Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# The role of alkylamine in the stabilization of CuO nanoparticles as a determinant of the Al/CuO redox reaction

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**S1. Mass spectra of CuO_air (a) and CuO_$O_2$ (b).**

Mass spectrometry analyses of both synthesized CuO NPs are performed upon heating (10°C.min$^{-1}$) under argon atmosphere. Figure S1 shows MS results for both CuO_air and CuO_$O_2$. All detected m/z species, during the CuO_air and CuO_$O_2$ ramping are given in Table S1.

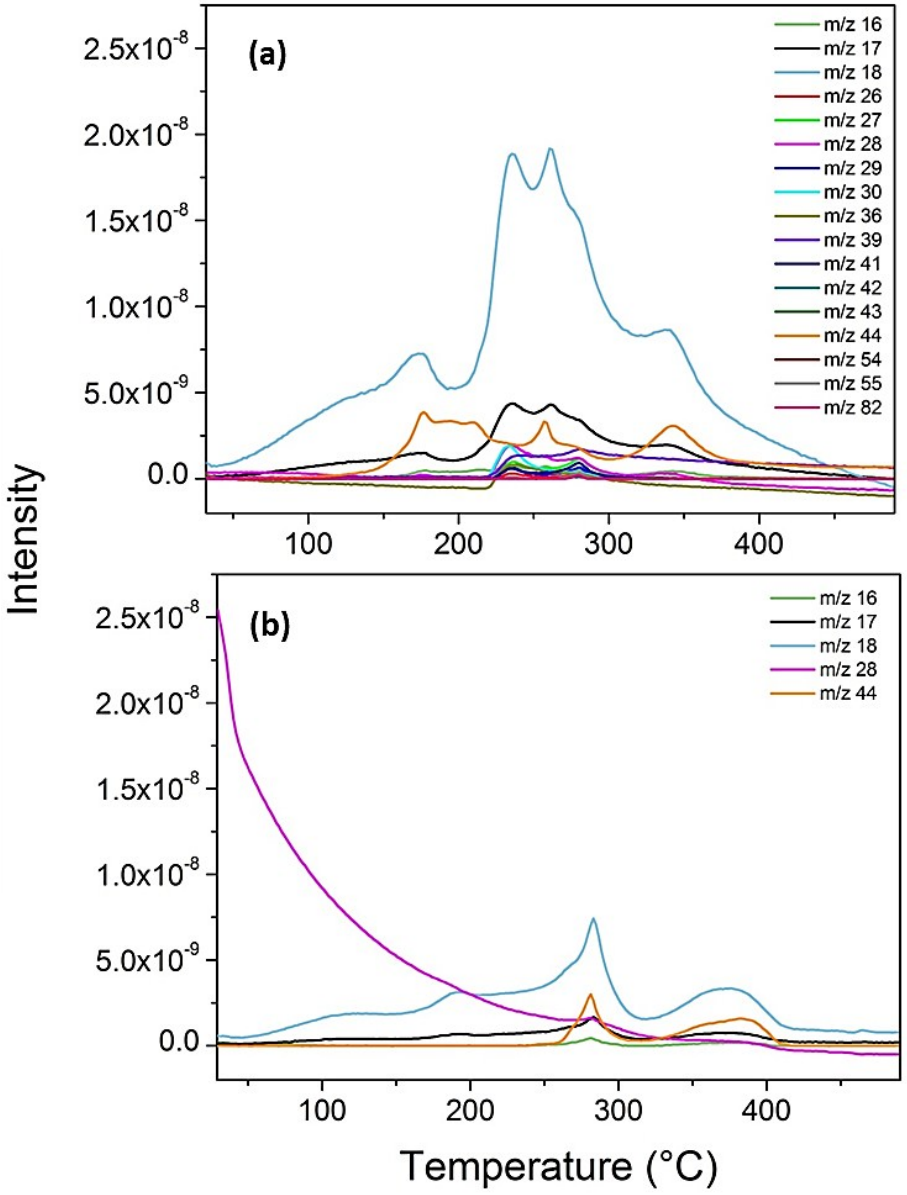


**Figure S1.** Mass spectra of (a) CuO_air and (b) CuO_$O_2$.

**Table S1.** Common neutral fragments present in mass spectra:[1]

| m/z | Molecules fragments | m/z | Molecules fragments |
|---|---|---|---|
| **16** | $CH_3$ | **39** | $C_3H_3$, $HC_2N$ |
