

Supplementary Material

The facile microwave-assisted coprecipitation route to obtain polyoxoniobate ($\text{Na}_7(\text{H}_3\text{O})\text{Nb}_6\text{O}_{19.14}\text{H}_2\text{O}$) nanorods modified with copper for CO_2 photoreduction

Joelma R. C. Souza¹, Juliana A. Torres², Lucas S. Ribeiro³, Jose B. G. Filho¹, Fabiana L. Santos¹, Nicholas Malgioglio⁴, Luiz Fernando Gorup^{2,5,6}, Alexandre H. Pinto^{4*}, André E. Nogueira^{1*}

¹Department of Chemistry, Institute of Exact and Biological Sciences (ICEB), Federal University of Ouro Preto—UFOP, Ouro Preto 35400-000, Brazil

²Embrapa Instrumentation, São Carlos 13560-970, Brazil; julianaarriel@hotmail.com

³Interdisciplinary Laboratory of Electrochemistry and Ceramics (LIEC), Department of Chemistry, UFSCar—Federal University of São Carlos, São Carlos 13565-905, Brazil

⁴Department of Chemistry & Biochemistry, Manhattan College, 4513 Manhattan College Parkway, Riverdale, NY 10471, USA

⁵ Institute of Chemistry, Federal University of Alfenas, Alfenas 37130-001, Brazil

⁶ School of Chemistry and Food Science, Federal University of Rio Grande. Rio Grande 96203-900, Brazil

*Correspondence: alex.pinto@manhattan.edu (A.H.P.); andre.esteves@ufop.edu.br (A.E.N.);

Tel.: +1-718-862-7211 (A.H.P.); +55-31-3559-1707 (A.E.N.)

