanostructure congregates to form large clusters (Fig. 2a). A closer view of the leaf-shaped structure revealed that NLs of CuO were uniformly formed (Fig. 2b) even at a short sonication time (5 min) and were strikingly similar to the morphology observed *via* the conventional synthesis method at 25 °C





Fig. 2. (a) Low and (b) high magnification of SEM images of CuO nanoleaves synthesized by low-frequency ultrasound (c) SEM images of CuO nanoleaves synthesized by conventional method; (d) low magnification TEM; (e) high magnification TEM image; (f) SAED pattern of CuO nanoleaves.

within 40 h (Fig. 2c). For detailed morphological characterization, TEM and HR-TEM were employed. TEM images of the as-synthesized CuO NLs (Fig. 2d) were consistent with the SEM observations, and revealed the leaf-like morphology of the as-synthesized CuO. The HR-TEM revealed that CuO NLs are composed of many small particles and the assembly of the nanoparticles results in the formation of the observed leaf-like morphology. A clear and continuous lattice fringe with a lattice spacing between two neighboring fringes of 0.23 nm (Fig. 2e) corresponded to the distance of the [111] plane of the monoclinic CuO and confirmed the highcrystalline nature of the leaf-like morphology with the same crystallographic orientation.<sup>48</sup> Figure 2f represents the corresponding selected area electron diffraction (SAED pattern) showing discrete spots and indicating the highly crystalline and monoclinic structure of the synthesized CuO NLs. The N<sub>2</sub> adsorption-desorption isotherm of the CuO NLs (Fig. S1) was in perfect agreement with the SEM and TEM analysis, revealing a type II isotherm with a type H<sub>3</sub> hysteresis loop attributed to a macroporous material and the formation of plate-like particles, respectively, according to the IUPAC classification. A surface area of 20 m<sup>2</sup>g<sup>-1</sup> was obtained for the as-synthesized CuO NLs.

XPS analysis of as-prepared CuO NLs confirmed the formation of  $Cu^{2+}$  with the binding energy centered at 934.1 eV and attributed to the core level of Cu  $2p^{3/2}$  (Fig. 3a). The additional

#### Journal Name

peaks observed at 935.3, 943.9 and 941.3 eV are due to the shakeup satellite peaks, and the analysis of the Cu LMM spectra revealed an intensity with kinetic energy of 917.1 eV<sup>69</sup> (Fig. S2, characteristic of a CuO nano-structured material), ruling out the possibility of the existence of a Cu<sub>2</sub>O phase. The O 1s spectra of the synthesized CuO revealed distinctive peaks at 529-530 and 531-532 eV attributed to the bulk lattice oxygen of CuO and surface adsorbed oxygen with low coordination, respectively.<sup>52, 70</sup> The high intensity at 531-532 eV suggests rich adsorbed dioxygen on the CuO surface. The peak centered at 533-534 eV corresponds to the water molecule, which confirms the formation of CuO NL in the hydrated form.<sup>71</sup>



Fig. 3. XPS analysis of CuO NLs. (a) Cu  $p_{3/2}\,\text{peak}$  fitting and (b) O 1s peak fitting

## Catalytic oxidation of glycerol on CuO NLs

Glycerol oxidation of glycerol was performed over CuO NLs as the catalyst, in the presence of  $H_2O_2$  as an oxidizing agent, at the reaction temperature of 80 °C and a reaction time span of 1-7 h (Table 1). The reaction conditions provided here were optimized, as demonstrated in the Supplementary Information. The reaction conditions provided here were optimized, as demonstrated in the Supplementary Information. It is important to mention here that glycerol

