

## Electronic Supplementary Information (ESI)

Green Synthesis of Starch-capped Cu<sub>2</sub>O Nanocubes and Their Application  
in the Direct Electrochemical Detection of Glucose

Antonio Jiménez-Rodríguez,<sup>a</sup> Eduardo Sotelo,<sup>a</sup> Lidia Martínez,<sup>b</sup> Yves Huttel,<sup>b</sup> María Ujué González,<sup>c</sup> Alvaro Mayoral,<sup>d,e,f</sup> José Miguel García-Martín,<sup>c</sup> Marcelo Videa<sup>a,\*</sup> and Jorge L. Cholula-Díaz<sup>a,\*\*</sup>

<sup>a</sup> *School of Engineering and Sciences, Tecnológico de Monterrey, Eugenio Garza Sada 2501, Monterrey 64849, NL, Mexico.*

<sup>b</sup> *Materials Science Factory. Instituto de Ciencia de Materiales de Madrid, ICMN-CSIC, Sor Juana Inés de la Cruz 3, Madrid 28049, Spain.*

<sup>c</sup> *Instituto de Micro y Nanotecnología, IMN-CNM, CSIC (CEI UAM+CSIC), Isaac Newton 8, Tres Cantos 28760, Spain.*

<sup>d</sup> *Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Pedro Cerbuna, 50009, Zaragoza, Spain.*

<sup>e</sup> *Center for High-Resolution Electron Microscopy (C<sub>H</sub>EM), School of Physical Science and Technology (SPST), ShanghaiTech University, 393 Middle Huaxia Road, Pudong, Shanghai, 201210, China.*

<sup>f</sup> *Laboratorio de Microscopias Avanzadas (LMA), Universidad de Zaragoza.*

\* Corresponding author: [mvidea@tec.mx](mailto:mvidea@tec.mx)

\*\* Corresponding author: [jorgeluis.cholula@tec.mx](mailto:jorgeluis.cholula@tec.mx)

