This document is the accepted manuscript version of the following article:
Dörner, L., Schmutz, P., Kägi, R., Kovalenko, M. V., & Jeurgens, L. P. H. (2020).
Electrophoretic deposition of nanoporous oxide coatings from concentrated CuO
nanoparticle dispersions. *Langmuir*, 36(28), 8075–8085.
<https://doi.org/10.1021/acs.langmuir.0c00720>

Electrophoretic deposition of nanoporous oxide coatings from concentrated CuO nanoparticle dispersions

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Abstract

Electrophoretic deposition (EPD) of nanoporous oxide coatings is an interesting research avenue owing to the experimental simplicity and broad scope of applications and materials. In this study, the properties of concentrated (up to 5000 mg/L), non-aqueous CuO nanoparticle (NP) dispersions were tailored to produce micrometer thick, nanoporous CuO films by EPD. In particular, we performed a systematic investigation of the electrophoretic mobilities and size distributions of dispersed CuO aggregates and developing agglomerates in different organic solvents for concentrations ranging from 50 to 5000 mg/L with and without surfactant addition. Time-resolved DLS analyses showed that aggregate mobilities and agglomeration rates decrease with increasing hydrocarbon chain length of the organic solvent (from ethanol to hexanol) and thus with increasing viscosity. The highest electrophoretic mobility was obtained for CuO NP aggregates and agglomerates dispersed in ethanol as a solvent. However, the addition of ≥ 0.5 wt.% acetylacetone (AcAc) as a surfactant is required to stabilize these dispersions for subsequent EPD and at the same time introduce a net attractive (electrostatic) interaction between neighboring agglomerates on the substrate to promote layer formation during the EPD step. The produced micrometer thick nanoporous CuO coatings can serve as high-surface area nanostructured materials or nanoporous scaffolds in catalysis, combustion, propellants and nanojoining.

KEYWORDS: Copper oxide, nanoparticle dispersion, electrophoretic deposition, mobility, aggregation, agglomeration, surface charge.

Table of Contents Graphic: Tailoring of CuO nanoparticle dispersions towards efficient fabrication of nanostructured coatings by electrophoretic deposition.

Introduction

Particle aggregation and coagulation in colloidal systems are crucial phenomena for a broad range of applications.¹⁻⁴ For example, suppressing particle aggregation and coagulation processes in colloidal dispersions is decisive to extend the shelf-life of nanoparticle (NP) suspensions and pastes, as applied in different industrial and consumer products (e.g. cosmetics^{5,6}, paint^{7,8}, food⁹, Ag nanopaste for joining¹⁰). The stability of a colloidal dispersion of solid particles in a liquid medium principally depends on the applied solvent and the types and concentrations of dispersed particles and chemical stabilizing agents. According to the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO), particle-particle interactions in colloidal dispersions are governed by the balance between the attractive Van der Waals forces between neighboring particles and the repulsive electrostatic interactions between the interfacial double layers at their particle surfaces.¹¹⁻¹³ The 'true' potential of the interfacial double layer can hardly be assessed by the experiment and is therefore usually approximated from the so-called Zeta-potential, defined as the potential difference between the dispersion medium and the outer boundary of the interfacial double layer. The Zeta-potential can be deduced from the measured electrophoretic mobility of the dispersed particles in the solution.^{14,15} In aqueous systems with high salt concentrations and weakly charged particles, the electrostatic repulsion between neighboring particles is relatively weak; hence the attractive van der Waals forces dominate, resulting in fast aggregation kinetics. On the contrary, for highly charged particles and low salt concentrations, the strong repulsive double layer forces between the charged particles obstruct particle aggregation, thus stabilizing the colloidal suspension. The interaction between particles in a colloidal dispersion can be tailored by adding so-called surfactants, which specifically interact with the particle surface and thereby alter the interacting forces between the diluted particles to promote or hinder aggregation.²

Evidently, the aggregation rate is suppressed in highly diluted particle dispersions, since the average distance between the dispersed particles is relatively large. With increasing particle concentration, aggregation starts by the initial formation of small particle dimers, which gradually coalesce into larger aggregates.^{16,17} In concentrated particle dispersions, the individual aggregates can