| **17** | OH | **41** | $CH_2{=}CHCH_2^{\bullet}$ |
| **18** | $H_2O$ | **42** | $CH_2{=}CHCH_3^{\bullet}$, $CH_2{=}C{=}O$, NCO, $NCNH_2$ |
| **26** | $CH{\equiv}CH$, $^{\bullet}C{\equiv}N$ | **43** | $C_3H_7^{\bullet}$, $CH_3C{=}O^{\bullet}$, $CH_2{=}CH{-}O^{\bullet}$, HCNO |
| **27** | $CH_2{=}CH^{\bullet}$, $HC{\equiv}N$ | **44** | $CO_2$ |
| **28** | CO | **54** | $CH_2{=}CH{-}CH{=}CH_2$ |
| **29** | $CH_3{-}CH_2^{\bullet}$, $^{\bullet}CHO$ | **55** | $CH_2{=}CHCHCH_3$ |
| **30** | $NH_2{-}CH_2^{\bullet}$, $CH_2O$, NO | **82** | $CH{\equiv}C{-}(CH_2)_4$ |
| **36** | $2\ H_2O$ | | |

## S2. Kinetics of $CO_2$ (a) and $H_2O$ (b) MS signal intensity

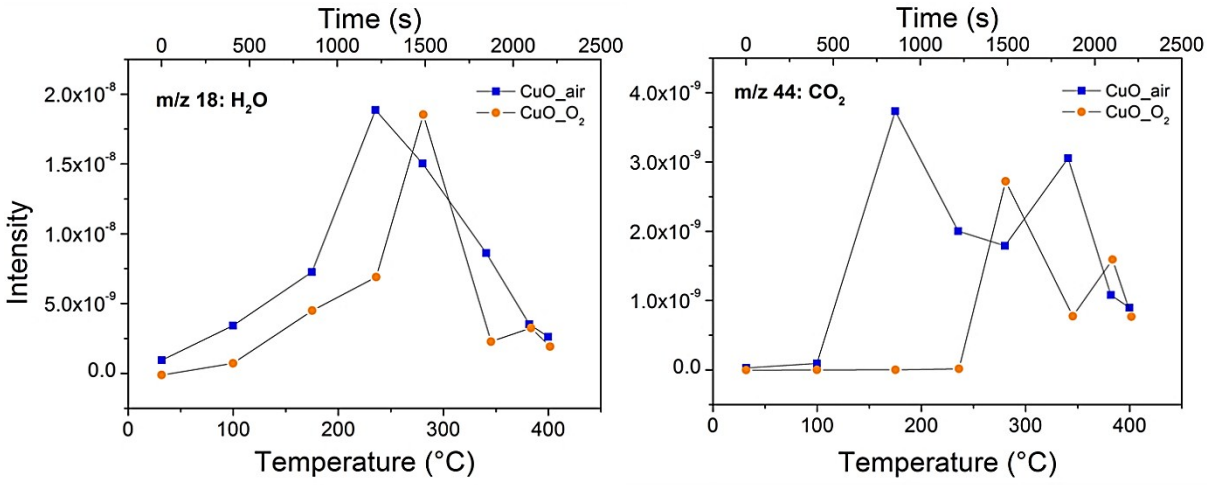


**Figure S2.** Evolution of the signal intensity for (a) $CO_2$ (m/z 44) and (b) $H_2O$ (m/z 18) as a function of temperature and time (kinetics).

