**Supporting information**

**Formation of Copper Nanoparticles in LTL Nanosized Zeolite: Kinetics Study**

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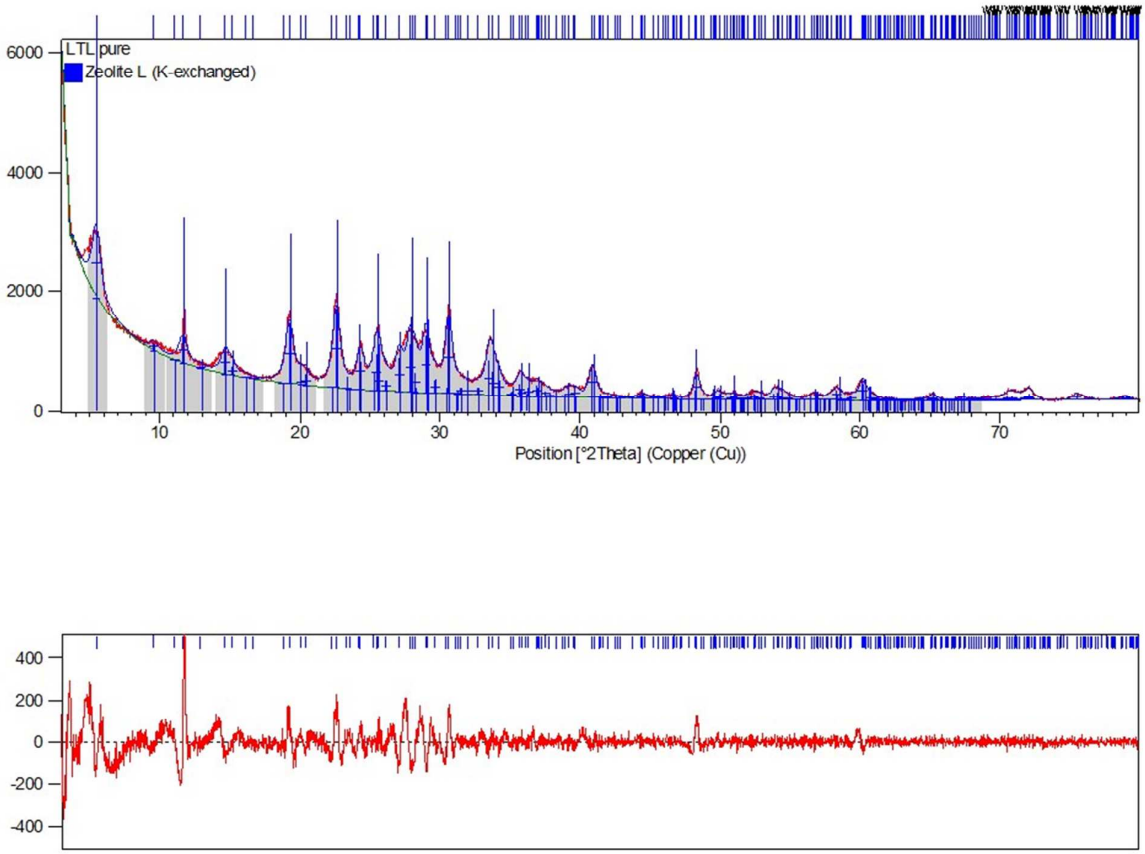
(A)



(B)