oxidation in the presence of H<sub>2</sub>O<sub>2</sub> but without CuO NL did not lead to any detectable product in the liquid phase (Table 1, entry 1), suggesting that a free OH radical mechanistic reaction pathway is less likely to occur.<sup>72, 73</sup> Glyceric acid (yield: 10 %) was observed for reactions performed over CuO NLs in the absence of  $H_2O_2$  within 4 h (Table 1, entry 2) but the complete reduction of CuO to Cu<sub>2</sub>O and Cu was observed by XRD at the end of the reaction (Fig. S3). When the reaction was performed in the presence of  $H_2O_2$  and CuO NLs, characterization of the spent CuO NLs catalyst did not reveal any surface reduction, suggesting (i) the regeneration of the CuO NLs catalyst in the presence of H<sub>2</sub>O<sub>2</sub> and (ii) both CuO NLs and  $H_2O_2$  are required for the transformation of glycerol to OXA and TAR. Additionally, glycerol oxidation was performed in labelled hydrogen peroxide- ${}^{18}O_2$  solution (H $_2{}^{18}O_2$ ). Analysis of the reaction products by mass spectrometry revealed the insertion of  $^{18}\mbox{O}$  into OXA (Fig. S4), demonstrating that  $H_2O_2$  is the preferred oxidizing agent for the reaction and CuO doesn't supply oxygen for the reaction, like that in the Mars van Krevelen type mechanism.

After 4 h, 95% of glycerol was converted. Analysis of the reaction mixture over time showed that glyceraldehyde and glyceric acid were the primary products of the reaction. Their yields reached a maximum of 36% (glyceric acid) and 18% (glyceraldehyde) after 1h of reaction time (Table 1, entry 3). When the reaction time was extended, the yield of glyceraldehyde and glyceric acid decreased and. concomitantly, OXA and TAR were produced with a maximum yield of 56% and 22%, respectively after 4 h, i.e. an overall yield in dicarboxylic acids of 78% (Table 1, entry 5). Glycolic and formic acids were also detected but their amounts remained rather low (< 5% yield). At 95% conversion of glycerol, the carbon mass balance was 88%, suggesting that gaseous products (mainly CO<sub>2</sub>), presumably from over oxidation of glycerol and products, were also formed. The kinetic data suggests that glycerol was first oxidized to glyceraldehyde and then to glyceric acid. Glyceric acid is then further oxidized to TAR. OXA would be produced via (1) C-C bond cleavage after glyceraldehyde formation to give  $C_1$  and  $C_2$ precursors for formic acid and OXA, respectively; (2) C-C bond cleavage of glyceric acid, releasing glycolic acid (further oxidized to OXA) and formic acid and/or (3) decarboxylation of TAR to glycolic acid followed by the oxidation to OXA (Scheme 1). At reaction temperatures higher than 80 °C (Table 1 entry 8), OXA yield decreased (from 56 to 35 %, at 100 ° C) and the yield of C1 acids increased, suggesting additional C-C bond cleavage. However, this increase in temperature (100 ° C) was innocuous to the formed TAR, as its yield (20 %) was observed to be somewhat stable.

DOI: 10.1039/C8GC00961A

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Table 1: Reactant conversion and product yields for the CuO NL-catalyzed oxidation of glycerol. Glycerol amount = 0.100 g, Reaction temperature =80 °C, reaction time =1-7 h, CuO catalyst = 0.05 g, volume of solvent (H<sub>2</sub>O) = 2mL. The optimum glycerol/H<sub>2</sub>O<sub>2</sub> molar ratio is 0.5.



<sup>*a*</sup> Oxidation of glycerol was performed in the presence of  $H_2O_2$ , without CuO catalyst. <sup>*b*</sup> Oxidation of glycerol was performed in the presence of CuO catalyst, without  $H_2O_2$ . <sup>*c*</sup> Reaction temperature = 100 °C

For benchmarking purposes, CuO synthesized via the conventional method, following a synthesis protocol reported earlier<sup>48</sup> and denoted herein as CuO (CM) with a surface area of 18 m<sup>2</sup>g<sup>-1</sup>, was also tested. Glycerol oxidation was conducted under similar conditions with CuO NLs prepared by ultrasound irradiation. Results obtained with both catalysts were collected at *iso*-conversion (95 %). Results are summarized in Table 2. Using CuO (CM) as the catalyst, OXA and TAR were produced with 37% and 26% yields, respectively, after 6 h of reaction. It

corresponds to a total yield in dicarboxylic acid of 63%. This yield is lower than the yield obtained with CuO NLs (78%), after 4 h of reaction. It suggests that CuO NLs was not only more selective but also more active than CuO (CM). The presence of 13% of glycolic acid (reaction intermediate) at the end of the reaction with CuO (CM) suggests a lower oxidative activity towards OXA.

