Supporting Information

Chemical and Morphological Evolution of Copper Nanoparticles Obtained by Pulsed Laser Ablation in Liquid

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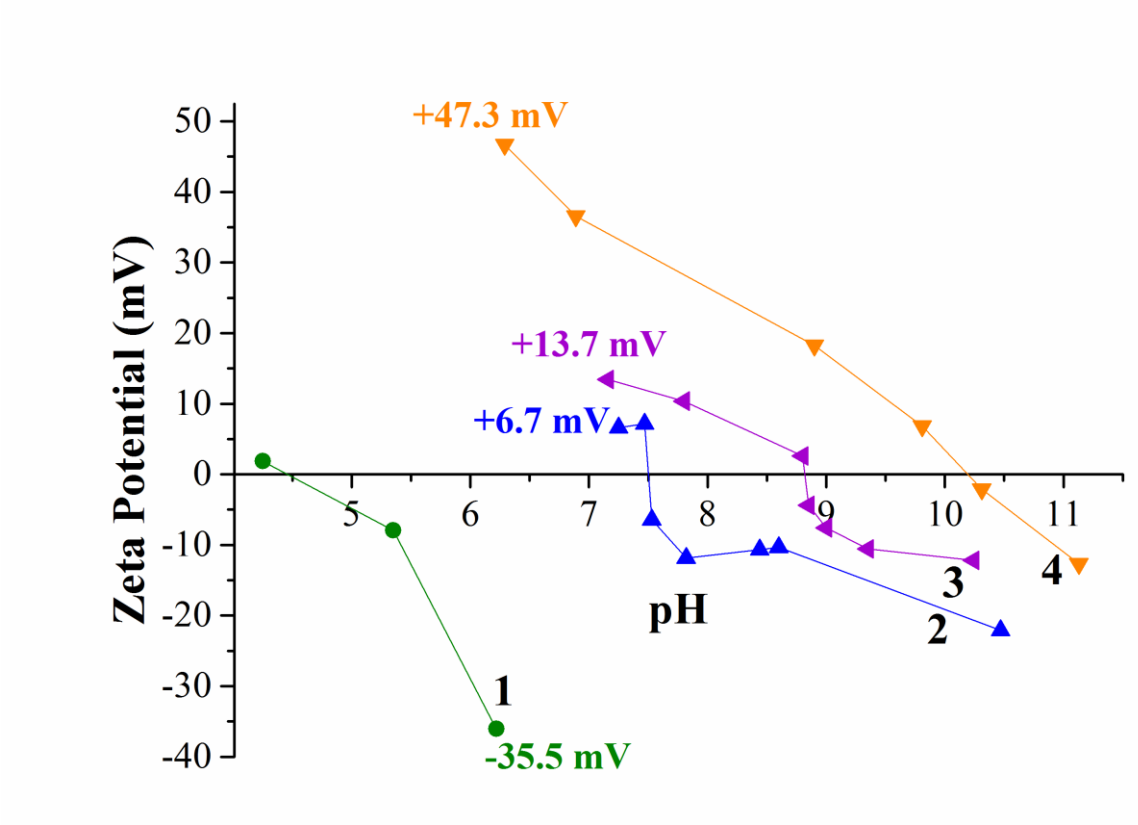

Figure S1. Titration curves in the pH-zeta coordinates of a colloidal solution Cu_2O (1), CuO prepared from $Cu(NO_3)_2$ (2) and $Cu(OH)_2$ (3), $Cu(OH)_2$ (4).