## S3. FTIR analysis of CuO_air, CuO_$O_2$ samples after being washed

Cuprite phonon modes at 616 $cm^{-1}$ is evidenced at 200 °C for both samples, whereas they disappear at 500 °C when copper is formed. These effects are even stronger for

CuO_air with the formation of copper at 200 °C, due to the larger quantity of ligands and water at the surface.

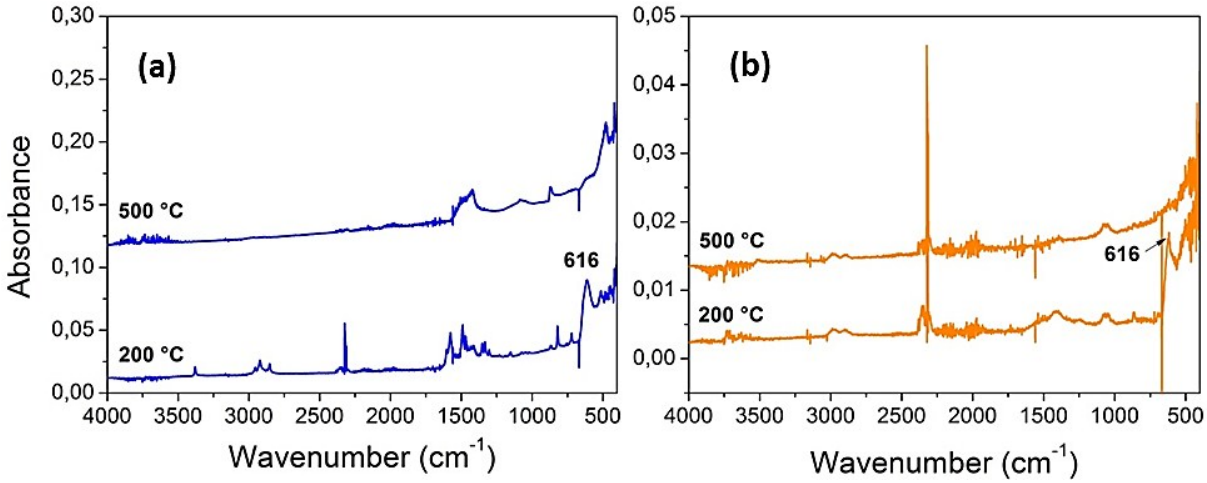


**Figure S3.** FTIR spectra of annealed (a) CuO_air and (b) CuO_$O_2$ at 500 and 200°C under argon.

**S4. X-Ray analysis of CuO_com annealed at 200 and 500 °C under argon.**

The initial CuO_com structure doesn't change until 500 °C, pointing the crucial role of the ligands in the CuO reduction process below 500 °C observed for CuO_air and CuO_$O_2$.