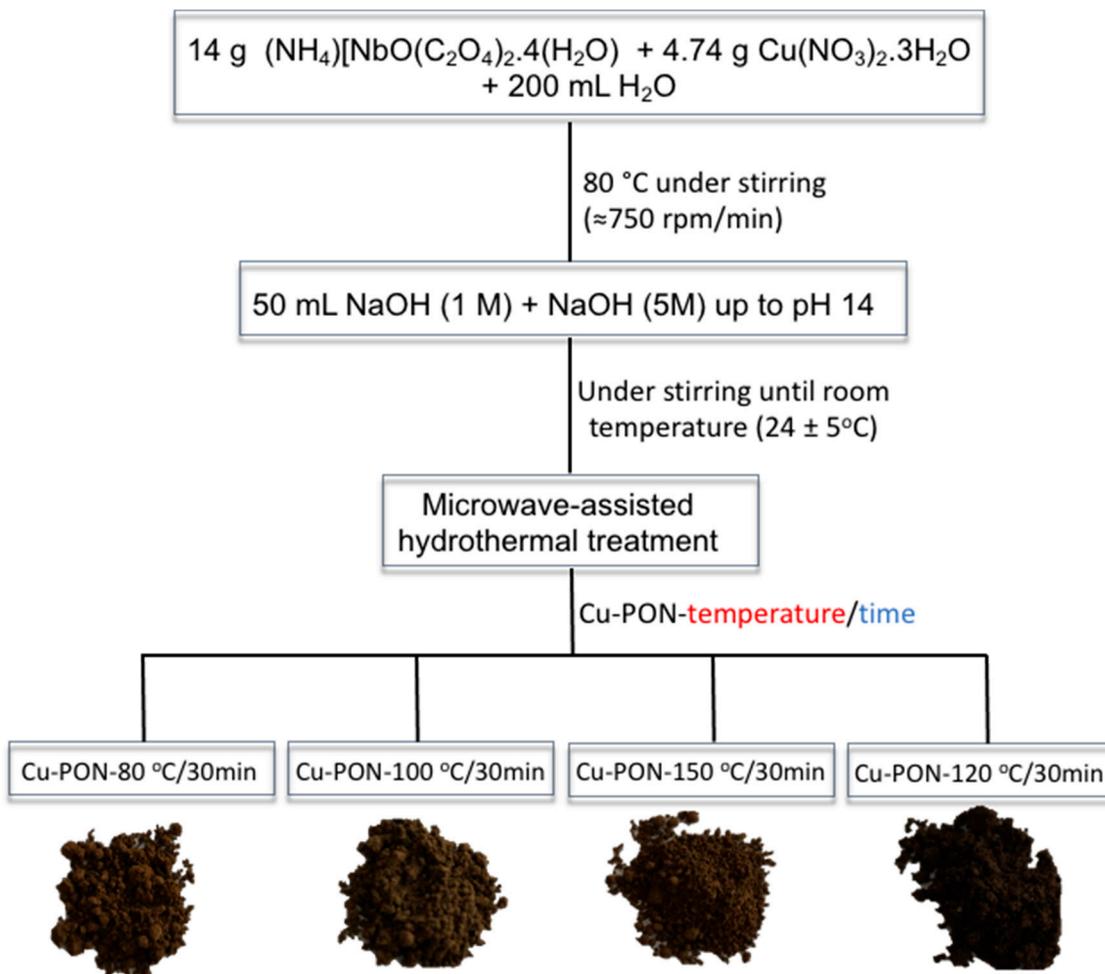


Figure S1. Flowchart of the synthesis process to obtain the pristine polyoxoniobate modified with copper.

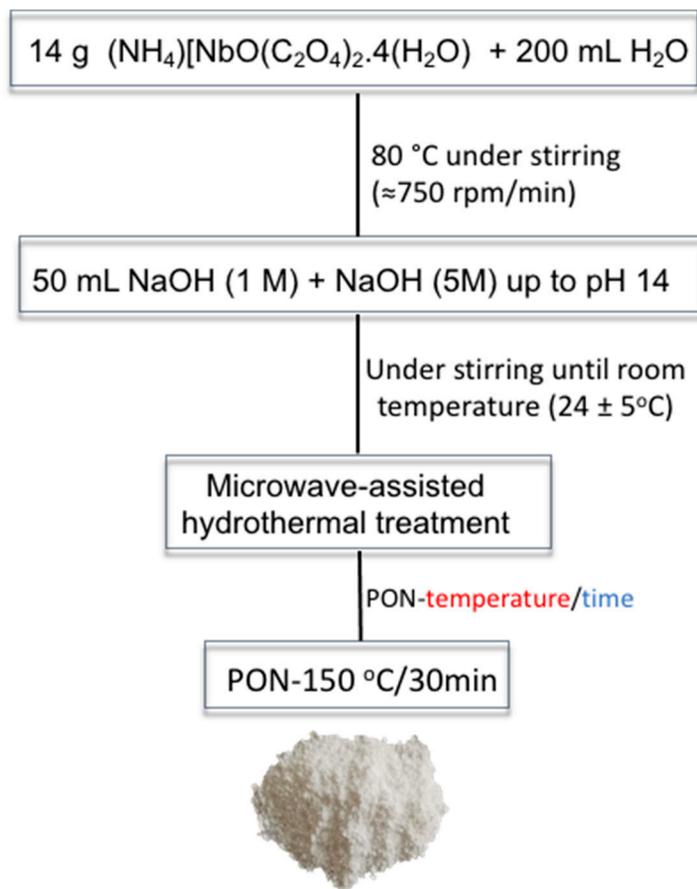


Figure S2. Flowchart of the synthesis process to obtain the pristine polyoxoniobate.