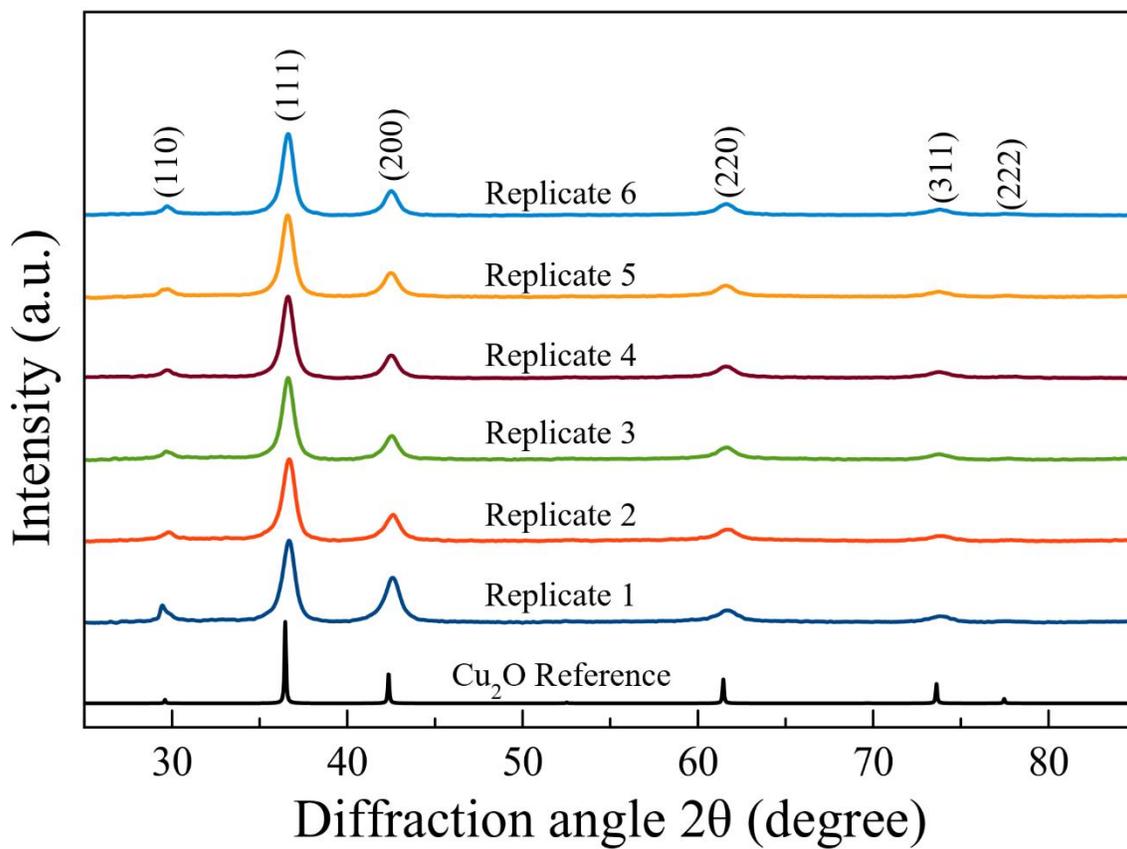


Figure S1. XRD patterns of replicates of Cu<sub>2</sub>O nanocubes fabricated with 1 mL of a 1% m/v starch solution from a total measurement of  $N = 6$  and a Cu<sub>2</sub>O reference [1]. Miller indexes corresponding to cubic phase with space group  $Pn\bar{3}m$ .

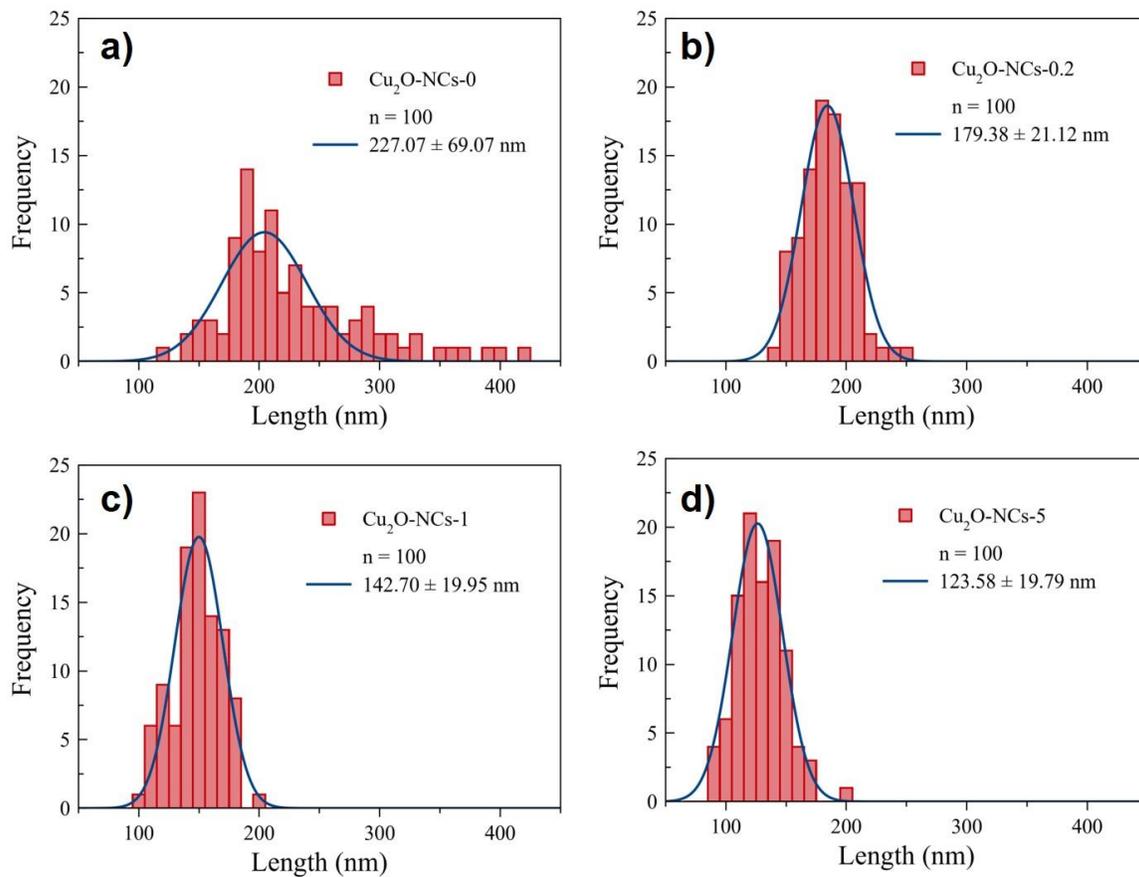


Figure S2. Size distribution of edge lengths of  $\text{Cu}_2\text{O}$  nanocubes ( $N = 100$ , in each case) synthesized (a) without starch, (b) 0.2 mL, (c) 1 mL and (d) 5 mL of a 1% w/v starch solution.