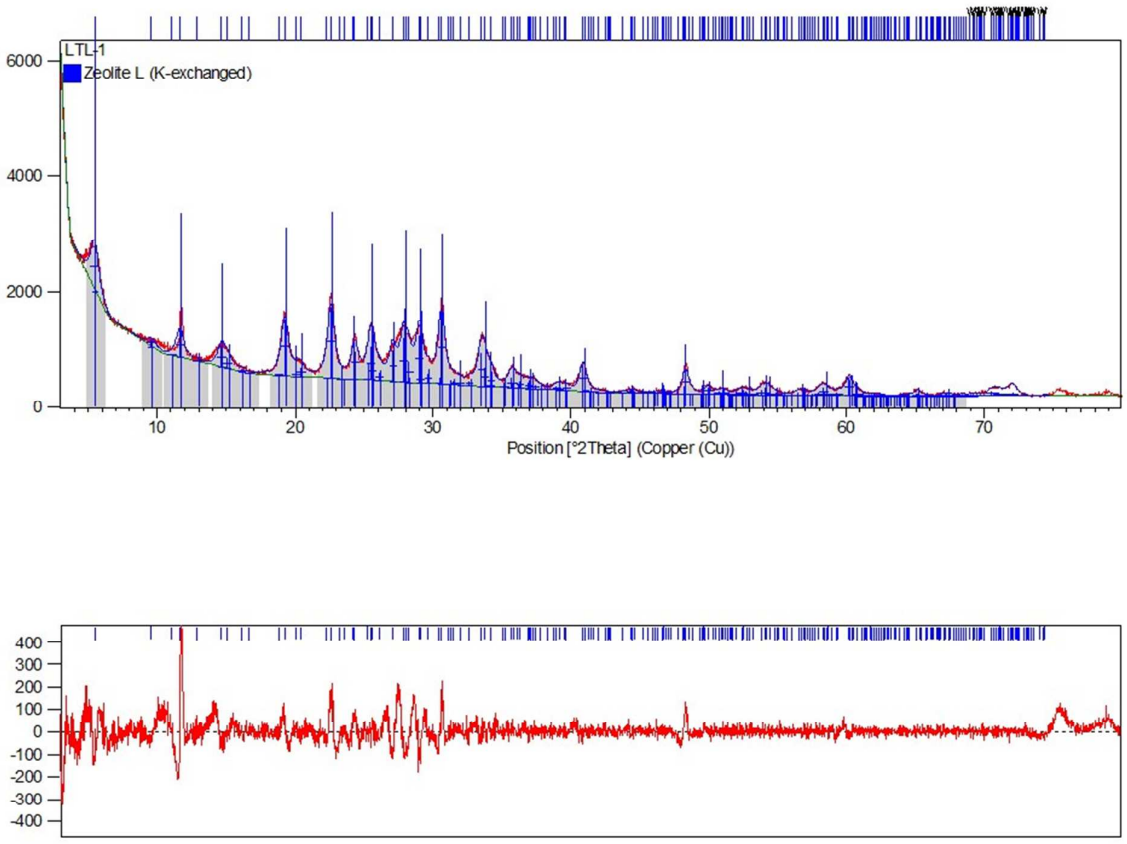



*Figure S1* Pawley fit of the XRD patterns and difference diagram between calculated and experimental data of (A) parent LTL and (B) $Cu^0$-LTL; a unit cell is used to generate the initial peak list, as a reference pattern the Zeolite LTL (K-exchanged) (No. 98-003-5486) was used.

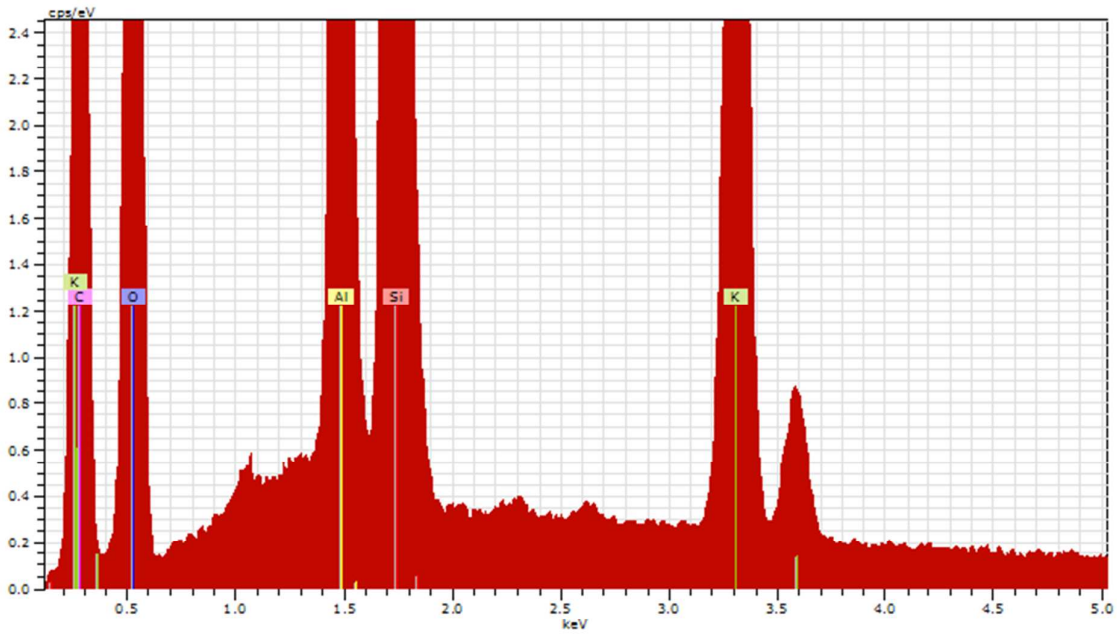
*Table S1* Agreement indices for the Pawley fit of the parent LTL and $Cu^0$-LTL.

| Agreement Indices | Parent LTL | $Cu^0$-LTL |
|---|---|---|
| **R expected** | 3.7244 | 3.6959 |
| **R profile** | 4.3126 | 4.1496 |
| **Weighted R profile** | 5.6025 | 5.8898 |
| **D-statistics** | 0.2734 | 0.3293 |
| **Goodness of Fit** | 1.5043 | 1.5936 |

*Table S2* Chemical composition of parent LTL and $Cu^{2+}$-LTL samples

| Element | Series | Parent LTL | | $Cu^{2+}$-LTL | |
|---|---|---|---|---|---|
| | | % wt. | % at. | % wt. | % at. |
| Silicon | K-series | 13.15 | 55.77 | 16.54 | 55.58 |
| Aluminium | K-series | 5.34 | 23.57 | 6.65 | 23.26 |
| Potassium | K-series | 6.78 | 20.66 | 7.8 | 18.83 |
| Copper | K-series | - | - | 1.57 | 2.33 |

(A)




(B)

