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Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

DTU Food
National Food Institute

Dispersion and characterization of surface-functionalized CuO nanoparticles for toxicity testing

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CuO engineered nanomaterial (ENM) is widely used in industry (e.g. microelectronics, antifouling agent, biocide in textiles) and has been reported to be highly toxic in comparison to other metal oxide ENM and bulk CuO[3]. The aim of this study was to develop and compare dispersion techniques for CuO ENM for later use in a wide range of toxicity studies[4].

Synthesis and dispersion of CuO ENM

The CuO ENM was synthesized by high-temperature decomposition of inorganic precursor. Its purity was measured by inductively coupled plasma mass spectrometry (ICP-MS), which revealed that traces of Fe, Sr, Ba and Pb were present.

The CuO ENM was subjected to dispersion by::

i. Ball-milling with Y_2O_3-stabilized ZrO_2 beads in 0.08 M acetic acid (pH =2.9);
ii. Dispersion in water by ultrasound probe sonication (Figure 1).

Size characterization by transmission electron microscopy (TEM) and dynamic light scattering (DLS) (Figure 1 and Table 1). showed that **ball milling** lead to generally smaller size distribution and mean hydrodynamic diameters than **probe sonication.**

Imaging by TEM showed that the **probe sonicated** ENM suspensions were composed of aggregates/agglomerates, but with constituent nanostructures around or below 100 nm.

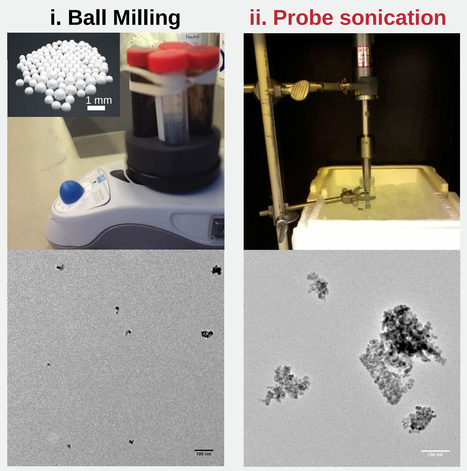

Figure 1 Dispersion of CuO ENM by ball-milling and probe sonication. Size characterization by TEM and DLS.

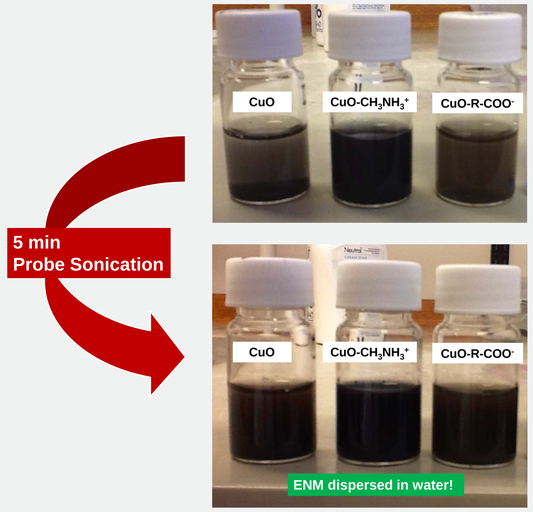

Figure 2 Dispersion of functionalized ENM by probe sonication in aqueous suspensions.

Table 1 Characterization of functionalized ENM by DLS and zeta potential.

ENM	Dispersion Technique	Z_{ave} (diam., nm)	ζ potential (mV)
CuO	Ball-milling	102.0 ± 6.9	36.2 ± 0.7
CuO	Probe sonication	1510 ± 61.8	20.7 ± 1.19
CuO-$CH_3NH_3^+$	Probe sonication	285.3 ± 6.7	33.7 ± 0.1
CuO-R-COO^-	Probe sonication	1247 ± 120.1	- 8.7 ± 0.6

Selection of dispersion techniques

Ball-milling may introduce artifacts that would affect toxicity studies such as:

- Partial dissolution of the aggregated material, (release of low molecular CuO clusters and/or Cu-ions into the acidic dispersant);
- Defects on the CuO crystal structure;

→Probe sonication preferred for ENM dispersion.

Probe sonication dispersion was also applied to CuO ENM functionalized with positively charged ammonium (–CH3NH_3^+), or negatively charged carboxylate (-R-COO^-) (Figure 2). The efficiency of probe sonication for dispersion depends on the surface functionality (Table 1).

The degree of ENM dispersion depends on the power output of probe sonication**.** Hence, the actual power delivered by the ultrasound probe was **calibrated by calorimetry**, enabling that similar ENM suspensions can be obtained across laboratories using different ultrasound probe equipment.

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"The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° [309329]."