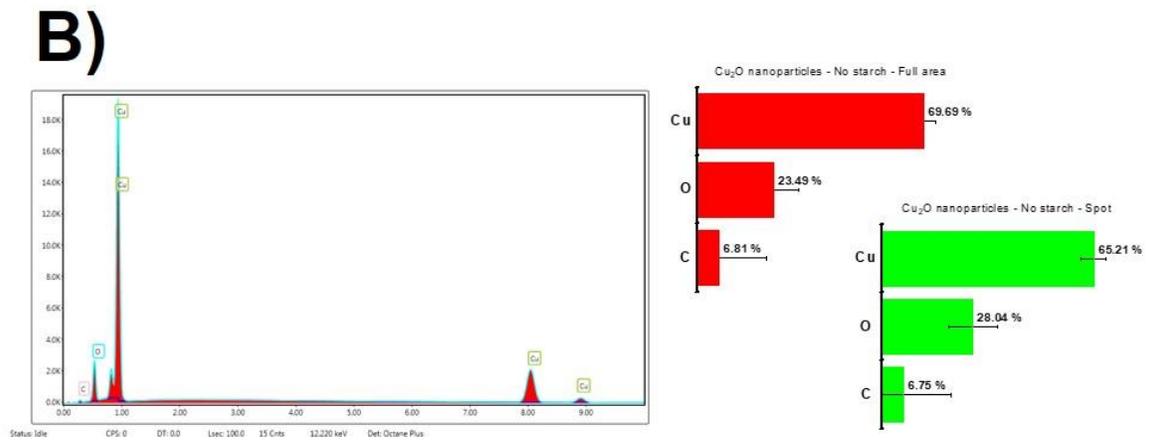
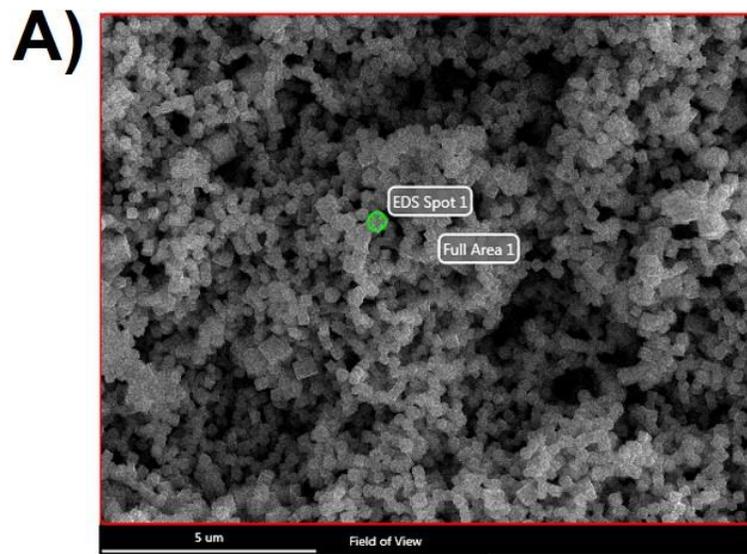
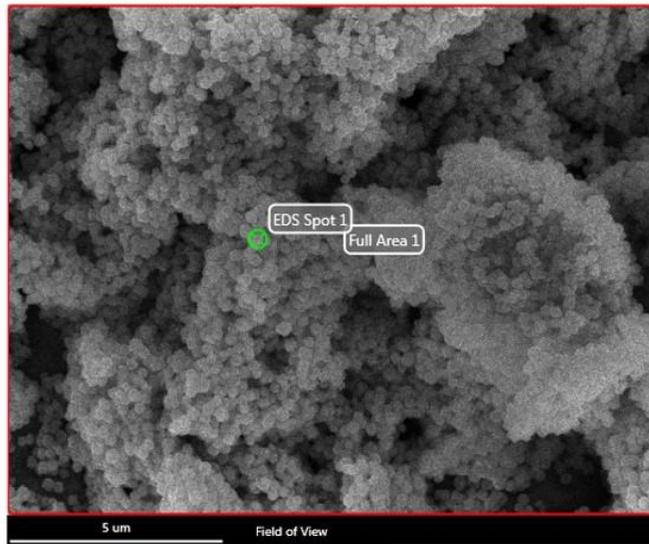


Figure S3. EDX analysis of sample Cu<sub>2</sub>O-NCs-0 (without starch). A) SEM image; B) EDX spectrum and chemical composition analysis.