Table 2. Product yields for the CuO-catalyzed oxidation of glycerol. Two different catalysts, CuO NLs and CuO (CM), were tested.	Glycerol = 0.100 g, R. T = Reaction time, CuO
catalyst = 0.05 g, volume of solvent (H $_2$ O) = 2mL (Product yields were determined at an iso-conversion of 95 %)	

HO OH Glycerol	СОН <u>H2O2, 80 °C</u> <u>CuO, 95 % con</u>	( ► HÓ	O O OH TAR		HO OH Glyceric acid	HO Glycol	OH HO O
					Yield (%)		
Catalyst	Time (h)	OXA	TAR	Glyce	eric acid d	Glycolic acid	Formic acid
CuO NLs	4	56±3.5	22± 1	.6 8±	± 0.5	0	2± 0.1
CuO (CM)	6	37±2.7	26±2.	.0 9:	±0.6	13±1.0	10±0.9

## Journal Name

## ARTICLE

To demonstrate the superior performances of highly crystalline CuO NLs, the recycling of CuO NLs and CuO (CM) was then investigated at 80 °C, with a glycerol/H<sub>2</sub>O<sub>2</sub> molar ratio of 0.5. As shown in Fig. 4, a rapid decrease in OXA and TAR yields was observed over CuO (CM) cycle after cycle. The total yield of dicarboxylic acids dropped from 63% to only 7% after 6 catalytic cycles. Conversely, CuO NLs were more robust than CuO (CM) and the total yield in dicarboxylic acids remained higher than 70% up to the 5th catalytic cycle (vs 78% for the first cycle). The lower activity and stability of CuO (CM) than those of CuO NLs could be a result of a lower purity, as well as the presence of Cu vacancies on the surface of CuO (CM). Such vacancies may 1) affect the activation of glycerol and hydrogen peroxide, thereby affecting the conversion of glycerol and selectivity towards dicarboxylic acids and 2) may accelerate the reduction of the copper oxide, leading to changes in the crystalline structure of CuO, as presented in Fig. S6a. The presence of oxygen vacancies is known to make metal oxides more amenable to reduction<sup>74</sup>. In addition, the pore diameter and pore volume are slightly different between both CuO samples (12 nm, 0.038  $\text{cm}^3/\text{g}$  and 9 nm, 0.019  $\text{cm}^3/\text{g}$  for CuO(US) and CuO(CM), respectively), which may also contribute to explain their difference of catalytic behavior. Inductively coupled plasma with optical emission spectrometer (ICP-OES) analysis of the filtrate collected after the 4th recycling with CuO NLs revealed a slight leaching of Cu of 20.6



Fig. 4. Recycle experiments over CuO NLs and CuO (CM) catalysts. Reaction conditions: 0.05 g of CuO (US), 0.1 g of glycerol, 80 oC reaction temperature, 2 mL of H2O, 4 h reaction time and glycerol/H2O2 molar ratio of 0.5.

ppm. In addition, FT-IR analysis (Fig. S5) revealed the adsorption of organic compounds on spent CuO NLs. All together, these factors contributed to the slight decrease in catalytic activity of CuO NLs during recycling experiments. We further carried out a hot filtration test to verify the heterogeneous nature of the reaction in the presence of CuO NLs. In this test, the CuO NLs catalyst was separated from the hot reaction mixture after 0.75 h (*i.e.* 50 % glycerol conversion) and the filtrate was heated at 80 °C for another 1 h. No increase in conversion was observed, thus confirming the heterogeneous nature of the catalytic process.

# Reaction mechanism of the conversion of glycerol to dicarboxylic acids on CuO(111) and the role of $\rm H_2O_2$

## Glycerol activation and oxidation on clean CuO(111) surface

To unravel the underlying reaction mechanism and to investigate the role of  $H_2O_2$  in enhancing the activity and stability of CuO NLs, we performed density functional theory (DFT) calculations. From the kinetic data presented in Table 1, glyceric acid is suggested to be the primary product in the initial stage of the reaction. The energy profile for the oxidation of glycerol to glyceric acid on a clean CuO(111) surface is shown in Fig. 5.