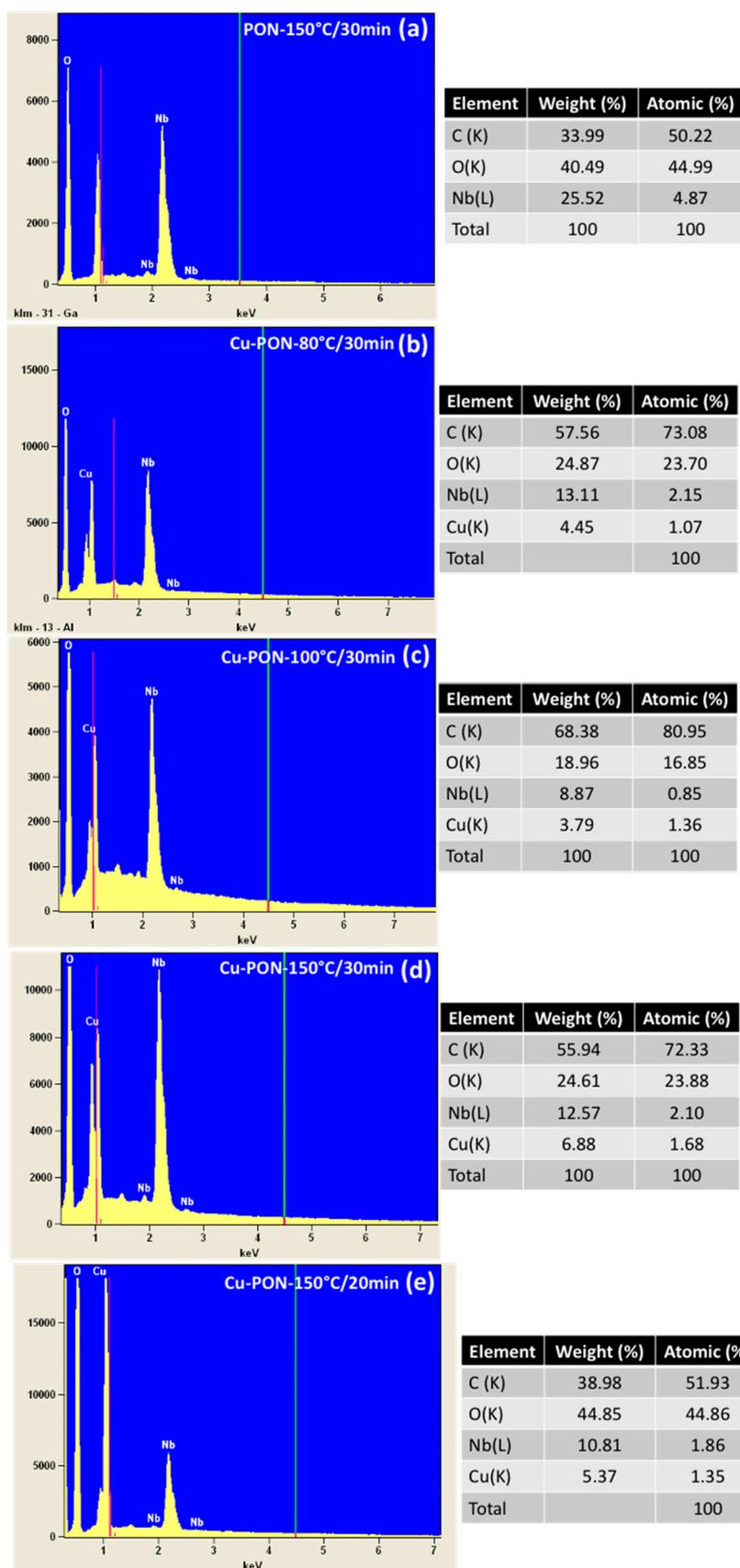


Figure S3. EDS spectra of the synthesized materials: (a) PON-150°C/30min, (b) Cu-PON-80°C/30min, (c) Cu-PON-100°C/30min, (d) Cu-PON-150°C/30min and (e) Cu-PON-150°C/20min.

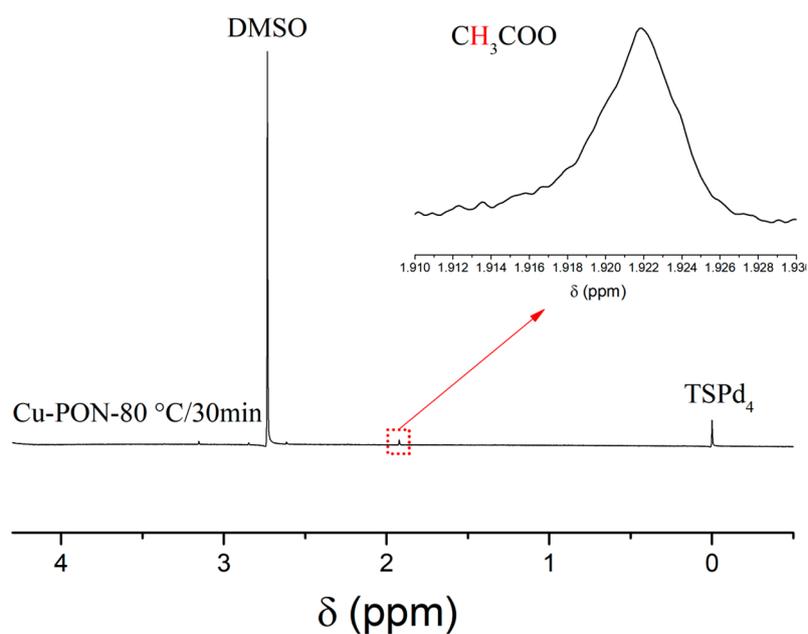


Figure S4. NMR spectrum acetate obtained in the liquid phase after CO₂ photoreduction with Cu-PON-80 °C/30 min.