A)



B)

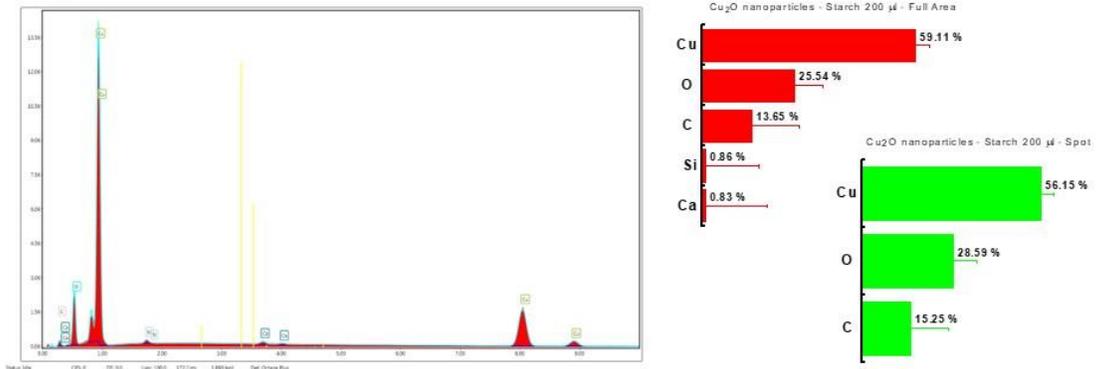
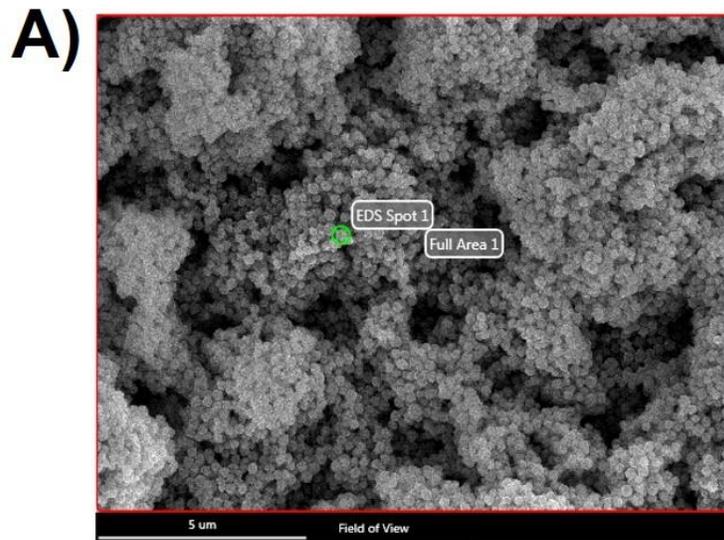


Figure S4. EDX analysis of sample Cu<sub>2</sub>O-NCs-0.2 (with 0.2 mL of a 1% w/v starch solution). A) SEM image; B) EDX spectrum and chemical composition analysis.



**B)**

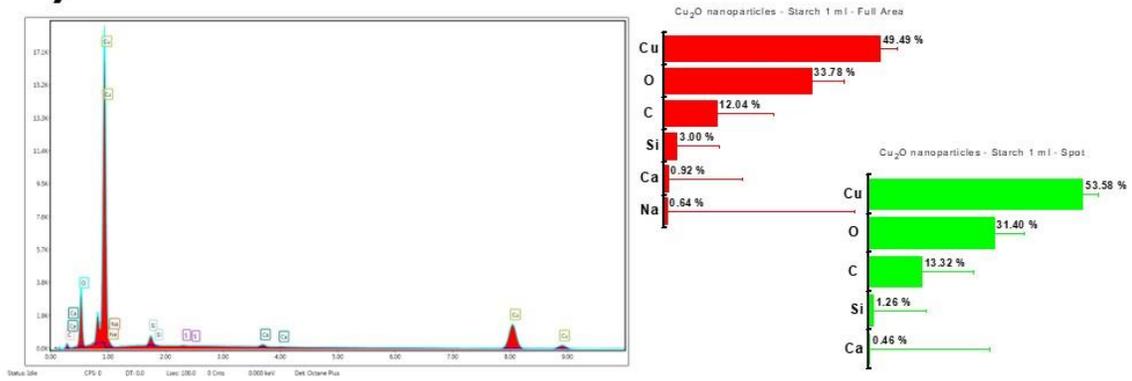
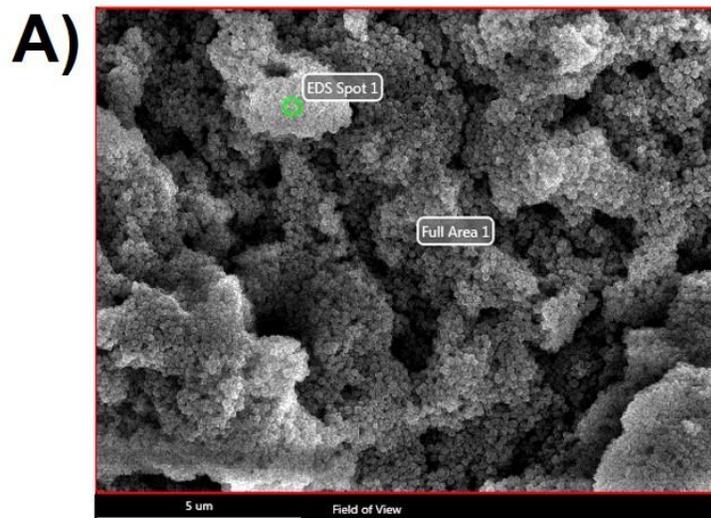