Under-coordinated  $O_3$  and  $Cu_3$  sites have been reported as active sites for C-H and N-H bond activations on the CuO surface.<sup>51, 52</sup> On clean CuO(111) surface, glycerol is initially activated via the abstraction of H from the primary OH, facilitated by the surface  $O_3$  site, with the barrier of only 49 kJ/mol (TS1 in Fig.5b). All other competitive pathways involving the C-H activation as the first step have barriers greater than 130 kJ/mol (Supplementary Information, Fig. S13). The preference of initial OH activation observed here is also consistent with the recently reported results of Zhao et al.,75. After the terminal OH is cleaved, the C-H bond can be activated by the surface  $O_3$  site with the activation barrier of 63 kJ/mol (TS2, Fig.5c), forming glyceraldehyde. Adsorbed glyceraldehyde is subsequently oxidized to glycerate via a twostep process involving the formyl C-H bond activation with the barrier of 74 kJ/mol (TS3, Fig 5d), followed by the incorporation of the surface lattice oxygen into glyceraldehyde (structure I5, Fig.5f). It is important to mention that the incorporation of CuO lattice oxygen into glyceraldehyde forming glycerate (step from I4 to I5) is energetically downhill by -21 kJ/mol, similar to the oxidation mechanism of glucose to gluconic acid, reported earlier.48 Glycerate is then protonated by the surface hydrogen (has been confirmed by both, calculations and isotope labelling study<sup>48</sup>) with the

DOI: 10.1039/C8GC00961A Journal Name



Fig. 5. (a) Energy profile for the conversion of glycerol to glyceric acid on clean CuO(111) surface; (b) Transition state for the initial primary O-H activation (TS1); (c) Transition state for the subsequent C-H activation (TS2); (d) Transition state for the formyl C-H activation (TS3); (e) Intermediate after the formyl C-H activation (I4); (f) glycerate formation generating the surface lattice oxygen vacancy (I5) and (g) Transition state for the protonation of glycerate to form glyceric acid (TS4). Activation barriers (Ea) are indicated in kJ/mol. Big red and big salmon balls represent Oxygen (O) and Copper (Cu) atoms of the CuO surface, respectively; while small white, grey and red balls represent Hydrogen (H), carbon (C) and oxygen (O) atoms of glycerol/glyceric acid, respectively.

barrier of 94 kJ/mol and finally is converted to glyceric acid (TS4, Fig.5g). Our DFT results explain the formation of glyceraldehyde and glyceric acid as initial products of the reaction, as shown in Table 1. After glyceric acid is formed, it reorients on the surface to a more stable configuration and adsorbs on the surface via the primary OH (16 kJ/mol more stable, Fig. S14). The oxidation of the other primary CH<sub>2</sub>OH group in glycerol would proceed via the same mechanism, resulting in the formation of tartronic acid (TAR). The formation of oxalic acid (OXA) via C-C bond cleavage is discussed later in section called C-C cleavage.

## The role of H<sub>2</sub>O<sub>2</sub>

DFT calculations on the clean CuO surface reveal the activity of CuO for glycerol oxidation. However, the surface lattice oxygen is consumed during the reaction (Structure step from I4 to I5, Fig.5), resulting in the reduction of CuO and the deactivation of the catalyst.<sup>48, 50</sup> Indeed, without the presence of  $H_2O_2$  in experiments, CuO was reduced to  $Cu_2O$  and Cu after the reaction, as shown in Supplementary Information, Fig. S3. Additionally, the surface  $O_3$  sites, as shown in TS1,2,3 (Fig.5b,c,d), will be blocked due to the strongly bound dissociated H atoms from C-H and O-H cleavages. At sufficiently high coverage on the surface, these adsorbed hydrogens would combine with the lattice oxygen, forming water, thereby generating oxygen vacancies on the surface

and partially reducing the CuO structure, as was observed both theoretically<sup>76</sup> and experimentally.<sup>52, 77</sup> In the absence of  $H_2O_2$ , reduction of CuO to Cu<sub>2</sub>O and Cu over the reaction time results in low conversion of glycerol (10%), as shown in Table 1, entry 2. The experimental results with and without  $H_2O_2$  clearly demonstrate that  $H_2O_2$  plays a crucial role in achieving the high conversion of glycerol and high yields of dicarboxylic acids, and the role of  $H_2O_2$  needs to be investigated.