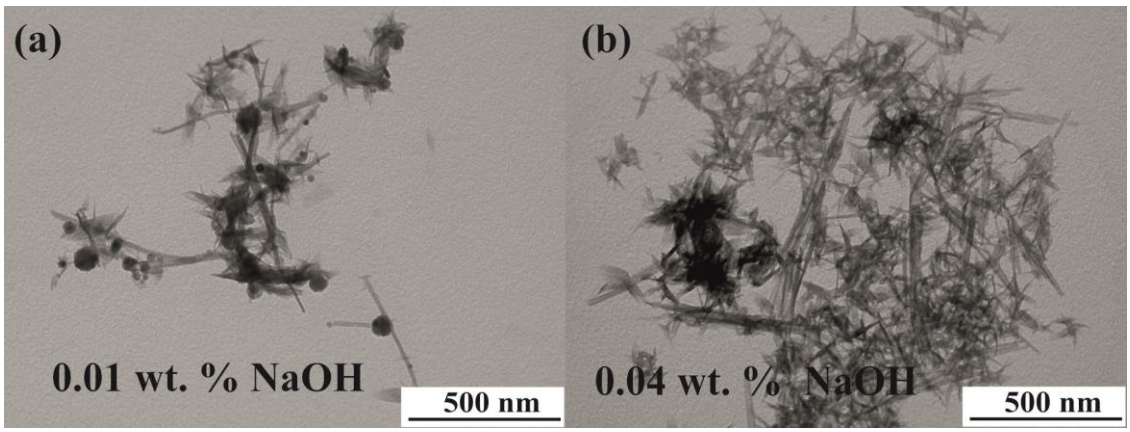

Figure S2. Typical TEM image of NPs of the fresh suspension obtained by PLA of copper in NaOH solution of 0.01 wt. % (a) and 0.04 wt. % (b).