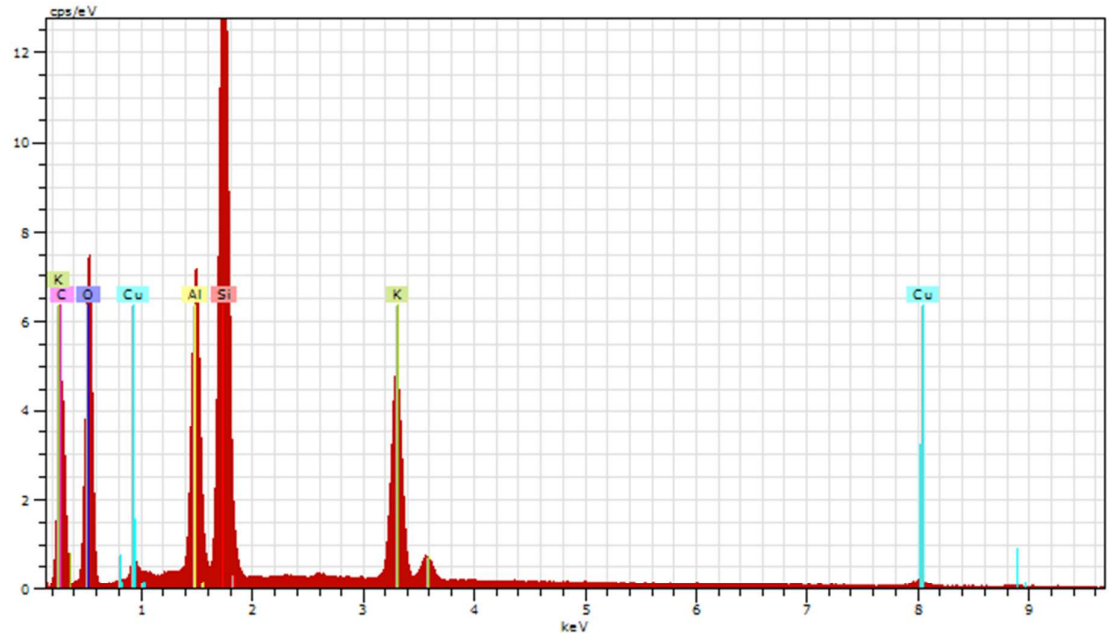



*Figure S2* Elemental composition of the (A) parent LTL and (B) $Cu^{2+}$-LTL samples measured by EDX-SEM (C corresponds to the carbon film)

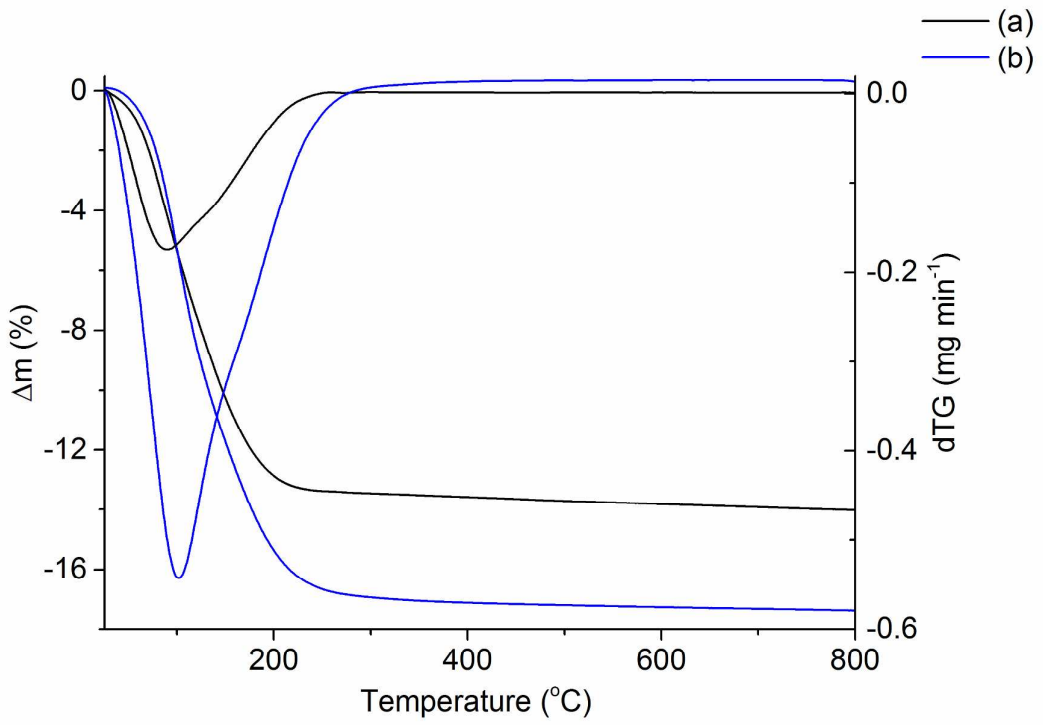



*Figure S3* TG and dTG curves for (a) parent LTL and (b) $Cu^{2+}$-LTL samples. The weight loss below 200 °C corresponds to removal of water. The total amount of water for parent LTL and $Cu^{2+}$-LTL was about 14.5%, 17.9%, respectively