The presence of  $H_2O_2$  can generate OH groups adsorbed on the CuO surface by the decomposition of  $H_2O_2$  into two OH fragments, catalyzed by CuO. The free energy change at the reaction temperature of  $80^{\circ}$ C for the formation of adsorbed OH species from  $H_2O_2$  on CuO(111) is -28 kJ/mol and the activation barrier is only 22 kJ/mol (Supplementary Information, Fig. S16). The surface OH species from  $H_2O_2$  can react with the H on the O<sub>3</sub> site to form water, with the barrier of only 27 kJ/mol (Fig. S16c), thus, regenerating the active O<sub>3</sub> site and enhancing the activity of the catalyst.

Next, we evaluated the involvement of surface OH, generated from  $H_2O_2$ , in altering the mechanism of glycerol oxidation on CuO. Activation barriers for the alternate pathway assisted by surface OH are shown in Fig. 6.



**Fig. 6.** Mechanism and energy profile of the conversion of glycerol to glyceric acid on CuO(111), in the presence of  $H_2O_2$ ; Activation barriers (E<sub>a</sub>) are indicated in kJ/mol. Red values are activation barriers for surface lattice oxygen catalyzed reaction steps and green values are barriers for the surface OH facilitated reaction steps. Key transition states are also shown. Big, blue arrows indicate the preferred reaction pathway. Color code for atoms is the same as in Fig.5.

For comparison, the pathway catalyzed by the lattice oxygen of CuO is also shown. Surface OH can activate the primary OH group of glycerol with the barrier of only 14 kJ/mol (TS5, Fig.6), much lower than the direct activation by the surface lattice  $O_3$  site (49 kJ/mol, TS1, Fig.5b), consistent with many earlier studies.<sup>78-80</sup> The subsequent C-H activation assisted by surface OH has almost the same barrier (67 kJ/mol, Supplementary Information, Fig. S17a) as that of the direct activation by the

#### Journal Name

surface lattice  $O_3$  site (63 kJ/mol). However, the pathway assisted by the surface OH species leads to the "on-the-fly" transfer of hydrogen from glycerol to the surface OH (TS5, Fig.6), and does not generate any hydrogen on the active  $O_3$ site. This would prevent the surface reduction of CuO due to the increased coverage of hydrogen, as discussed earlier. Additionally, the oxidation of glycerol to glyceric acid on the clean CuO surface involves the incorporation of lattice oxygen of CuO into the acid product, resulting in the reduction of the catalyst.48, 50 This key step can also be avoided by the assistance of surface OH, produced due to the dissociation of H<sub>2</sub>O<sub>2</sub>. The presence of surface OH on transition metals can facilitate alcohol oxidation by an OH insertion mechanism into the intermediate aldehyde, as reported by Zope et al.<sup>78</sup> Using DFT calculations and isotope labelling experiments, they revealed that the added oxygen in the carboxylic acid originated from water (forming surface OH), instead of the dissolved molecular oxygen.<sup>78</sup> Similarly, we show here that the surface OH species originating from H<sub>2</sub>O<sub>2</sub> combines with glyceraldehyde to form an intermediate complex, with the activation barrier of only 21 kJ/mol (TS6 in Fig.6). This complex subsequently undergoes H-abstraction, preferably catalyzed by the surface lattice  $O_3$  site (TS7 in Fig.6) with the barrier of 27 kJ/mol to form the acid. The H-abstraction step assisted by the surface OH is unlikely due to a relatively higher barrier of 92 kJ/mol (Supplementary information, Fig. S17b). The barrier for the surface OH insertion into glyceraldehyde is much lower than the value of 74 kJ/mol for the formyl C-H activation (TS3, Fig.5d), which otherwise is the key step for its conversion to acid. More importantly, this OH insertion pathway does not require the insertion of a lattice oxygen from CuO for the oxidation process, as described earlier, and therefore does not generate any surface oxygen vacancy, keeping the structure of CuO unchanged and intact after the reaction. This suggests that H<sub>2</sub>O<sub>2</sub> preferentially supplies oxygen for the reaction, instead of CuO, via the aforementioned OH insertion pathway, in excellent agreement with the observed experimental isotope labelling study using H<sub>2</sub><sup>18</sup>O<sub>2</sub>. The most preferred pathway for the oxidation of glycerol, in the presence of H<sub>2</sub>O<sub>2</sub> on CuO, is highlighted by blue arrows in Fig.6. It involves the surface OH assisted initial activation of the primary OH group of glycerol, subsequent C-H activation to form glyceraldehyde (could be either by surface lattice  $O_3$  or assisted by surface OH), insertion of surface OH into glyceraldehyde and finally deprotonation to glyceric acid facilitated by the surface lattice