The comparison of the morphology of the particles obtained in H_2O_2 and NaOH

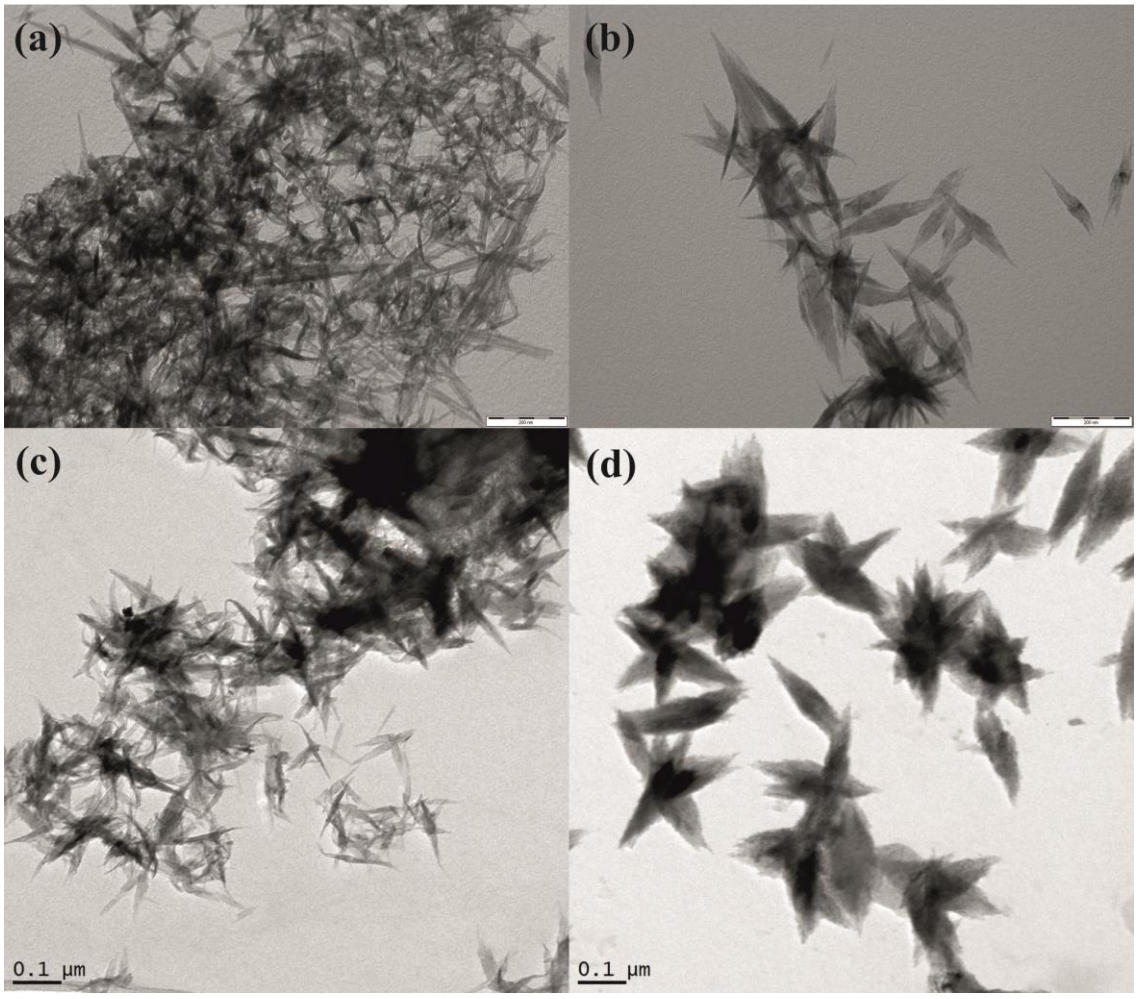

Figure S3. Typical TEM images for NPs obtained by PLA of copper in NaOH solution (a, c); Typical TEM images for NPs obtained by PLA of copper in H_2O_2 water solution (b, d) by electron microscope CM 12, Philips (Netherlands) (a, b) and a JEM-2200FS, JEOL (Japan) (c, d).

Study of NPs obtained by PLA of copper in ethanol covered by an amorphous phase

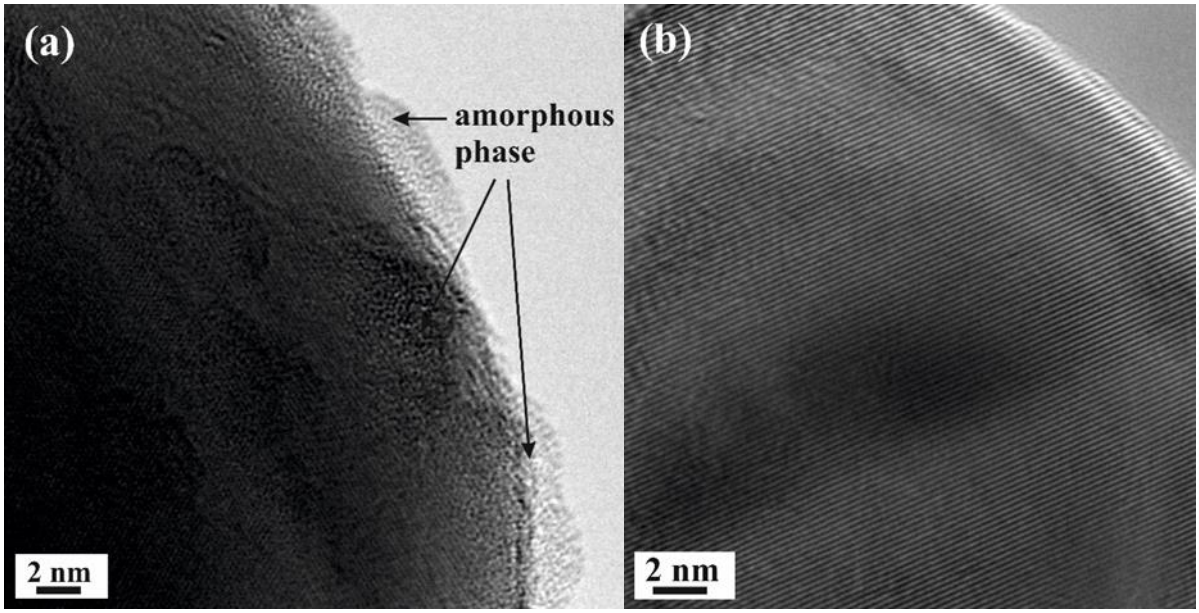

Figure S4. HR TEM images of NP obtained by PLA of copper in ethanol covered by an amorphous phase: initial (a) and after action of the electron beam (b).

Some NPs coated with an amorphous phase were observed during the sample examination by HR TEM (Figure S4). However, this amorphous phase was unstable and removed under the electron beam during examination. It was attributed to the ethanol adsorption layer on the particle surface. This was additionally confirmed by the IR spectroscopy of powder obtained by PLA of Cu in ethyl alcohol. (Figure S5). The corresponding IR spectrum contains bands at 1003, 1031, 1407, 1546, 2875 and 2917 cm^{-1} those are typical for ethanol adsorbed.[1]