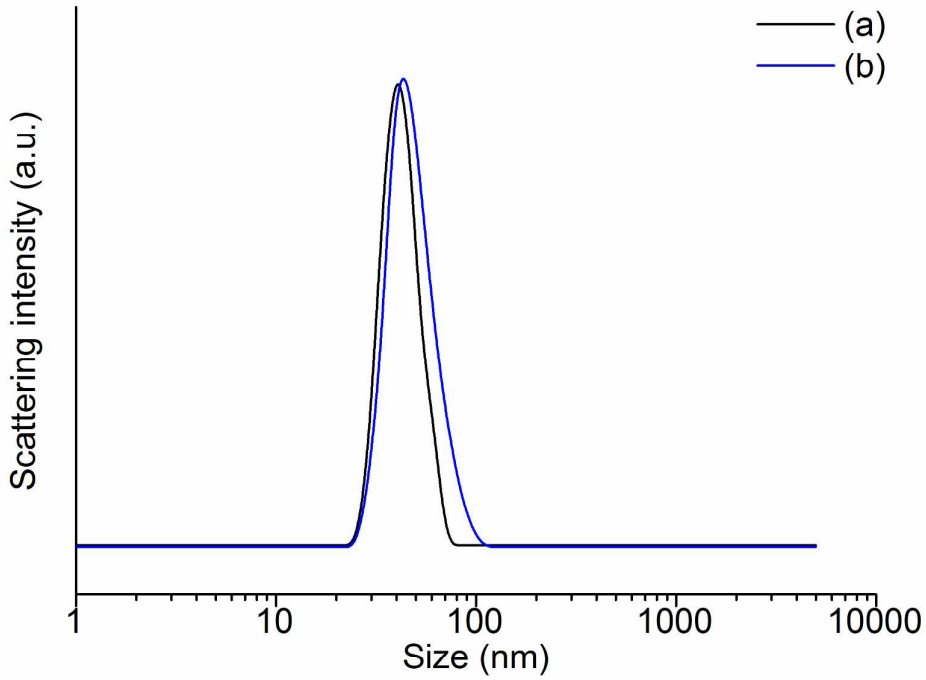



*Figure S4* Particle size distribution of (a) parent LTL and (b) $Cu^{2+}$-LTL samples measured by DLS. As the particles are not spherical, DLS gives the diameter of a sphere that has the same average translational diffusion coefficient as the particle being measured. The DLS-curves show that both materials have monomodal particle size distribution. Parent LTL and $Cu^{2+}$-LTL exhibit maximum values at around 40 nm. While TEM images show rectangular crystalline domains with well-defined edges with the size of 10 – 15 nm that are aggregated to bigger entities presented by the DLS curves.

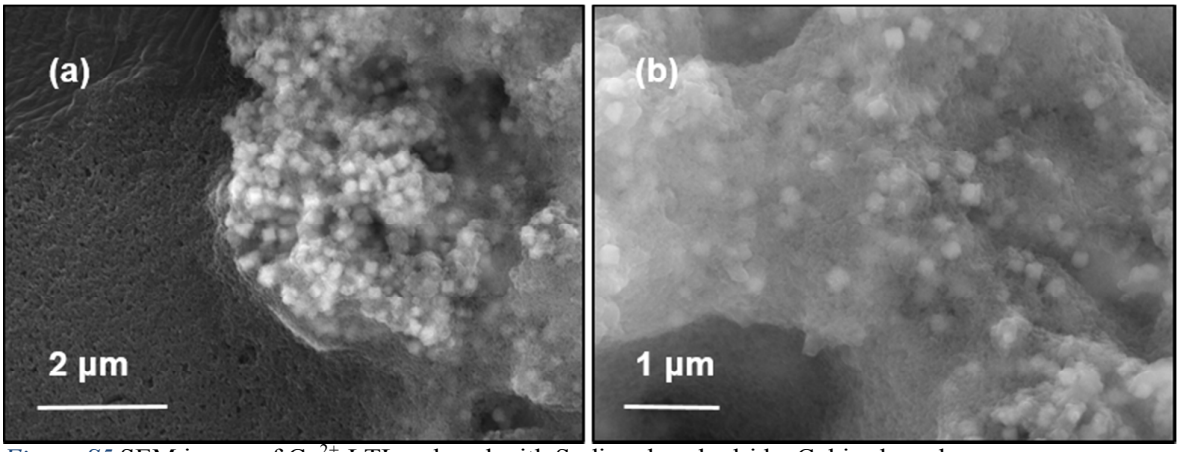
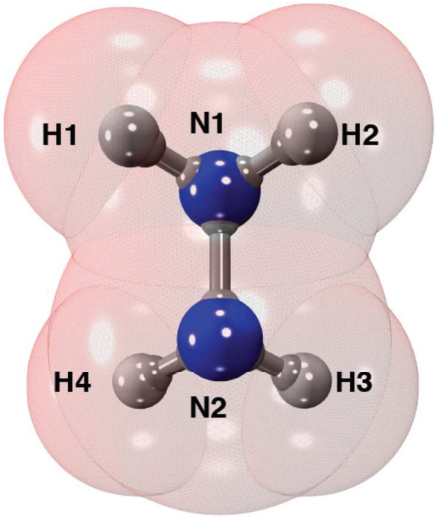



*Figure S5* SEM image of $Cu^{2+}$-LTL reduced with Sodium borohydride. Cubic shaped copper nanoparticles on the surface of nanosized LTL crystals are observed.




*Van der Waals surface*

| Atoms | d, Å |
|---|---|
| **H1-H2** | 1.62 |
| **H1-H3** | 2.90 |
| **H1-H4** | 2.41 |
| **N1-N2** | 1.44 |

| Atoms | Radii, Å |
|---|---|
| **H** | 0.53 |
| **N** | 0.56 |

*Figure S6* Van der Waals size of Hydrazine molecule

*Table S3* Analysis of Bragg peak area of the XRD patterns collected at different key times of the reaction.

| **Sample $Cu^{2+}$-LTL** | **$X_{beg}$** | **$X_{end}$** | **$Y_{max}$** | **$X(Y_{Max})$** | **Peak Area** |
|---|---|---|---|---|---|
| **0 min** | 42.90 | 43.70 | 43.08 | 43.61 | 0.04 |
| **70 min** | 42.90 | 43.70 | 37.19 | 43.65 | -0.06 |
| **190 min** | 42.90 | 43.70 | 140.00 | 43.29 | 44.24 |
| **280 min** | 42.90 | 43.70 | 263.00 | 43.33 | 56.23 |
| **430 min** | 42.90 | 43.70 | 258.00 | 43.31 | 64.25 |
| **960 min** | 42.90 | 43.70 | 309.00 | 43.33 | 92.42 |