Finally, we also evaluated the possibility of  $H_2O_2$  providing oxygen to compensate the generated oxygen vacancies on the surface. Two possible mechanisms for the replacement of lattice oxygen's are:

$Cu_nO_{n-1} + 0.5H_2O_2 \rightarrow Cu_nO_n - H$	(3)
$Cu_nO_{n-1} + H_2O_2 \rightarrow Cu_nO_n + H_2O_1$	(4)

 $O_3$  site of CuO.

The computed free energies of reactions (3) and (4) at  $80^{\circ}$ C (the entropy, zero-point energy and enthalpy correction were

depicted in the Supplementary Information, Fig. S18. To summarize, the presence of  $H_2O_2$  can (i) compensate the generated Oxygen vacancy and keep the structure of CuO and its morphology intact, (ii) form surface OH groups and remove the H atoms that block the active  $O_3$  site on CuO surface and regenerate it, and most importantly (iii) provide an alternate lower energy barrier pathway to oxidize glycerol to acid without utilizing the surface lattice oxygen of CuO.

## C-C cleavage

The formation of glycolic acid, OXA and formic acid (Table 1), requires C-C bond cleavage. Three possible routes for the C-C cleavage are illustrated in Scheme 1, as were proposed in the literature for the catalytic oxidation of glycerol to mono acids and diacids.<sup>81, 82</sup> They involve the C-C cleavage after glyceraldehyde formation (route 1), after glyceric acid formation (route 2) and after tartronic acid formation (route 3). DFT calculations were implemented to evaluate all these pathways and the transition states of C-C cleavages via these routes are presented in Fig. 7.



Scheme 1. Different routes for the C-C cleavage

In route 1 involving glyceraldehyde, the C-C bond cleavage is likely to be preceded by the activation of its primary OH group, forming a structure which is adsorbed via both the terminal (1,3) oxygen atoms. The activation barrier for the C-C cleavage in this precursor is 82 kJ/mol (TS8, Fig.7a) and forms C<sub>1</sub> and C<sub>2</sub> fragments which could be further oxidized to formic acid and glycolic acid, respectively. Similarly, along route 2, the C-C dissociation is also preceded by the abstraction of H from the primary OH in glyceric acid to form a structure adsorbed via its terminal oxygen (1,3) atoms. However, the C-C cleavage in this precursor from glyceric acid has lower activation barrier of

## ARTICLE

Green Chemistry Accepted Manuscript

DOI: 10.1039/C8GC00961A Journal Name

vield of 78 % (OXA; 56 %, TAR acid; 22%) at 95 % conversion of glycerol was obtained. DFT calculations provided detailed insights into the reaction mechanism and identified the synergistic role of H<sub>2</sub>O<sub>2</sub> and CuO catalyst in the overall oxidation reaction. The proposed CuO nanoleaves catalyst can eliminate disadvantages of using expensive noble metal catalysts for oxidation reactions and the results shown here shed light, for the first time, on the synergistic role of CuO and  $H_2O_2$  in the selective oxidative conversion of glycerol to dicarboxylic acids and in maintaining the stability of the

## **Conflicts of interest**

catalyst.