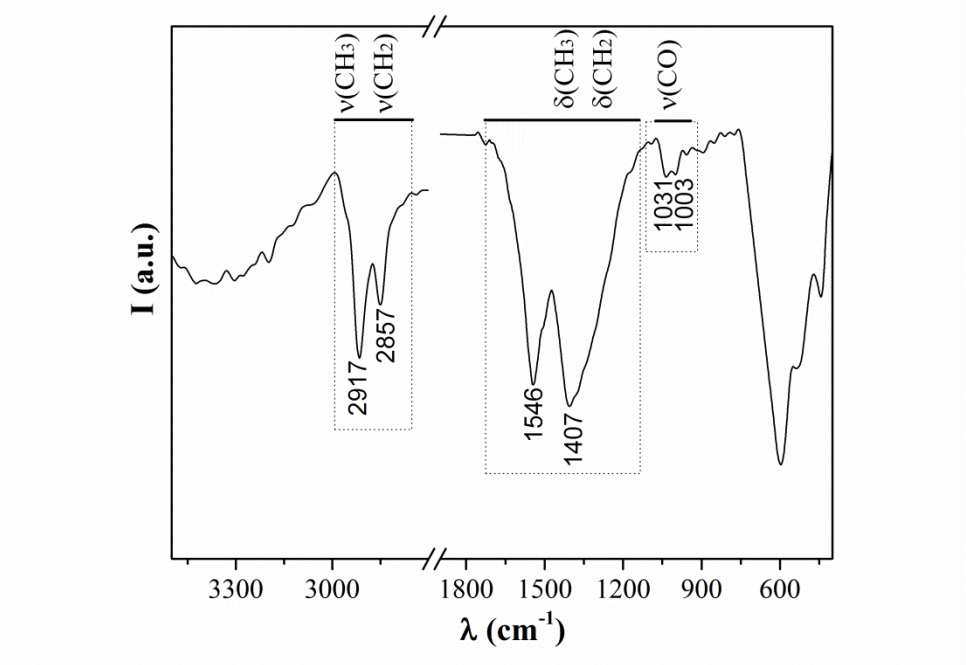

Figure S5. AT-FTIR spectrum of NPs obtained by PLA of Cu in ethyl alcohol.

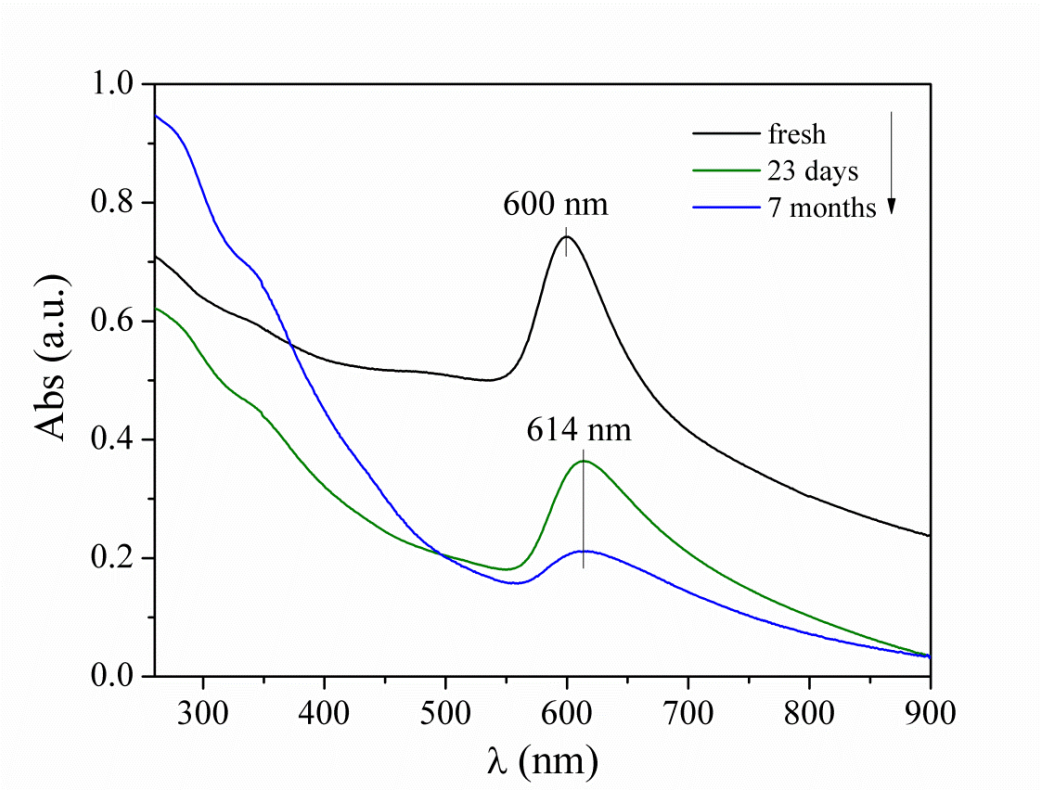

Figure S6. UV-vis spectra NPs obtained by Cu PLA in ethyl alcohol suspensions.