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3 agglomerate with time to form even larger irregular, reversible clusters of aggregates; such
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5 *agglomerated aggregates* should not be confused with the irreversible formation of more strongly
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7 bonded aggregates from individual colloidal particles. Sedimentation of larger aggregates and/or
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9 agglomerates can occur in parallel under the influence of gravitational forces.¹ For high particle
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11 concentrations, strong interlinking of aggregated clusters may result in the formation of a stable
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13 colloidal gel.^{18,19} Most studies on colloidal particle dispersions use diluted systems with particle
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15 concentrations of 0.5 mg/L – 5 mg/L to suppress the rates of aggregate and agglomerate formation.^{20,21}
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17 For similar reasons, most particle aggregation theories have been developed for low concentrations of
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19 dispersed single particles in water with various salt concentrations.
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24 In this study, the properties of concentrated (500 up to 5000 mg/L), non-aqueous CuO NP
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26 dispersions were systematically investigated and tuned to achieve fast electrophoretic deposition (EPD)
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28 of micrometer thick, nanoporous CuO films. Copper oxide finds applications in a wide range of different
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30 technologies, such as catalysis (electrochemical reduction of CO₂),²² magnetic storage, printable
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32 electronics, energy conversion and storage, joining and thermites.²³ Notably, the copper-oxygen system
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34 contains two stable stoichiometric oxides, cuprous (Cu₂O) and cupric (CuO) oxide. For our envisioned
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36 application in the field of Al/CuO nanothermites for joining, the use of single-phase cupric CuO NPs is
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38 preferred,^{24,25} since it presents the most stable Cu oxide phase according to bulk thermodynamics and
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40 has the highest caloric effect upon reduction.²⁶ Over the years, a wide variety of methods (e.g. sol-gel
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42 synthesis,²⁷ milling,²⁸ electrodeposition,²⁹ sonochemical synthesis,³⁰ ultrasonic spray pyrolysis,³¹
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44 hydrothermal synthesis^{32,33}) have been developed for synthesizing single-phase CuO NPs with
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46 controllable size and shape.^{34,35} We recently developed an economic green sol-gel synthesis route for
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48 easy production of submicron-sized, porous CuO NP aggregates with a very high specific surface area
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50 (>18 m²/g), which exhibit enhanced reactivity when processed in the form of a dispersion, paste or
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52 nanocomposite for the targeted application.²⁷
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59
60 ¹ Notably, dispersions of particles and particle aggregates sufficiently large for sedimentation are generally called suspensions, whereas dispersions of much smaller nanoparticles are usually denoted as colloids.

The first part of this work presents a systematic investigation of the size distribution, mobility and agglomeration behavior of CuO NP aggregates, dispersed in different primary organic solvents with and without surfactant for CuO NP concentrations in the range of 50 - 5000 mg/L. Very high CuO NP aggregate concentrations up to 5000 mg/L (i.e. much higher than the typically particle concentrations applied in oxide-NP dispersion studies in the range of 0.5 mg/L – 5 mg/L),^{20,21} are required to achieve micrometer-thick, nanoporous oxide layers through a fast and easily scalable EPD process.³⁶ Our aim was to develop a green, time- and cost-effective EPD process. We have chosen primary alcohols as suitable inexpensive and green solvents. Notably, aqueous-based dispersions cannot be used for EPD, since the external voltages applied in these processes by far exceed the equilibrium potential for the splitting of water into its elemental components H₂ and O₂.³⁷ The type and concentration level of surfactant in the CuO NP dispersions were selected on the basis of the following criteria: (i) sufficient mobility of the NP aggregates in the dispersion, (ii) sufficient interaction between the dispersed NP aggregates to promote layer formation during EPD, while maintaining a practical stability of the concentrated CuO NP dispersion throughout the synthesis procedure; (iii) minimization of carbon residue in the electrophoretically deposited CuO coating. Zeta-potential measurements were applied to determine surface charge, effective mobility and conductivity of the dispersed particles and the solvent for each combination of solvent and surfactant. The initial increase in agglomerate size with time was investigated by time-resolved dynamic light scattering analysis (DLS). Static light scattering characterization was conducted to evaluate the stability of the dispersions after aging up to 24 hrs. The desired properties of the concentrated, nonaqueous CuO NPs dispersions could be tuned for the targeted EPD step.