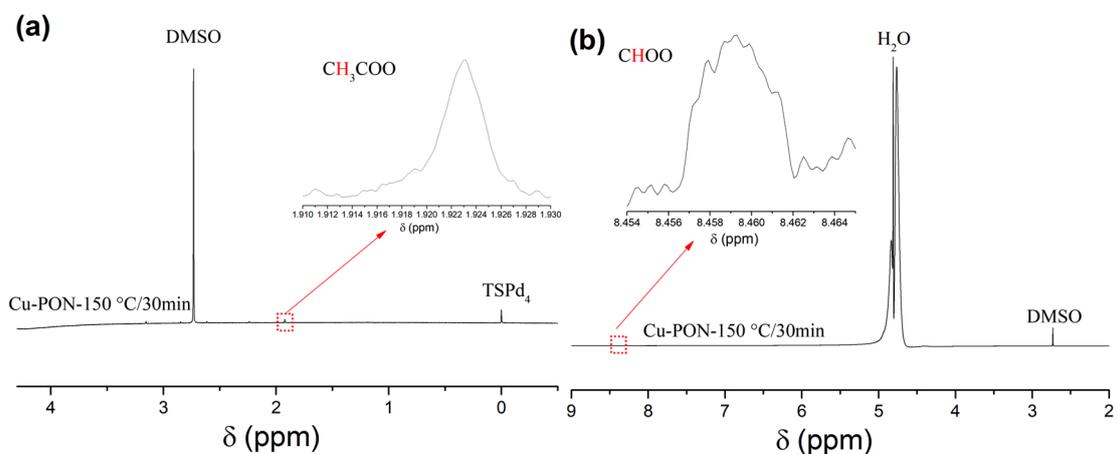


Figure S5. NMR spectrum of the products obtained in the liquid phase after CO₂ photoreduction with Cu-PON-150 °C/30 min: (a) acetate, and (b) formate.

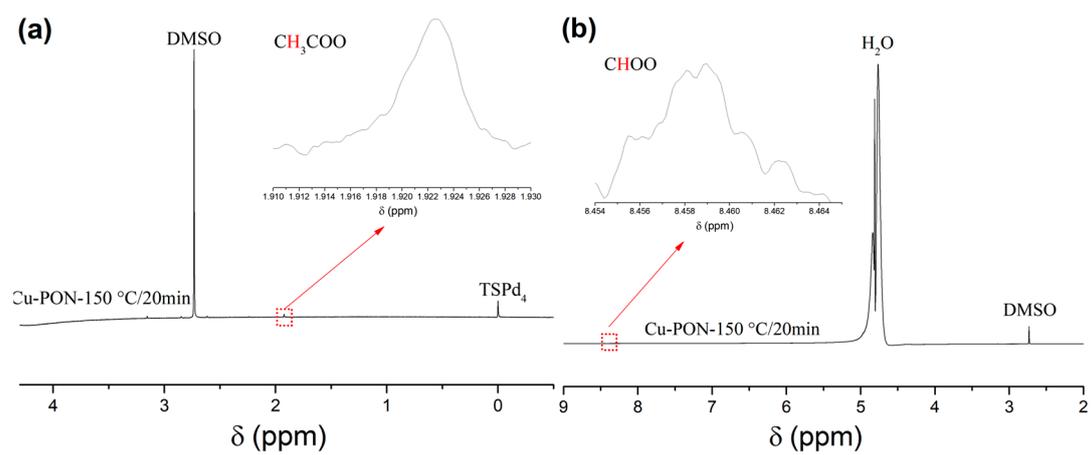


Figure S6. NMR spectrum of the products obtained in the liquid phase after CO_2 photoreduction with Cu-PON-150 $^\circ\text{C}/20\text{ min}$: (a) acetate, and (b) formate.