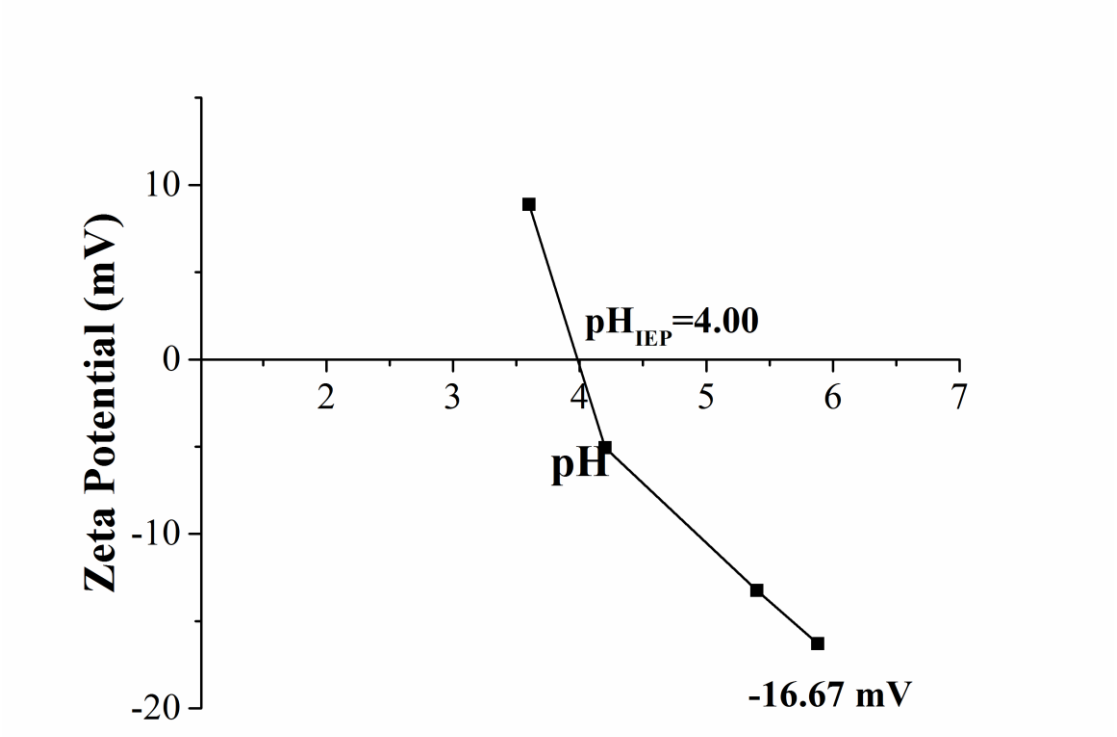

Figure S7. Zeta potential at different pH values for water suspension prepared using powder obtained by drying in ethanol suspension.