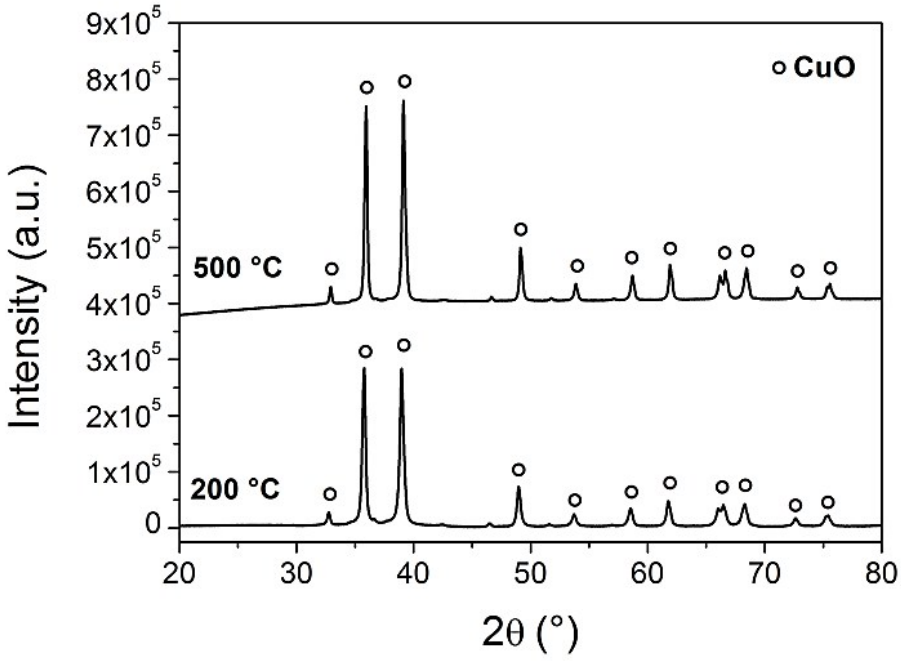


**Figure S4.** X-ray diffraction patterns of CuO _com at 200 and 500 °C upon annealing with a ramping of 10°C.min$^{-1}$ and under argon.

**S5. Chemical analysis of commercial CuO nanoparticles functionalized with one monolayer of OA ligands.**

The FTIR characterization of CuO_com@OA shows alkyl chain of OA at the stretching mode in the area of 3000 cm$^{-1}$, proving that bonding is realized between OA and commercial CuO. Mixed with Al NPs, the thermal response shows an exothermic peak at 258 °C **(o)**, two others ones at 580 **(i)** and 783 °C **(j)** identified as reaction between Al and CuO NPs. Before 500 °C, the exothermic peak is therefore associated to OA oxidation. XRD analysis, of annealed CuO_com@OA demonstrates that at 500 °C, CuO phase is partially reduced into $Cu_2O$ and Cu phases. The CuO_com@OA mixed with Al exhibits a heat released of 0.79 kJ.g$^{-1}$ between 450 and 900 °C. This points out the role of OA in the reduction process of CuO nanoparticles but also that the CuO

remaining in the system after 500 °C, allows the exotherms reactions. Therefore, CuO nanoparticles size has to be taken into account to avoid reduction.

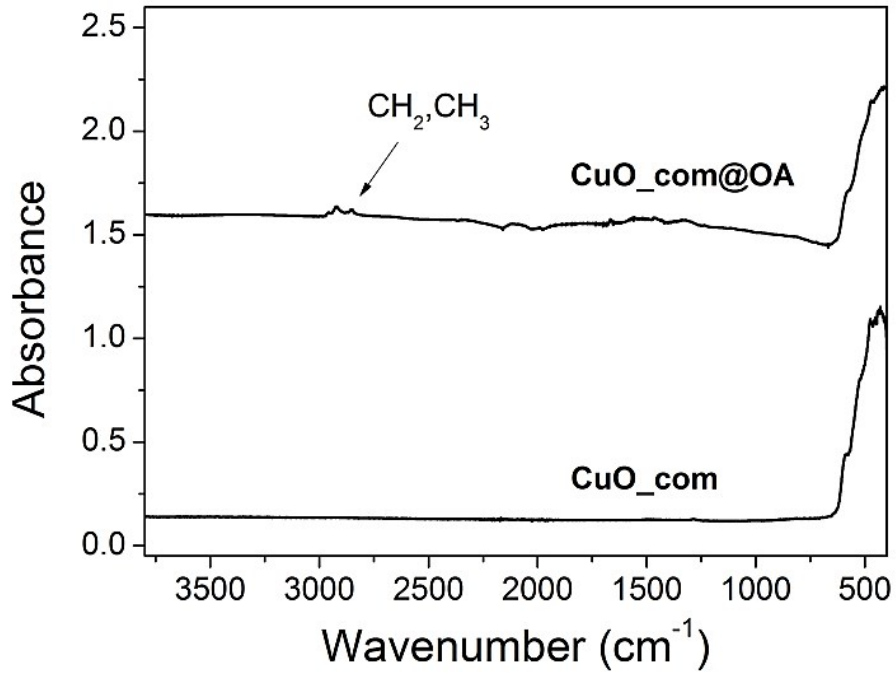


**Figure S5a.** FTIR spectra of CuO_com and CuO_com functionalized with OA. At around 3000 $cm^{-1}$, stretching mode of alkyl chain is identified.