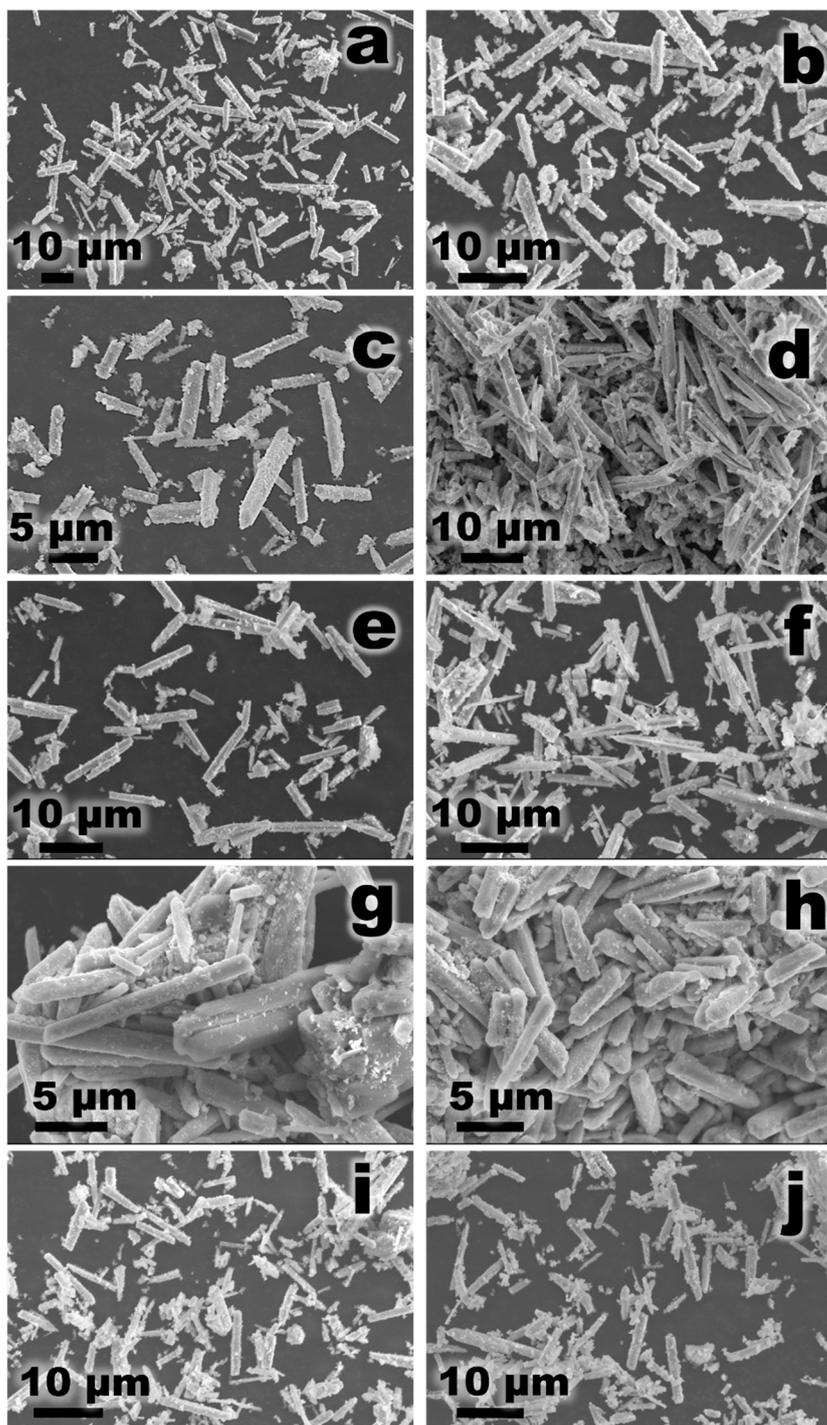


Figure S7. SEM micrographs of nanoparticles (a-b) PON-150 °C/30 min; (c-d) Cu-PON-80 °C/30 min; (e-f) Cu-PON-100 °C/30 min; (g-h) Cu-PON-150 °C/20 min; (i-j) Cu-PON-150 °C/30 min.

