Chemical and morphological stability study of copper oxide nanocubes in controlled and non-controlled atmospheres

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Background
Cu-based formulations are high-prospect catalysts for their remarkable performance in environmental reactions and their role as a substitute for expensive noble metals. Depending on the reaction of interest, Cu-based catalysts are exposed to different oxidizing/reducing environments, in a temperature regime that may span over 200-800ºC1. Temperature-programmed experiments under H2 or O2 atmospheres have shown that copper phases are susceptible to release or capture oxygen, changing its oxidation state from Cu0 to Cu2+. These variations are concomitant with structural, chemical, and morphological modifications 2.

In relation with the gas-catalyst interaction, each exposed crystallographic facet may exhibit a singular ability to generate/annihilate oxygen vacancies3, and, therefore, a specific reactivity. The diverse and irregular surface of Cu-based nanoparticles hinder a direct relationship between the observed performance and their surface termination. The use of nanoparticles with controlled morphology and well-defined facets4, such as nanocubes, is proving to be a promising approach to address this complexity because it provides particles with homogeneous and explicit facets, facilitating the investigation of the H2/O2 interaction with copper phases and its chemical and structural consequences. To this end, we propose to synthesize CuOx nanocubes and characterize them by means of HR-TEM and EELS after application of different reducing/oxidizing thermal treatments. It will be paid careful attention to aspects such as their oxidation state, crystallographic homogeneity and stability.

Methods
The structural, chemical and morphological evolution of copper oxide nanocubes synthesized in our laboratory using very dilute solutions of Cu(NO3)2.3H2O, NaOH and ascorbic acid5 have been investigated after exposing the catalysts to oxidizing/reducing atmospheres at different temperatures. We have employed a FEI Talos F200X electron microscope operating at 200kV, capable of both transmission and scanning/transmission (TEM/STEM) modes and equipped with a Gatan Continuum Electron Energy Loss Spectrometer (EELS). The Cu-L2,3 white line EELS signals have been the primary focus of this study towards the determination of the oxidation state, processed using DigitalMicrograph software. More specifically the spatial distribution of CuOx phases have been determined with the Multiple Lineal Least Squares (MLLS) method. High quality Cu0, Cu1+ and Cu2+ references have been previously registered to perform the fitting. The EELS data have been complemented with the analysis of HR-TEM images, extracting the copper phase maps from the Fourier periodicities.

Results
STEM-HAADF images of the as prepared samples unveil the success of the synthesis, with particles exhibiting a cubic morphology spanning over 30 and 60 nm in size. The crystallographic analysis carried out by HR-TEM allowed us to confirm the presence of Cu2O phase (Figure a-b). In addition, a zoomed image of the {100} faces reveals a rough surface assembled by low-dimension facets (Figure c). Aberration-corrected electron microscopy characterization will be used to better define this type of nanofacets.

To confirm the oxidation state of these systems, we conducted EELS analysis. The Cu-L2,3 EELS signal confirmed the presence of Cu2O, in agreement with the results obtained by HR-TEM. Prior to assessing the potential impact of different gas atmospheres on the initial state, we evaluated its stability over time. Thus, the morphology and Cu-L2,3 EELS features have been tracked after 1, 2 and 3 weeks (Figure d, e and f respectively). The evolution shows a progressive deterioration of the cubes, with areas exhibiting undefined morphologies which increase over time. These regions displayed Cu2+, indicating a transformation to CuO. Consequently, the samples are prone to capture O2 from air, triggering the destruction of the cubes. In contrast, when oxidation treatment was controlled in a muffle oven at 300ºC, the sample exhibited a hollow structure while preserving its morphology.

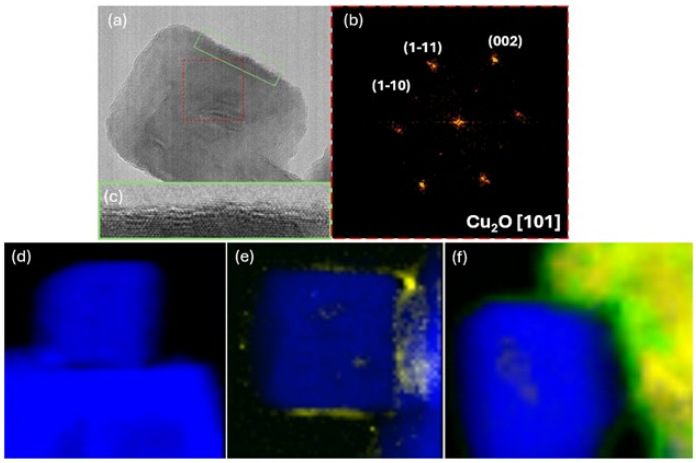
The pristine Cu2O nanocubes were also submitted to H2 at 100 and 150ºC. The reduction at 100ºC slightly altered the morphology, forming small nanoparticles on the surface of the nanocubes. However, at 150ºC, the HAADF images indicated sintering of the cubes, resulting in large (over 500 nm) aggregates, hindering a proper characterization.

An in-depth characterization is required to obtain the fine details ascribe to these thermal treatments. The implementation of Machine Learning routine to process HR-TEM images will provide a spatial distribution of each phase which will help determining the crystallography of the surface at the nanoscale.

Conclusion

In summary, the structural analysis highlights the morphological changes of Cu2O nanocubes under different oxidation conditions, with uncontrolled atmospheres leading to progressive oxidation while controlled treatments maintain morphology with a hollow structure. Further investigations are necessary to fully elucidate these phenomena. Additionally, observations in H2 atmosphere indicate a temperature-dependent morphological changes. Efforts to enhance accuracy in copper oxidation state studies through advanced methodologies are underway, promising deeper insights into nanomaterial behaviour.

Graphic:



Keywords:

Copper oxide, nanocubes, EELS, HR-TEM

Reference:

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