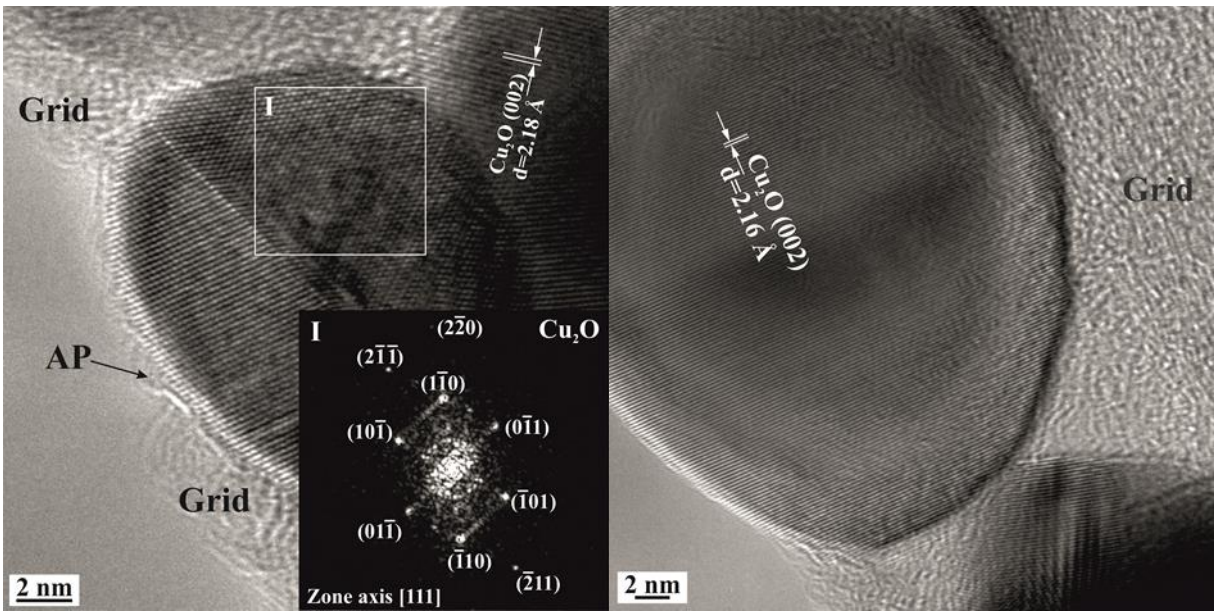

Figure S8. Typical HRTEM images and FFT pattern of NPs in the suspension aged for 48 hours obtained by Cu PLA in ethyl alcohol containing 20 wt.% water. AP is an amorphous phase due to ethanol adsorption.

Study of the evolution of the Cu NPs in the ethanol suspensions diluted with water

To study the evolution of the Cu NPs in the ethanol suspensions diluted with water, a fresh suspension prepared by PLA of copper in ethanol with concentration 200 mg/L was diluted 20 times with distilled water and ethanol in parallel. The diluted suspensions were analyzed by UV-Vis absorption spectroscopy for several days.