Figure S5. EDX analysis of sample Cu<sub>2</sub>O-NCs-1 (with 1 mL of a 1% w/v starch solution). A) SEM image; B) EDX spectrum and chemical composition analysis.



**B)**

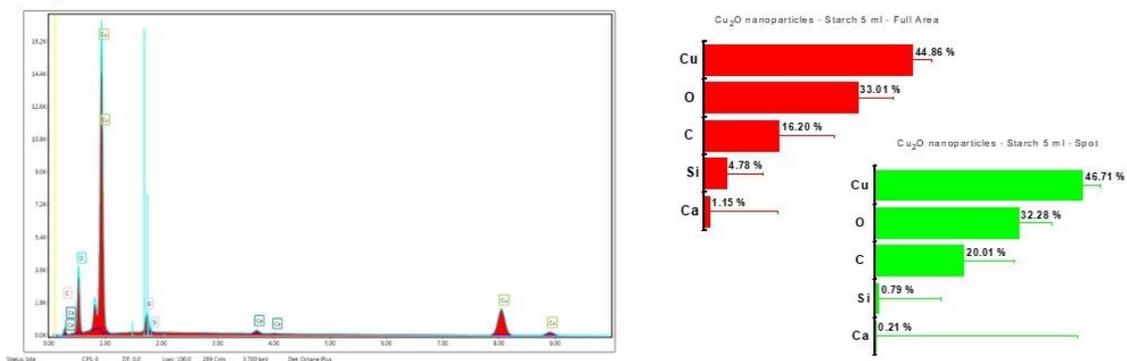


Figure S6. EDX analysis of sample Cu<sub>2</sub>O-NCs-5 (with 5 mL of a 1% w/v starch solution). A) SEM image; B) EDX spectrum and chemical composition analysis.

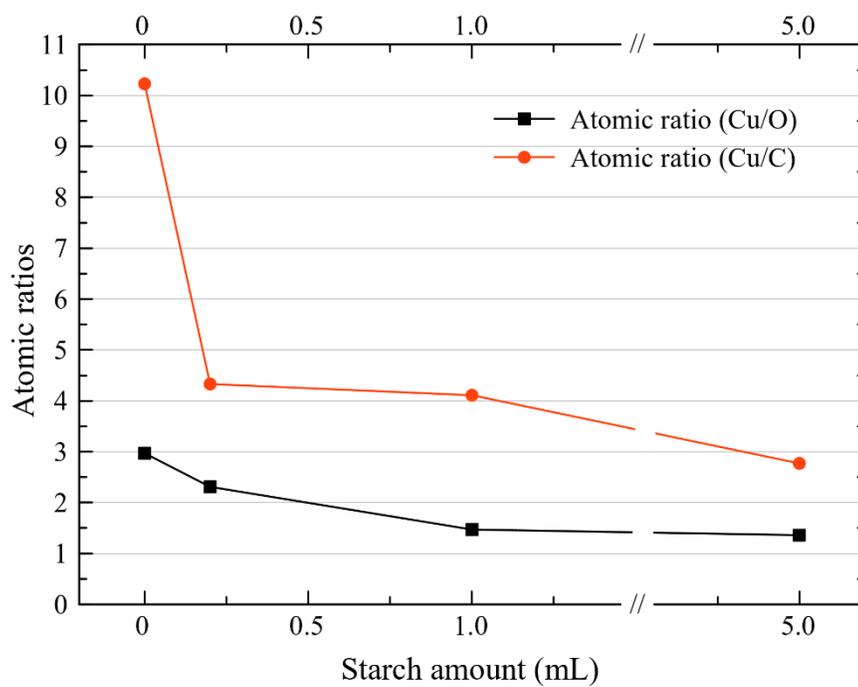


Figure S7. Atomic ratios Cu/O and Cu/C deduced from EDX experiments as a function of the amount of starch solution.