Authors declare no competing financial interest.

## Acknowledgements

Authors are grateful to the CNRS, the Ministry of Research and the Région Aquitaine-Limousin-Poitou-Charentes for their financial support. Funding from the International Consortium on Ecoconception and Renewable Resources (FR CNRS INCREASE 3707) and the chair "TECHNOGREEN" is also acknowledged. This research is also supported by the National Research Foundation (NRF), Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) program.

## Notes and references

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**‡ Supplementary Information:** Experimental details and conversion and yield data. Effect of operating conditions on the conversion and yield. Details of computational methods. DFT studies on adsorption of glycerol on CuO(111) surfaces. Transitions states for the oxidation of glycerol to glyceric acids and C-C cleavages from different precursors. Surface OH adsorbed on CuO(111) surface, the regeneration of active surface lattice O<sub>3</sub> site and the compensation of oxygen vacancies by  $H_2O_2$ .

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only 58 kJ/mol (TS9, Fig7b). The precursor for the C-C cleavage in route 3 is also a structure adsorbed via both the terminal oxygen atoms (1,3), resulting from the H-abstraction of both the -COOH groups of tartronic acid. The H-abstraction of the terminal COOH groups proceeds with an activation barrier of 34 kJ/mol, as shown in the Supplementary Information Fig. S15f. The C-C cleavage which is a decarboxylation reaction (one of the fragments is CO<sub>2</sub>) has an activation barrier of 103 kJ/mol (TS10, Fig.7c). The  $C_2$  fragments in all three routes are precursors for the formation of oxalic acid which is the dominant product of the oxidation reaction. The activation barrier for C-C cleavage in route 3 is the highest among all three routes and therefore the C-C cleavage in tartronic acid would be limited. This DFT result can explain why the amount of tartronic acid is not reduced even when the oxalic acid is formed in large yields, as shown in Table 1 (entry 5). The activation barrier for C-C cleavages in route 2 (from glyceric acid) is the lowest among all three routes. It is worth mentioning that this activation barrier (58 kJ/mol) is even lower than the barrier for the subsequent C-H activation (~63 kJ/mol, TS2, Fig.5c) in the minimum energy pathway indicated in Fig.6 for the oxidation of glyceric acid to tartronic acid. This implies that the formed glyceric acid would kinetically prefer to undergo further decomposition to form  $C_2$  and  $C_1$ fragments, consistent with the higher yield of oxalic acid (product of C-C cleavage) than that of tartronic acid (product of oxidation), as observed in Table 1 (entry 5). Although the C-C cleavage from glyceraldehyde is feasible at reaction conditions, the activation barrier (82 kJ/mol) is higher than the barrier for subsequent oxidation of glyceraldehyde (21 kJ/mol for the OH insertion, TS6, Fig.6) and therefore results in the formation of glyceric acid as the primary product in the initial stage of the reaction (Table 1).



Fig. 7. Transition states (TS) for C-C cleavages from (a) glyceraldehyde, TS8, Route 1; (b) glyceric acid, TS9, Route 2 and (c) tartronic acid, TS10, Route 3. Mechanisms corresponding to routes 1, 2 and 3 for C-C cleavages are depicted in Scheme 1. Color code for atoms is the same as in Fig.5. Activation barriers ( $E_a$ ) are in kJ/mol and C-C distances in the transition states are also indicated.

## CONCLUSIONS

In summary, the catalytic performances of non-noble CuO prepared by a fast (5 min) and simple sonochemical approach is reported in the oxidation of glycerol to OXA and TAR, in base-free and mild conditions. A significant advantage of this sonochemical synthesis technique is the incredibly fast synthesis time along with in-situ pseudo-calcinations of the CuO nanostructured material. An overall dicarboxylic acids

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Glycerol was oxidized selectively to oxalic and tartronic acid in 78% yield over a highly crystalline CuO catalyst prepared within few minutes by a sonochemical synthesis.