$X_{beg}$-$X_{end}$ – peak position

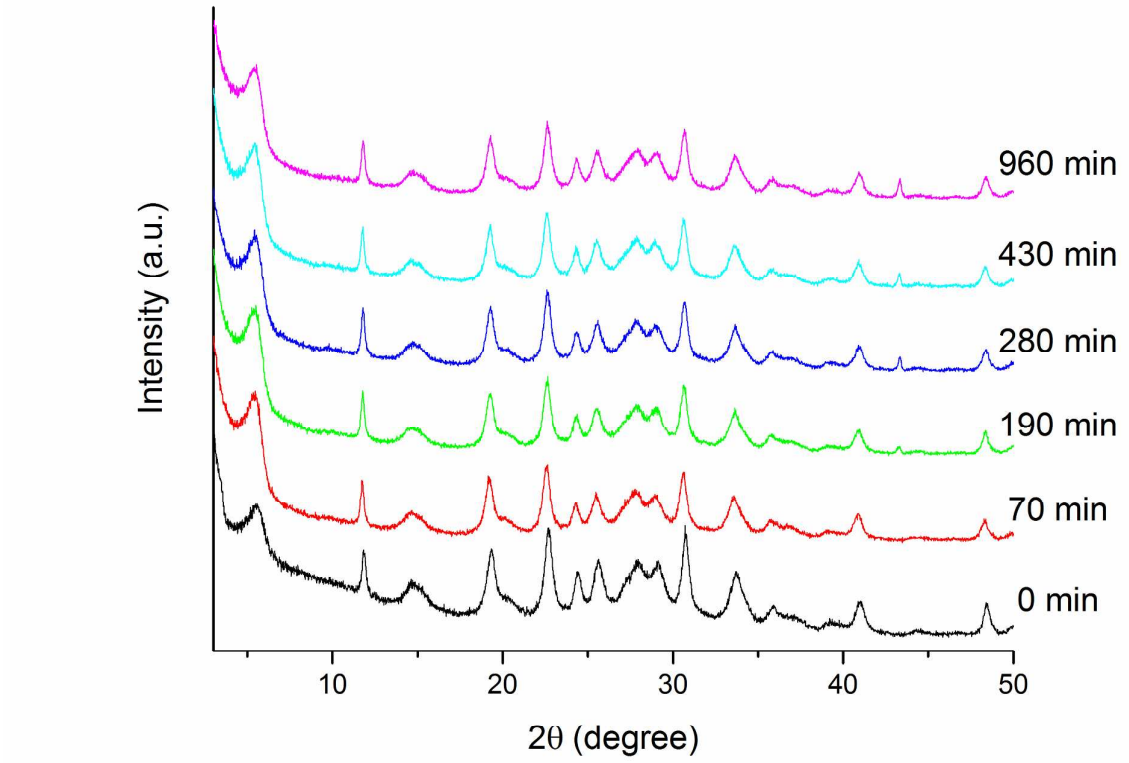
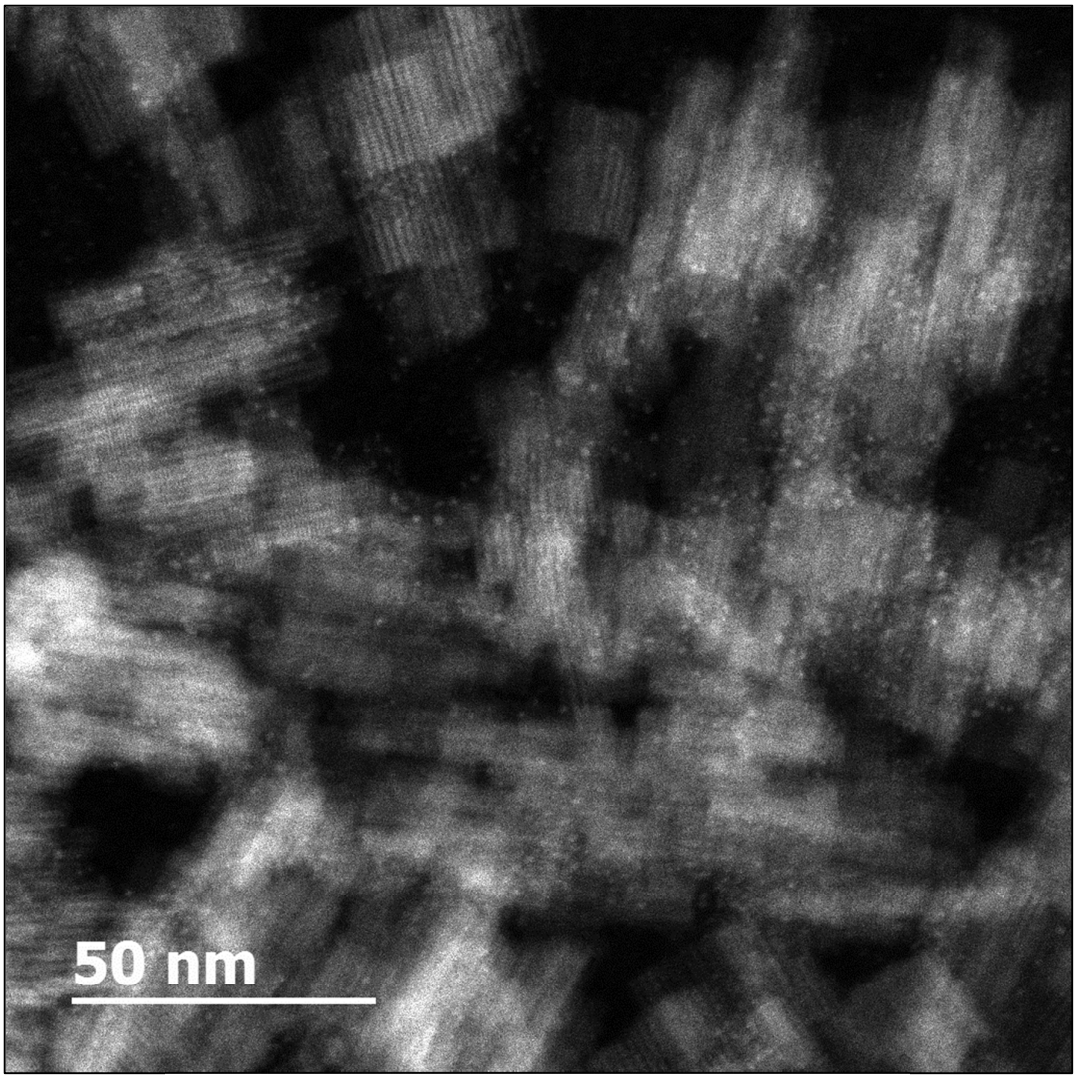
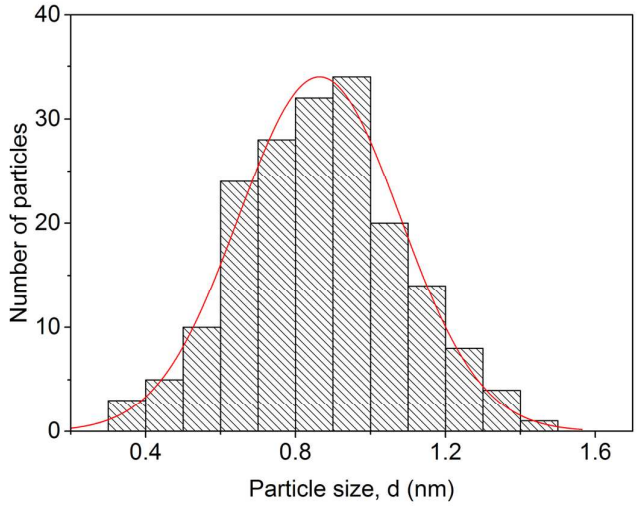