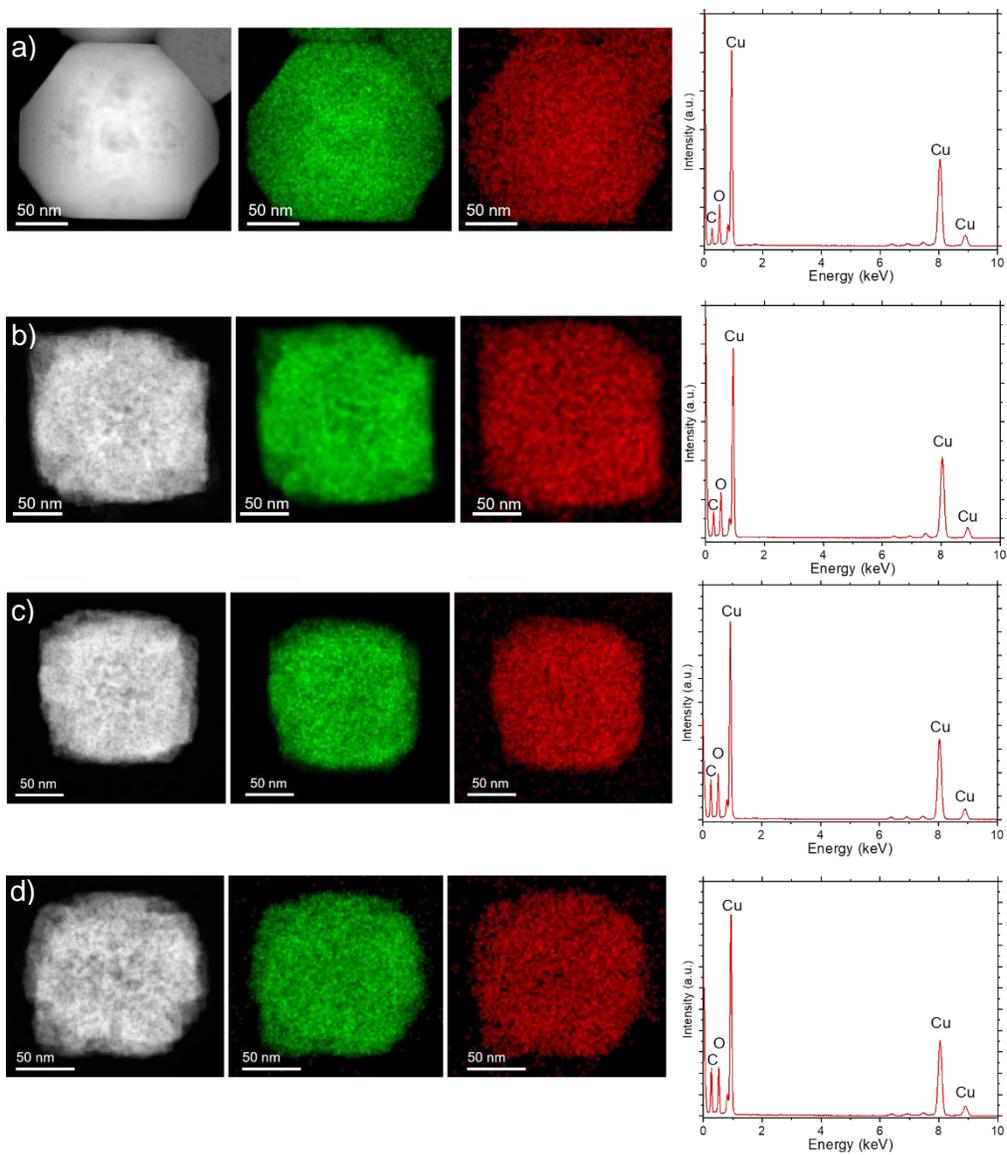


Figure S8. Chemical analysis of  $\text{Cu}_2\text{O}$  nanocubes synthesized (a) without starch ( $\text{Cu}_2\text{O}$ -NCs-0), with (b) 0.2 mL ( $\text{Cu}_2\text{O}$ -NCs-0.2), (c) 1 mL ( $\text{Cu}_2\text{O}$ -NCs-1) and (d) 5 mL ( $\text{Cu}_2\text{O}$ -NCs-5) of a 1% w/v starch solution. In each set, the respective EDX spectrum is presented. Color code: Cu in green and O in red.