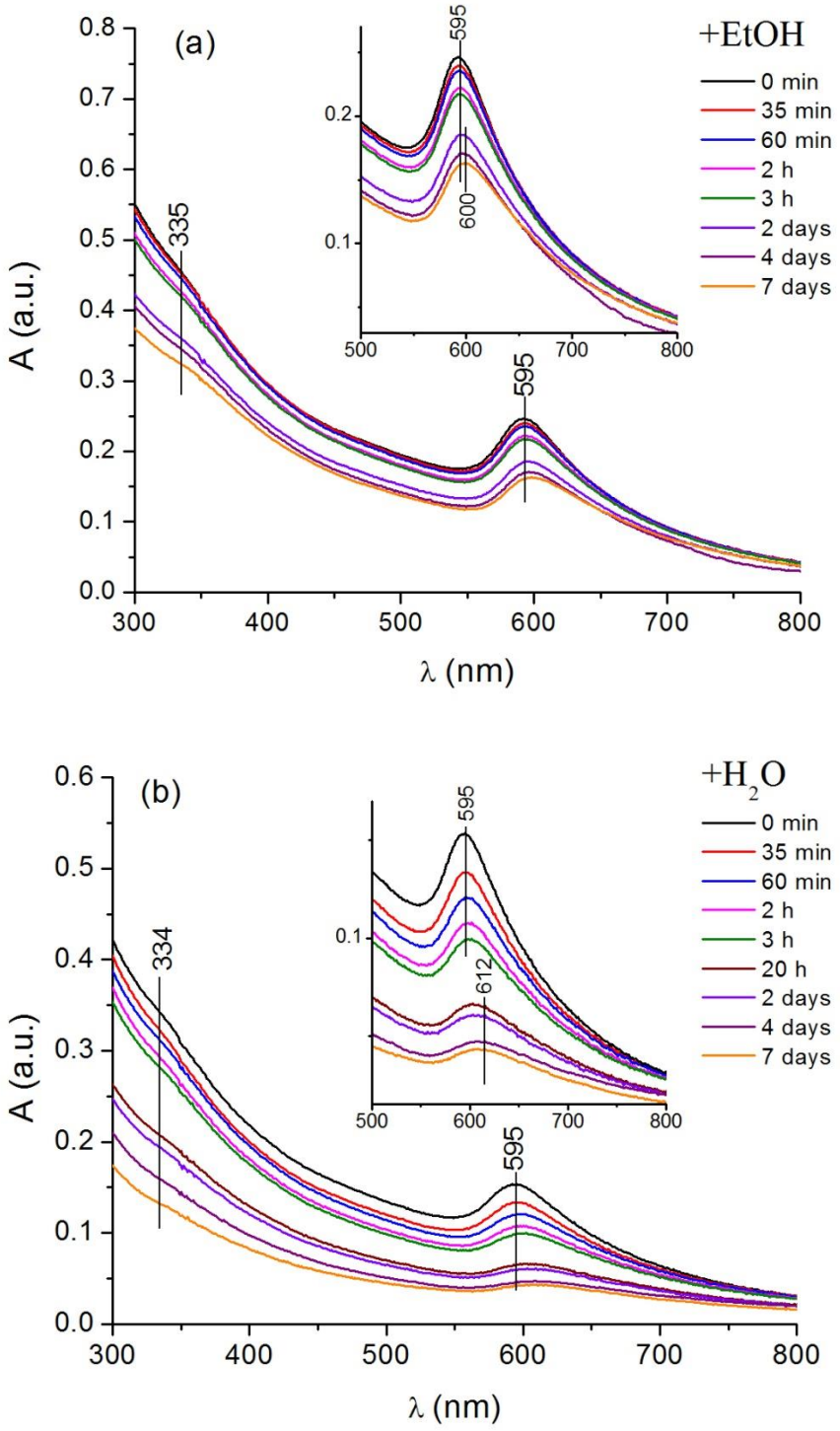

Figure S9. The absorption spectra of colloidal solutions obtained by PLA of copper in alcohol followed by 20 times dilution collapsed with ethanol (a) and water (b).

The results of the study are presented in Figure S9. The spectra of the initial suspensions are characterized by the intense peak of SPR absorption of Cu NPs at 595 nm with a sub-monolayer of Cu_2O and a broad extinction in the region of below 500 nm caused by scattering due to Tyndall effect as well as Cu_2O NPs presented in the sample. No significant changes are observed in the spectra of the suspension diluted with ethanol for 4 days (Figure S9a). Some drop in spectrum intensity associated with the agglomeration of the NPs takes place, but no shift of the SPR peak occurs. There is a slight shift of the SPR peak to 600 nm indicating a slow oxidation of the particles in the spectrum of the suspension after 7 days. However, the position of the peak corresponds to the formation of a thin (on or before monolayer) layer on the surface of Cu NPs.[2]

No significant changes are also observed in the spectra of suspension diluted with distilled water for 1 hour (Figure S9b). However, a noticeable shift of the SPR peak to 600 nm indicating the oxidation of Cu NPs to form Cu_2O up to a monolayer[2] is observed already after in 2–3 hours. For a longer time (> 20 h), A significant decrease of intensity of the SPR peak accompanied by its shift up to 612 nm and broadening are observed in spectra after 20 h and beyond, which is associated with the oxidation of Cu NPs with the formation of a thick (more than 2 monolayer) Cu_2O film[2] and CuO overlayer.

The data obtained confirms that the observed slow oxidation of Cu NPs in ethanol suspension can be caused by adsorption of ethanol molecules on NP surface preventing dissociative adsorption of oxygen on Cu as well as Cu_2O layer oxidation to CuO, which requires interaction of Cu^+ ions with surface OH groups. The high dilution of ethanol suspension with water results in partial or primarily desorption of ethanol from the particle surface, which results in respectively fast oxidation of copper particle.

On the other hand, the data obtained indicates that there is not significant particle oxidation during the first 1 h in the suspension diluted with water. This makes it possible to study the dependence of the zeta potential on the pH for the dispersion obtained in ethyl alcohol using suspensions diluted 20 times with distilled water.

References

(1) Caglar, B.; Olus Ozbek, M.; Niemantsverdriet, J. W. (Hans); Weststrate, C. J. (Kees-J. The Effect of C–OH Functionality on the Surface Chemistry of Biomass-Derived Molecules: Ethanol Chemistry on Rh(100). *PCCP* **2016**, *18* (43), 30117–30127.

(2) Cure, J.; Glaria, A.; Collière, V.; Fazzini, P.-F.; Mlayah, A.; Chaudret, B.; Fau, P. Remarkable Decrease in the Oxidation Rate of Cu Nanocrystals Controlled by Alkylamine Ligands. *J. Phys. Chem.* C **2017**, *121* (9), 5253–5260.