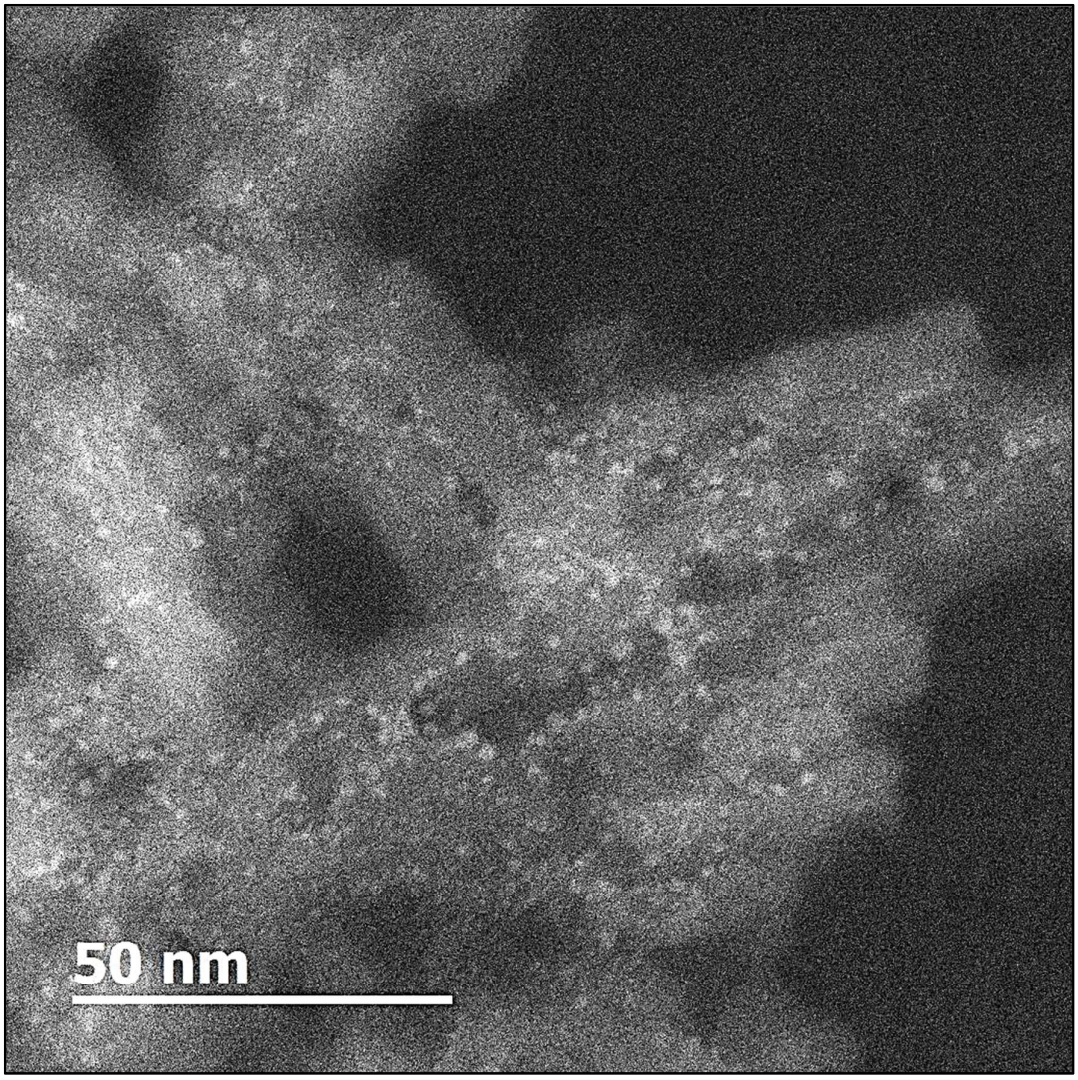

*Figure S7* XRD patterns of samples at different reaction time in the region 4 - 50 º2θ. The LTL zeolite structure stays intact during the reduction process.

(A)


50 nm


40
30
20
10
0
Number of particles
0.4
0.8
1.2
1.6
Particle size, d (nm)

(B)



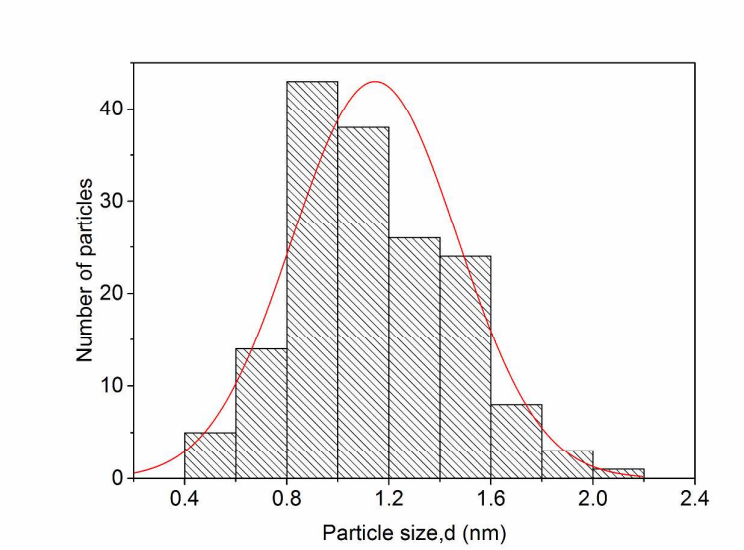




*Figure S8* HAADF-STEM images of zeolite samples reduced with hydrazine for (A) 190 min, (B) 280 min with histograms of particle size distribution. The bright spots represent copper nanoparticles.

