Controlling the Morphology of Silica-Copper Oxide Nanostructures from Laser Ablation in Liquid

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**Motivation**
Green and sustainable way of synthesizing oxide-metal composite nanomaterials: use photons to initiate chemical reactions rather than wet chemicals as reducing and stabilizing agents.

Pulsed Laser ablation in liquid (PLAL) is a common method for generating bare-surface metal nanoparticles by focusing intense laser pulses onto the surface of a solid target immersed in liquid.¹

When the liquid contains metal ions, they may interact with the ablated clusters from the target, forming supported metal nanoparticles. This is referred to as femtosecond- Reactive Laser Ablation in Liquid (fs-RLAL), when femtosecond laser pulses are used.²

Silica-supported copper nanoparticles are valued for their catalytic activity toward various reactions such as CO₂ hydrogenation to form methane and methanol.

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**Characterization**

*Counts*

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<th>CuL</th>
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Counts vs. Solution pH

Left: Representative SEM, EDS spectrum of Cu-silica-10.4 sample. Shows wt.% Si, O, and Cu quantified in samples fabricated from different pH solutions.

Right: TEM images of (a) Cu-silica-3.0, (b) Cu-silica-5.4, (c) Cu-silica-10.4. Histograms of (d) Cu-silica-5.4 and (e) Cu-silica-10.4

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**fs-RLAL Setup**

Ablated silicon wafer immersed in aqueous Cu(NO₃)₂ solutions (2 mM) with:

- HNO₃ (pH 3.0, Cu-silica-3.0)
- no additives (pH 5.4, Cu-silica-5.4), or
- KOH (pH 10.4, Cu-silica-10.4)

to see effect of pH on final morphology.

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**pH-Dependent Formation**

Low and medium solution pH: ablated silica clusters (oxidized silicon atoms upon interaction with water) are protonated, repel nearby Cu⁺ ions, resulting in low wt.% loading of Cu, and Cu-core/silica-shell morphology.

High solution pH: ablated silica clusters are deprotonated, attracting nearby Cu₂(OH)₂⁺⁺ clusters, generating high wt.% loading copper on silica

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**CO₂ Hydrogenation**

> Conversion increases from 4% at 450°C to 75% at 800°C

> Selectivity toward methanol below 600°C, and selective toward methane above 600°C

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**References**