The second part of this work demonstrates easy and fast electrophoretic deposition of micrometer thick, nanoporous CuO coatings on Ti-coated glass substrates from the tuned CuO NP dispersions. EPD is known since the early 19th century but has gained more attention recently since it enables facile and rapid deposition of nanostructured materials.³⁶ EPD is based on the directional migration of colloidal charged particles under an applied electric field between two electrodes for fast coating deposition.^{38,36} The EPD process involves two principle steps; the dispersed (charged) particles

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3 first move towards the oppositely charged electrode and subsequently accumulate on the surface of a
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5 (conducting) substrate.^{37,39,36}
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8 Noteworthy, *systematic* studies on the optimization of concentrated nonaqueous oxide NP
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10 dispersions for EPD, which is the main focus of this work, have very rarely been reported up to date. To
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12 the best of our knowledge, no systematic study on the dispersibility, stability and mobility of CuO NP
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14 aggregates dispersed in primary organic solvents with different types and concentrations of surfactants
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16 for coating deposition by EPD has yet been reported. First studies on the electrophoretic deposition of
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18 CuO from nanofluids date back about a decade ago⁴⁰. In recent years, there is an ever-increasing
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20 research interest in the electrophoretic deposition of CuO in combination with other particles, targeting
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22 at the production of nanocomposite materials, such as Al/CuO thermites⁴¹ and CuO/Carbon
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24 nanocomposites (with Carbon added in the form of nanotubes or graphene) for battery applications⁴²
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26 and antibacterial coatings⁴³. However, these studies typically use a predefined combination of solvent
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28 and surfactant for producing one specific functional nanocomposite deposit. Hence mainly the
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30 surfactant concentration, pH and/or EPD deposition parameters can be systematically varied to optimize
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32 the resulting nanocomposite deposit^{44,45}. Such an experimental strategy for producing a specific
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34 functional nanocomposite differs from the systematic approach presented here, which uses different
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36 combinations of organic solvents and surfactants (while also varying the concentrations of surfactants
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38 and CuO NPs) to reveal fundamental differences in the resulting dispersion properties (i.e. the kinetics
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40 of aggregation and agglomeration, the effective particle mobility, the solvent viscosity and conductivity).
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42 Previous aggregation studies have mainly been performed using polystyrene latex particles.^{20,21,46} In the
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44 current study, the deposition parameters of the EPD step were fixed to disclose the effect of the
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46 dispersion properties on the EPD process and resulting CuO deposit. Such a systematic approach by
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48 clearly separating dispersion- from deposition-related effects is generally not provided in previous
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50 works. Notably, the CuO dispersions in our work were optimized to minimize the carbon contamination
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52 from the surfactant in the EPD deposit; a fact that is often disregarded in other studies.
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Methods

Materials and chemicals

In this study, commercial CuO NP powder from AlfaAesar was used with an indicated mean primary NP size in the range of 20-40 nm and an indicated specific surface of 13 m²/g. Our own TEM and BET analyses of the commercial CuO NP powder indicated a slightly larger mean primary particle size of 60 ± 20 nm and a significantly lower specific surface area of 7 m²/g ($r = 0.99995$). The following primary alcohols were used as dispersant and solvent: Ethanol (99.8% C₂H₆O from Merck / Fluka Analytical), 1-Propanol (99.0% C₃H₈O from AnalaR NORMAPUR), 1-Butanol (99.9% CH₃(CH₂)₃OH from Merck), 1-Pentanol (>98% C₅H₁₂O from Merck), 1-Hexanol (>98.0% C₆H₁₄O from Merck). The following commonly used surfactants of different chemical nature were selected for this study: acetylacetone (AcAc; a bidental aprotic ligand with formula C₅H₈O₂ from VWR), sodium dodecylsulfate (SDS; an aprotic polar ionic ligand with formula C₁₂H₂₅NaO₄S from VWR Chemicals), polyethyleneglycol 1450 (PEG-1450; a short polar protic polymer with formula HO(C₂H₄O)_nH from Acros Organics), PEG-4000 (a longer chained protic polymer from Merck), Polyvinylpyrrolidone K12 (VP-K12; a short aprotic polymer with formula (C₆H₉NO)_n from Acros Organics) and PVP-K15 (a long aprotic polymer from PanReac).