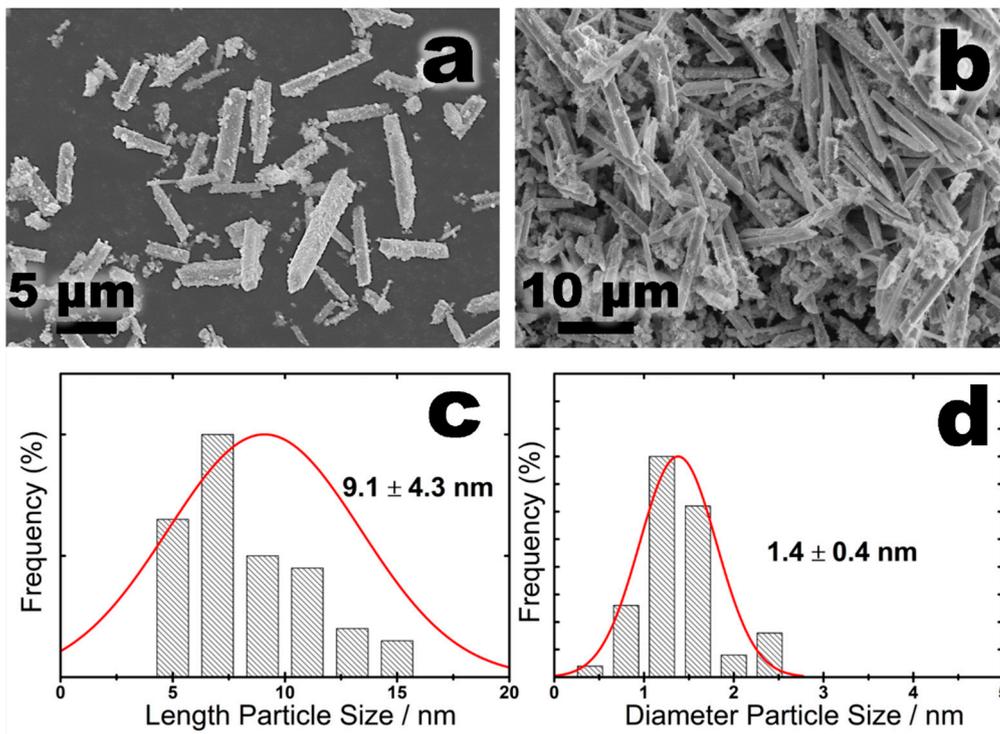


Figure S8. (a-b) SEM micrographs of nanoparticles CU-PON-80 °C/30 min; (c-d) Histogram showing the length and width of nanoparticles

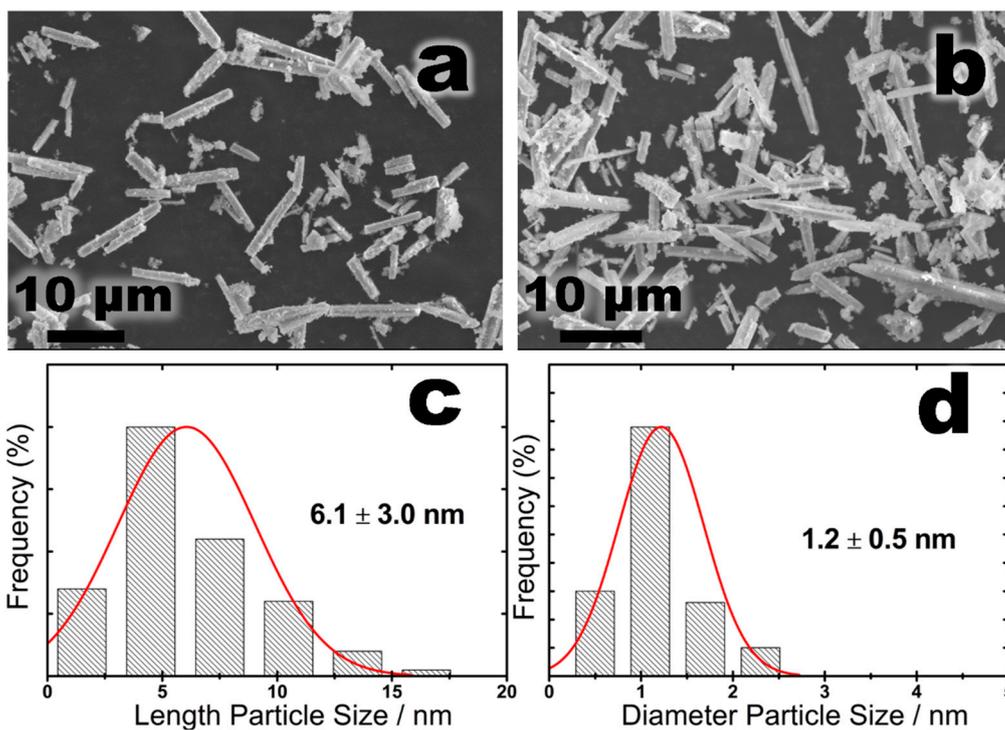


Figure S9. (a-b) SEM micrographs of nanoparticles CU-PON-100 °C/30 min; (c-d) Histogram showing the length and width of nanoparticles