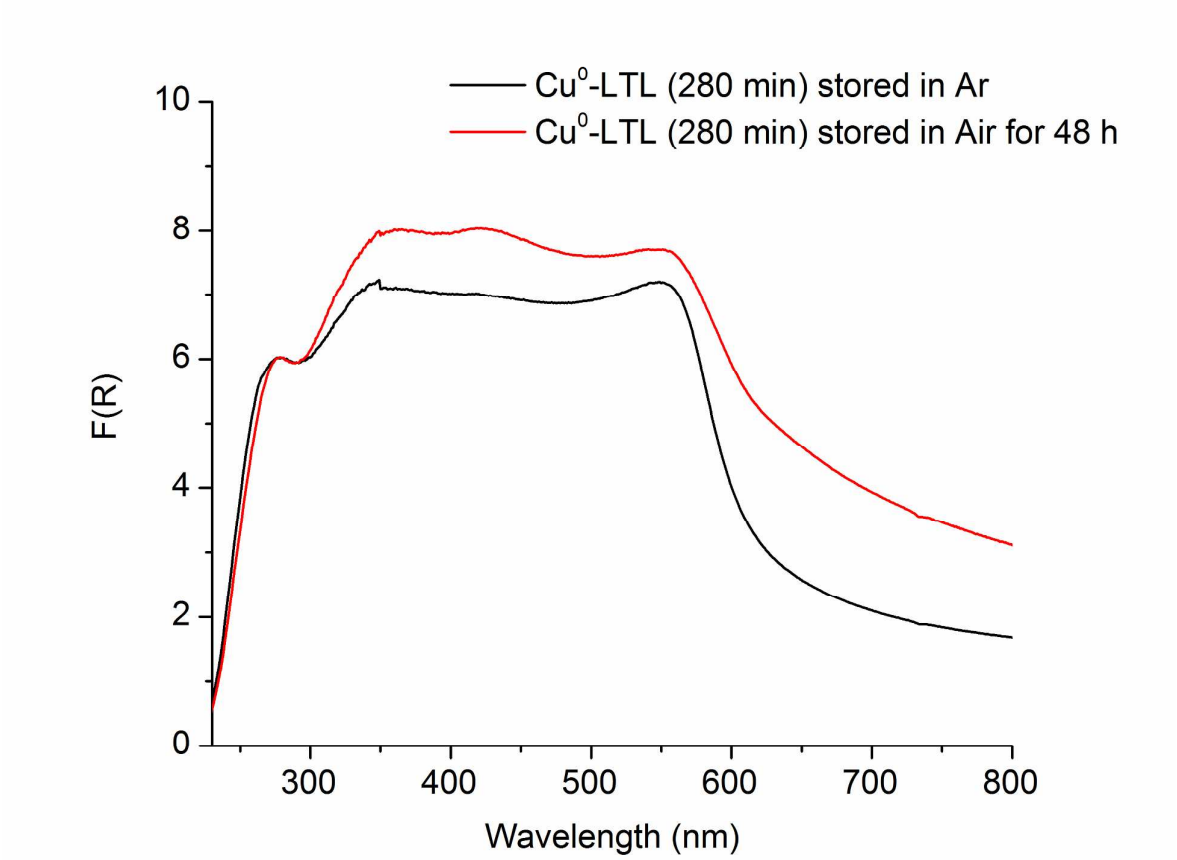



*Figure S9* UV-vis spectra of self-supported pellets of copper-containing LTL recorded after storing the sample in Ar atmosphere (black) and after storing in air for 48 hours (red). A new peak at 420 nm assigned to $Cu_2O$[1] appeared in the red spectrum.

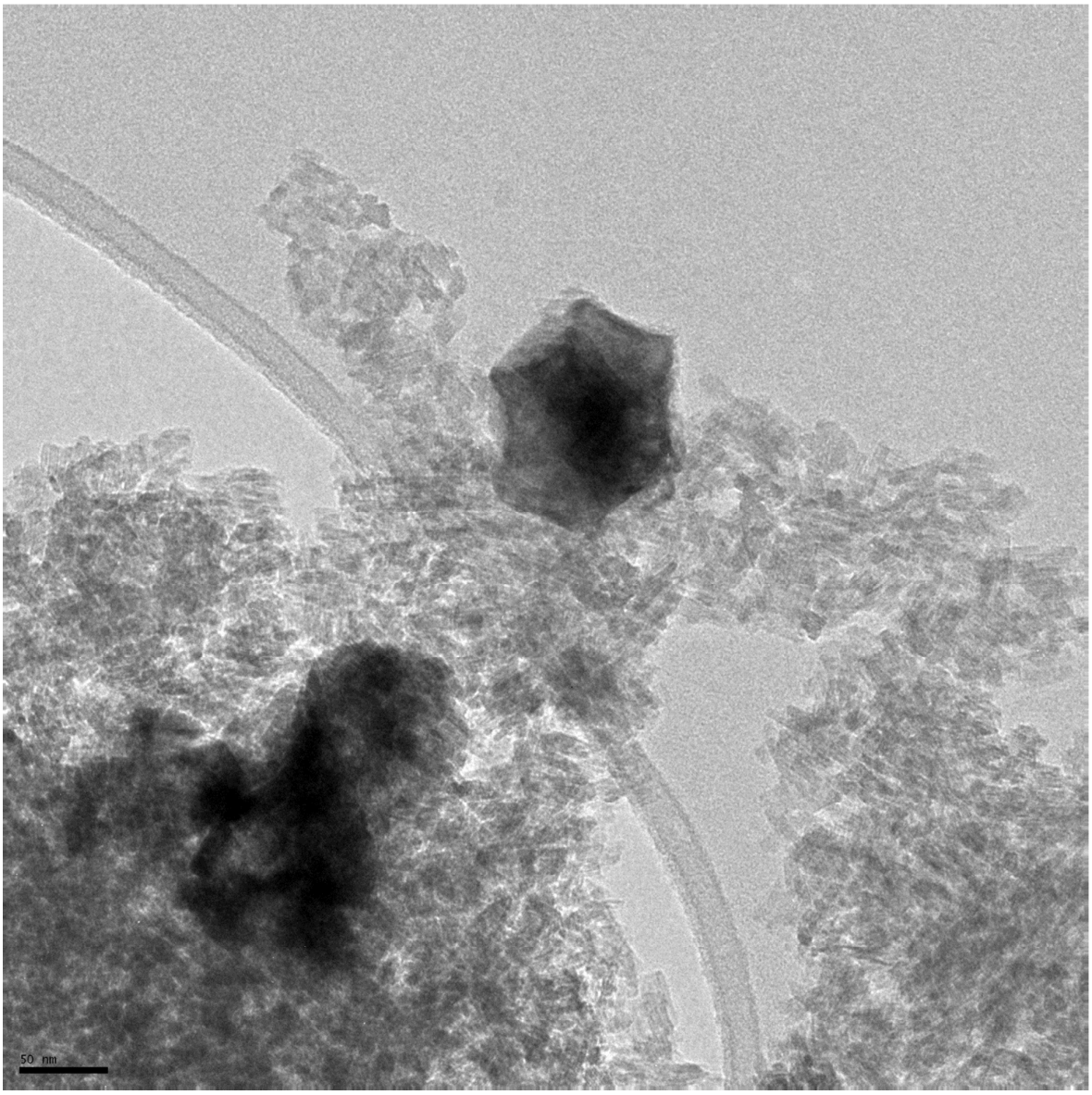



*Figure S10* TEM picture of sample $Cu^0$-LTL (280 min) after continuous heating under Ar flow at 400 ºC for 4 hours.

Reference

(1) Susman, M. D.; Feldman, Y.; Vaskevich, A.; Rubinstein, I. Chemical Deposition and Stabilization of Plasmonic Copper Nanoparticle Films on Transparent Substrates. *Chem. Mater.* **2012**, *24* (13), 2501–2508.