Oxide NP dispersions: preparation and analysis

To prepare the CuO NP dispersions, the solvent and the surfactant (if applicable) were mixed by stirring. Next, a weighted amount of the CuO NP powder was dispersed in the solution which was subsequently ultrasonicated to disrupt the weakly linked agglomerates in the original powder (using an UP200ST with VialTweeter from Hielscher). Unless indicated otherwise, all CuO dispersions were prepared with a default CuO NP concentration of 500 mg/L (0.06 wt.%) and a surfactant concentration of 4 g/L. Time-resolved DLS analysis was conducted directly after ultrasonification to trace the size distribution(s) of CuO NP aggregates and agglomerates during the first 15 minutes (using a Zetasizer Nano ZS from Malvern Instruments Ltd., Malvern, UK; equipped with a max 4 mW He-Ne laser emitting at 633 nm). Each DLS measurement was performed at the non-invasive backscatter angle (NIBS) of 173° at a temperature of 25 °C and was preceded by a 30 s equilibration time. The applied ultrasonic treatment procedure was

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3 optimized such that diluted dispersions yielded a stable minimal particle size (as verified by DLS). The
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5 optimized settings for the ultrasonic treatment were as follows: a sixfold repetition of ten cycles of a 1 s
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7 bursts at 30% of the device capabilities with a subsequent 1 s break, followed by a 10s break. Next, the
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9 dispersion was equilibrated for 60 s to reduce its temperature (to avoid boiling). The treatment described
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11 above was repeated three times in total. Zeta-Potential measurements were performed to determine the
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13 effective mobility of the dispersed CuO aggregates/agglomerates and the conductivity of the dispersion.
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15 To this end, the same Zetasizer Nano ZS device equipped with a ZEN1002 dip cell was used, employing
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17 automatic voltage selection. The standard deviations as well as their respective mean sizes, effective
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19 mobilities and conductivities were calculated from 10 successive measurements. Static light scattering
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21 experiments were conducted after a prolonged saturation time of more than 24 h (LS 13 320 instrument
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23 with a micro-liquid module from Beckman-Coulter) to evaluate the agglomerate size after ageing. For
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25 the analysis by transmission electron microscopy (TEM; JEOL JEM-2200FS operated at accelerating
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27 voltage of 200 kV) the particles were dispersed in ethanol and transferred onto a gold grid (300 mesh,
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29 TED PELLA, INC).

30 31 32 33 34 35 36 37 *Electrophoretic deposition procedure*

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39 Electrophoretic deposition of the CuO nanostructures from the tuned CuO NP dispersions was
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41 conducted using a Keithley Sourcemeter 2400. Ti-coated and Au-coated float glass cuvette slides with
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43 sizes of 7×50 mm² (coated using physical vapor deposition; PVD) were used as a counter electrode and
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45 working electrode, respectively. Electrodes were placed parallel at a 1 mm distance, while immersing an
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47 electrode area of 7×7 mm² into the dispersion. The EPD step was performed potentiostatically using
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49 successive pulses at 75 V with a duration of 120 s, which each precedes a ramp from 0 V to 75 V taking
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51 30 s. Between, the pulses, a 60 s resting period with a fixed potential of 1 V was inserted. After the EPD
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53 step, the electrodes were carefully removed from the dispersion and gently rinsed with ethanol.
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59 *Characterization of the electrophoretic deposits* 60

The substrate surfaces after electrophoretic deposition were analyzed by optical light microscopy. Moreover, the morphology and elemental composition of the oxide deposits were investigated using a Hitachi S-3700N scanning electron microscope (SEM), equipped with an energy-dispersive X-ray detector (EDX) (Ametek EDAX, Octane Pro). Cross-sections of the deposited nanoporous oxide layers were prepared by fracturing the samples and milling the fractured edge with an IM4000 Ion Milling System (Hitachi) using an Ar ion beam (6 kV accelerating voltage, 1.5 kV discharge and 0.09 cm³/h Ar gas flow). The thickness of the deposited layers was determined using a profilometer (Bruker Dektak XT) with a stylus radius of 2 μm, stylus force of 3 mg and trace resolution of 0.833 μm/pt.