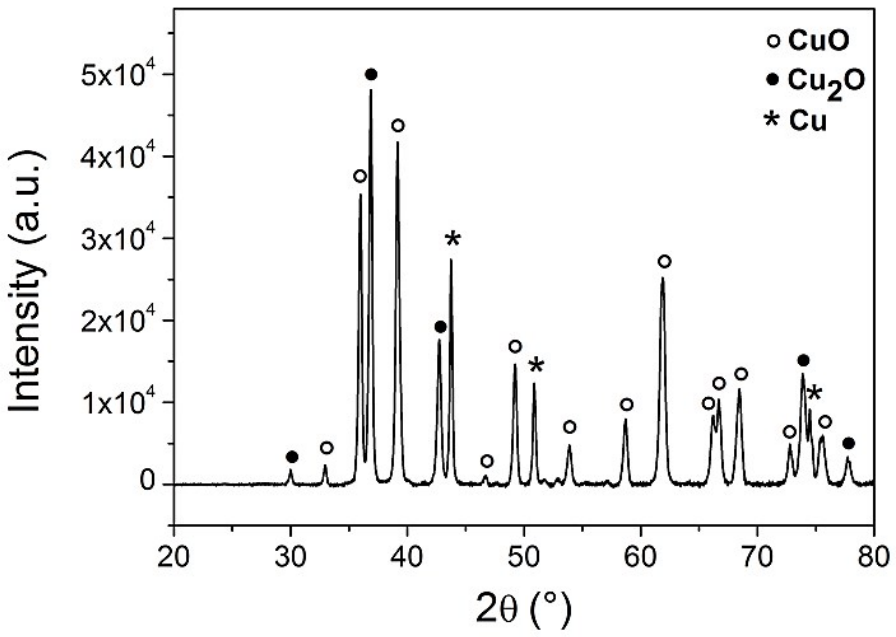


**Figure S5b.** X-ray diffraction pattern of CuO_com@OA annealed at 500°C under argon.

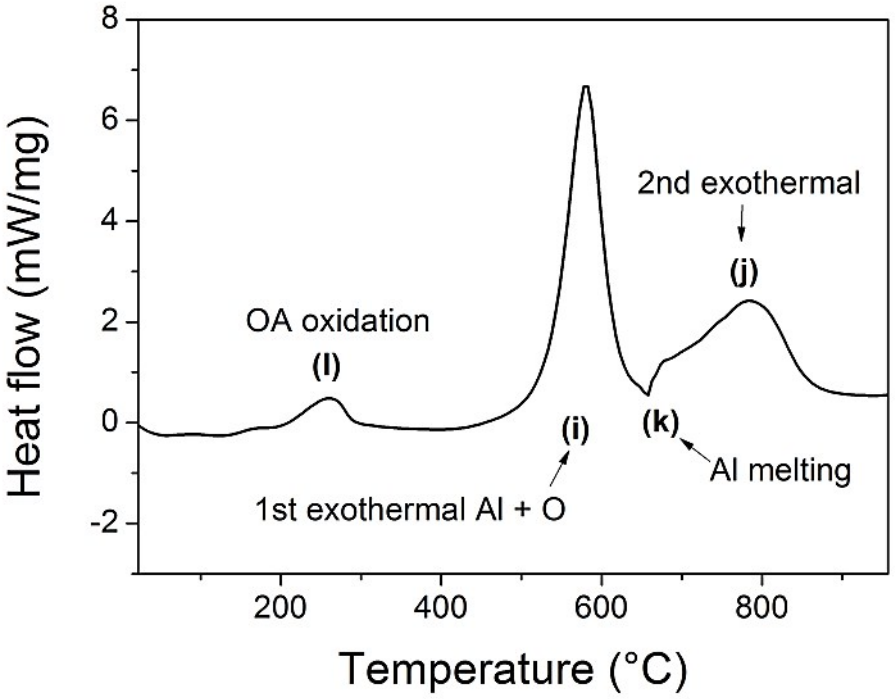


**Figure S5c.** DSC curve of Al/CuO_com@OA.

**S6. EDX analysis of mixtures composed of Al/annealed CuO NPs**

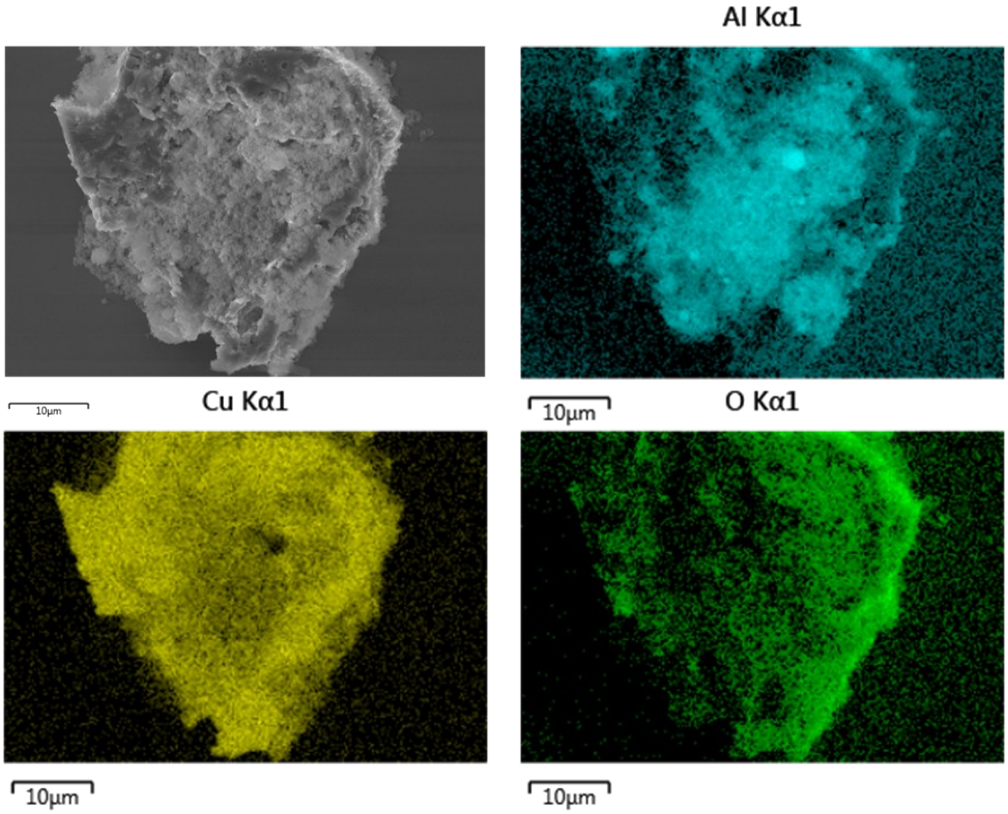


**Figure S6.** SEM image of assembly Al/annealed CuO_air with associated EDS analyses for Al, Cu and O elements.

## References

[1] C. Bullen, P. Mulvaney, The Effects of Chemisorption on the Luminescence of CdSe Quantum Dots, Langmuir. 22 (2006) 3007–3013.