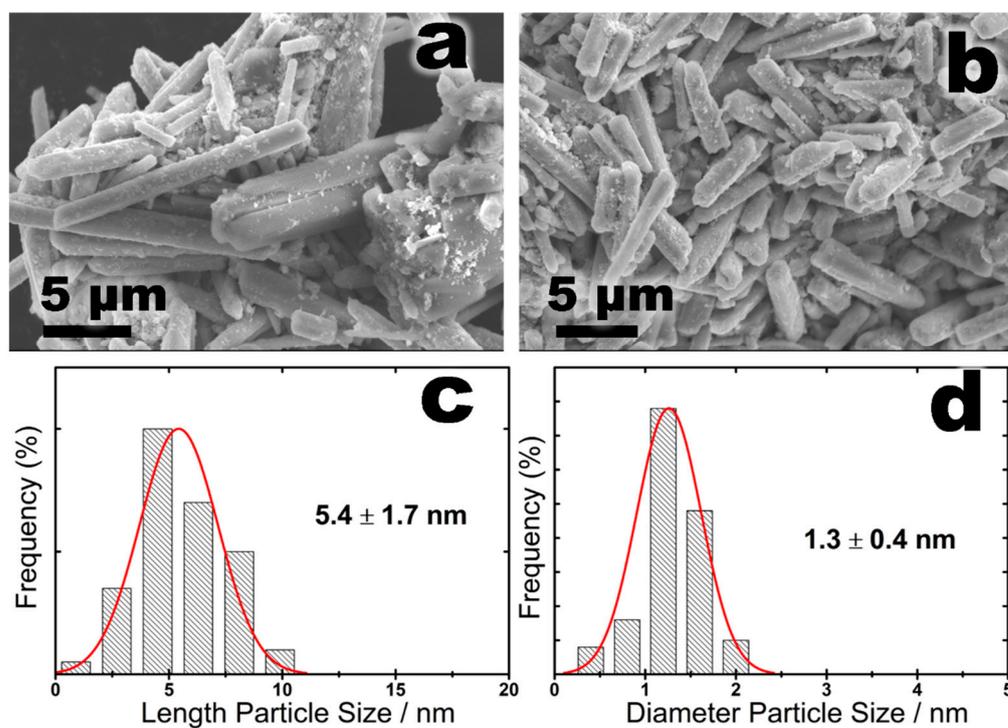


Figure S10. (a-b) SEM micrographs of nanoparticles Cu-PON-150 °C/20 min; (c-d) Histogram showing the length and width of nanoparticles

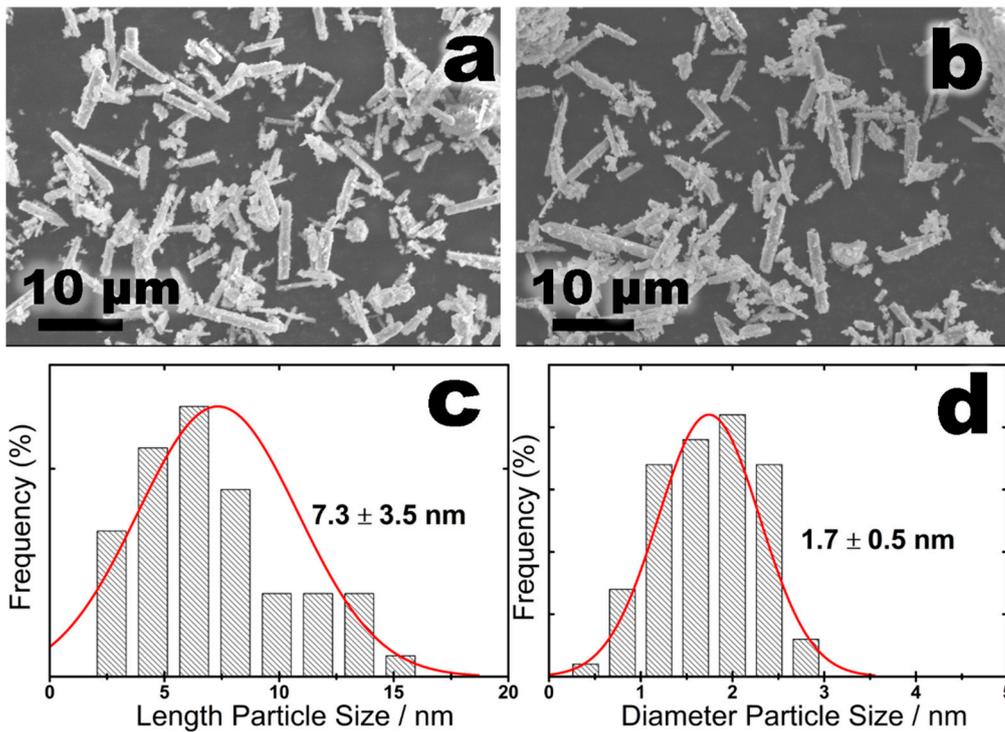


Figure S11. (a-b) SEM micrographs of nanoparticles Cu-PON-150 °C/30 min; (c-d) Histogram showing the length and width of nanoparticles