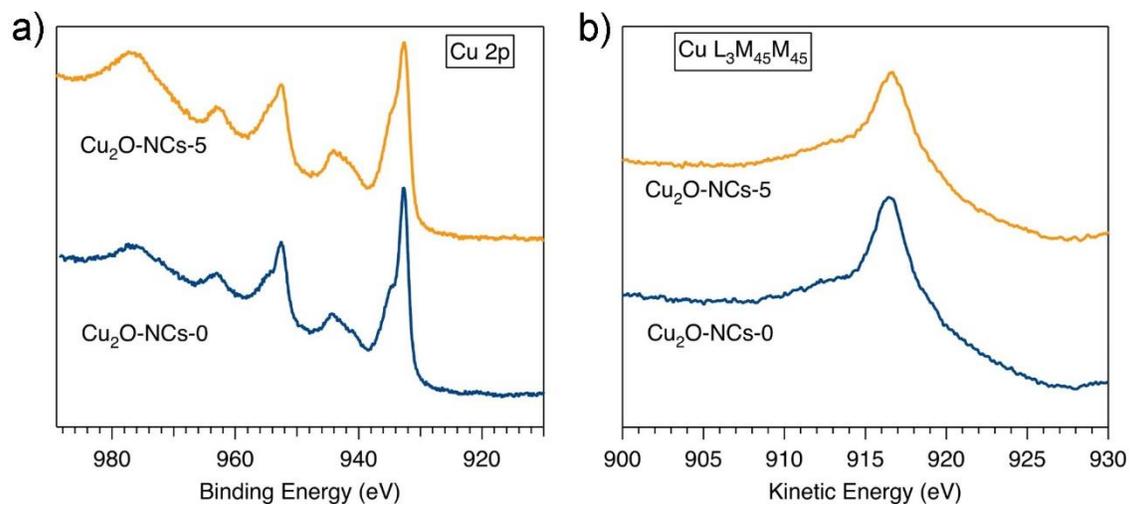


Figure S9. a) Cu 2p core level and b) Cu<sub>LMM</sub> Auger peak of the samples with and without starch (Cu<sub>2</sub>O-NCs-5 and Cu<sub>2</sub>O-NCs-0, respectively).

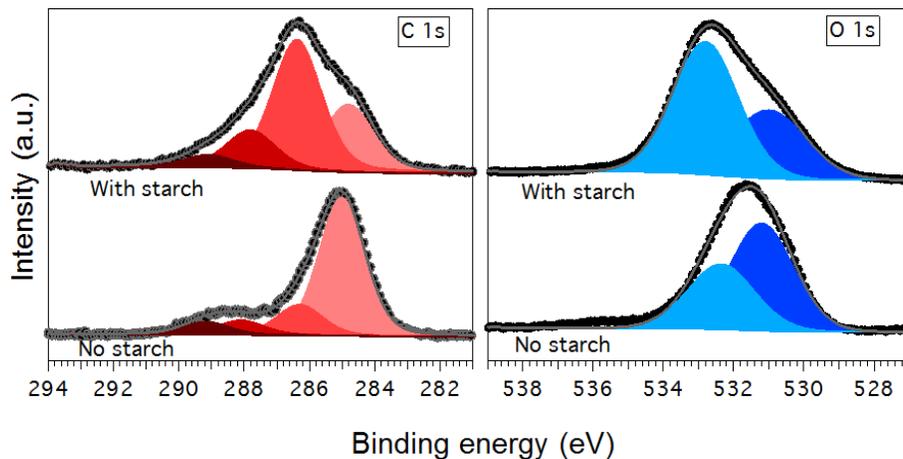


Figure S10. (left) C 1s and (right) O 1s core level peaks of the samples with and without starch (Cu<sub>2</sub>O-NCs-5 and Cu<sub>2</sub>O-NCs-0, respectively).

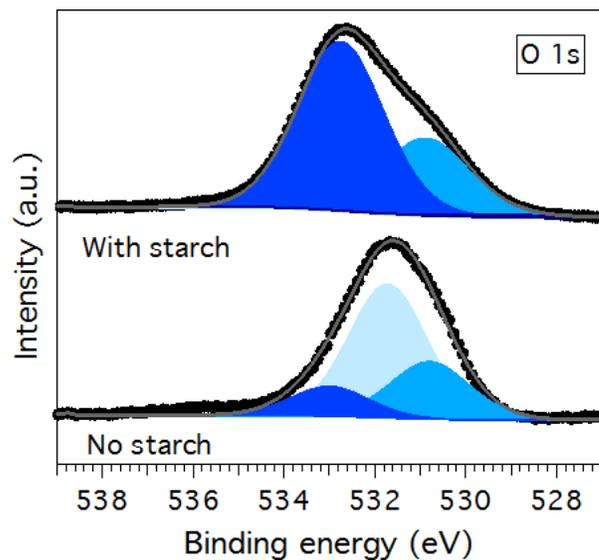


Figure S11. Alternative O 1s core level analysis of the samples with and without starch (Cu<sub>2</sub>O-NCs-5 and Cu<sub>2</sub>O-NCs-0, respectively), forcing the fitting with components associated to CuO and CuOH.

Table S1. Components used for the fitting of the C 1s and O 1s core levels.