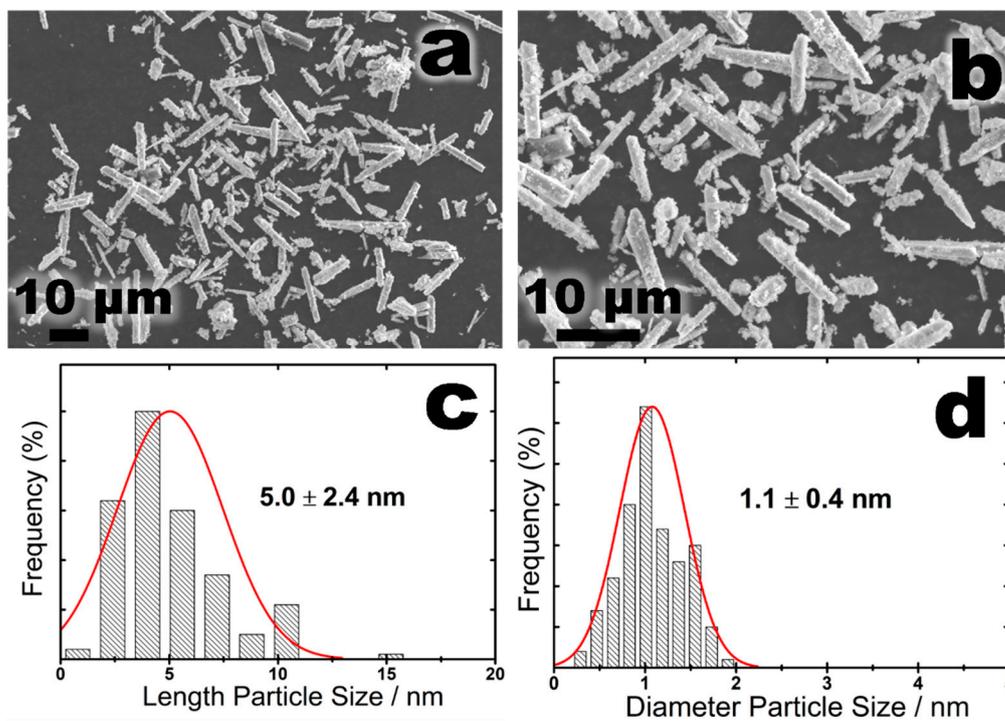


Figure S12. (a-b) SEM micrographs of nanoparticles PON-150 °C/30 min.; (c-d) Histogram showing the length and width of nanoparticles

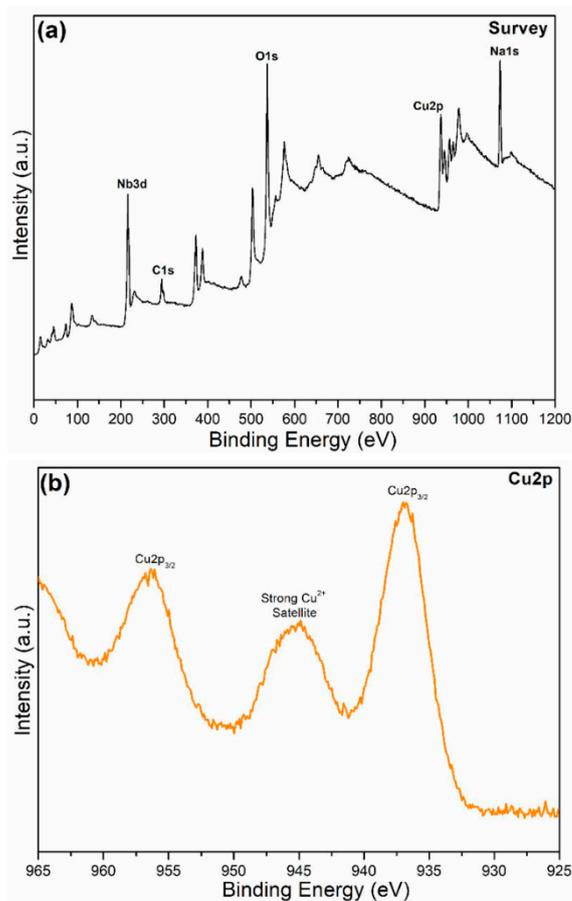


Figure S13. XPS spectra of Cu-PON-150 °C/30 min: (a) survey spectrum (b) Cu 2p.

We obtained useful information through spectral profiles, primarily concerning Cu2p. Our results indicate a 2⁺ oxidation state for copper in the material in question. Unfortunately, the technique used does not provide us with additional information about the specific form of copper incorporation in the material structure.

As mentioned in our article, to conclusively determine whether Cu was incorporated into the polyoxoniobate structure as a doping ion or a counterion, more advanced techniques such as X-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) would be required. However, due to the extensive time required to perform these analyses, we were unable to explore these complementary techniques.