	O1	O2	C-C/C-H	C-O	C=O	O-C=O
Cu <sub>2</sub> O-NCs-0	35.1	64.9	69.4	16.0	7.7	6.9
Cu <sub>2</sub> O-NCs-5	16.4	83.6	26.3	53.1	15.5	5.1

## Non-linear fit of the response of the current as a function of glucose concentration.

As the expectation is that the sensor response to be linear with respect to the concentration of glucose, the practice is to fit a straight line, but the data obtained with our copper oxide-based nanomaterials at different amounts of starch can alternatively be described with a function such as the Langmuir isotherm [2]. This can be shown in more detail in the following log-log plot (Figure S12). The solid lines are fits to the following expression (Equation S1):

$$i = \frac{A[\text{glucose}]}{1 + B[\text{glucose}]}$$

which illustrates the curvature in the data for Cu<sub>2</sub>O-NCs-1 and Cu<sub>2</sub>O-NCs-5.

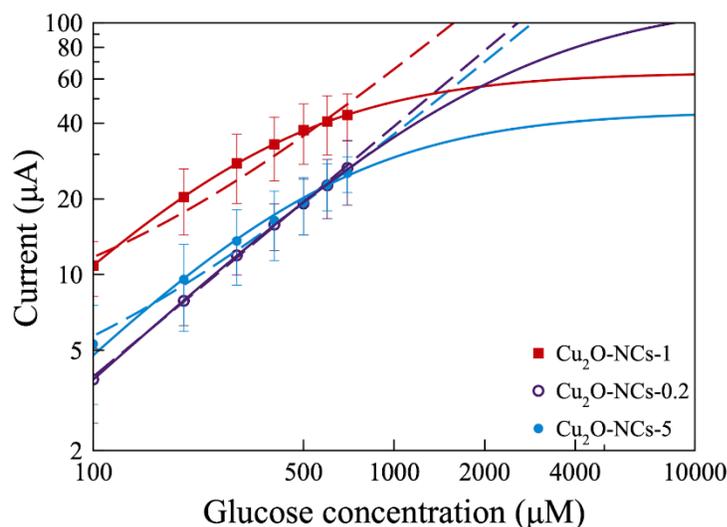


Figure S12. The dashed and solid lines correspond to linear and non-linear fits, respectively, obtained from current measured at 0.60 V vs. Ag|AgCl with Cu<sub>2</sub>O NCs synthesized using different amount of a 1% w/v starch solution, in the range from 100 to 700 µM of glucose (same experimental data as in Figure 10 in the main manuscript). Each point on the calibration curve represents the average value for three independent measurements with error bars showing the standard deviation for each set of measurements.

It seems to be that a saturation of the active sites in the nanomaterials was presented, suggesting an adsorption step in the oxidation of glucose in the concentration range studied. When a non-linear fit is carried out using a Langmuir expression, as is shown in Figures 10 and S12, we obtain a better description for the data. This is significant for Cu<sub>2</sub>O-NCs-1 (synthesized with 1 mL starch), but less important for the copper oxides produced with 5 mL of starch and not significant for the sample prepared with 0.2 mL starch.

The following table summarizes the fitting parameters obtained for the model. From these parameters a maximum measurable current and the concentration of glucose that saturates half of the active surface of the electrode ( $[\text{glucose}]_{0.5}$ ) can be estimated.

Table S2. Best fitting parameters obtained for the experimental data depicted in Figure S12 using the model described in Equation S1.

Sample	$A/\mu\text{A } \mu\text{M}^{-1}$	$B/10^{-3} \mu\text{M}^{-1}$	$i_{\text{max}} / \mu\text{A}$	$[\text{glucose}]_{0.5}/\mu\text{M}$
Cu <sub>2</sub> O-NCs-0	0.0253	0.217	116.7	4606
Cu <sub>2</sub> O-NCs-0.2	0.0401	0.075	535.7	13369
Cu <sub>2</sub> O-NCs-1	0.129	1.494	86.2	669
Cu <sub>2</sub> O-NCs-5	0.0553	0.779	71.0	1283

## References

- [1] A. Kirfel, K. Eichhorn, Accurate Structure Analysis with Synchrotron Radiation. The Electron Density in Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O. *Acta Crystallographica Section A*, A46 (1990) 271–284. DOI: <https://doi.org/10.1107/S0108767389012596>.
- [2] X. Strakosas, J. Selberg, P. Pansodtee, N. Yonas, P. Manapongpun, M. Teodorescu, M. Rolandi. A non-enzymatic glucose sensor enabled by bioelectronic pH control. *Scientific Reports* 9 (2019) 10844. DOI: <https://doi.org/10.1038/s41598-019-46302-9>.