Results & Discussion

Initial CuO nanoparticle aggregate size in ethanol solvent

The main goal is to develop a green and cost-effective electrophoretic deposition process, which is transferrable to an industrial scale. Therefore, only non-toxic primary alcohols with a successively increasing hydrocarbon chain length were considered as dispersant and solvent (the use of aqueous dispersions is not possible; see Introduction).

As a first step, the effect of the ultrasonic treatment on the initial CuO aggregate size distribution in primary organic solvent without surfactant was investigated by time-resolved DLS. We focused on the dynamic light scattering technique over static light scattering to start our investigation due to its compatibility with Zeta-potential measurements. Additionally DLS measures intensity fluctuations due to particle movement which allows better assessment of the dynamics in the dispersions. Among the primary organic solvents (Table 1) employed in this study ethanol has the lowest viscosity, consequently, the ultrasonic treatment is expected to be most effective in disrupting initial CuO agglomerates of the dispersed nanopowder using ethanol as a solvent. The applied ultrasonic treatment procedure was optimized such that diluted dispersions yielded a stable minimal particle size after successive DLS measurements of the dispersion. Corresponding DLS analysis of the time-resolved particle size distribution for different CuO NP concentrations from diluted (i.e. 50 mg/L) to weakly (i.e. 500 mg/L) to

concentrated (i.e. 5000 mg/L) are presented in the contour plots of Figs. 1a-c, respectively. The intensity size distribution in Fig. 1 refers to the size distribution of the CuO particles and their aggregates in the dispersion during a defined time interval (t) after the sonification step ($t = 0$). The DLS measurements of the size distribution were performed over specific size ranges ("size bins", as defined by the instrument/software), which results in a pixelation of the contour plots.

Figure 1. Contour plots of the time-resolved CuO NP size distributions in ethanol (without surfactant), as measured by time-resolved DLS, for different CuO NP concentrations of: (a) 50 mg/L (diluted), (b) 500 mg/L (weakly concentrated) and (c) 5000 mg/L (concentrated). The color-coded scale bar indicates the corresponding particle size distribution scale. Photographs of the corresponding dispersions are also shown on the left.

DLS analysis of the diluted dispersions (i.e. 50 mg/L) directly after the ultrasonic treatment should reflect the initial aggregate size(s) present in the original CuO nanopowder. The DLS analysis for the diluted dispersion revealed a bimodal size distribution with mean sizes of 182 ± 12 nm and 584 ± 51 nm (Fig. 1a), which is also detected in the weakly concentrated 500 mg/L dispersion (Fig. 1b; mean particle sizes around 180 ± 24 nm and 580 ± 110 nm), but absent in the concentrated 5000 mg/L dispersion (Fig. 1c).

When considering spherical aggregates the volume of the smallest observed aggregates with a diameter of ~ 180 nm is about a factor of 27 larger than the primary CuO nanocrystallites in the nanopowder (diameter 60 ± 20 nm, as characterized by TEM). This indicates that the optimized ultrasonic treatment (for pure ethanol solvent) is effective in disrupting weakly-bound aggregates and agglomerates in the original nanopowder yielding the bimodal size distribution. The smallest aggregate size around ~ 180 nm reflects the mean CuO aggregate size in the original nanopowder. We cannot rule out that even smaller aggregate sizes (i.e. single nanocrystallites) were also present in the dispersion; however their presence would be overshadowed by the large amount of bigger aggregates and agglomerates, since the scattering intensity scales with the particle size.^{47,48} As reflected by the relatively broad DLS signals of the bimodal size distributions in Figs. 1a and 1b, the initial aggregates in the original nanopowder, as well as their agglomerates formed in the dispersion, have an irregular non-spherical shape, as verified through TEM analysis of particles dispersed in ethanol (Fig. S1).

The initial aggregates (~ 180 nm) have a very high mobility (through Brownian motion) in the pure ethanol dispersion (due to the relatively low viscosity of the solvent; see Table 1), which enables very fast agglomeration, especially towards higher concentrations. Consequently, the initial aggregate size of around ~ 180 nm is no longer detected for the concentrated 5000 mg/L dispersion (see Fig. 1c). The low viscosity of ethanol solvent also enables fast sedimentation of large agglomerates by gravity, which keeps the mean agglomerate size distribution in the dispersion below 1000 nm for all CuO NP concentrations studied (Fig. 1). The upper size of roughly 1000 nm thus represents an upper threshold of the largest CuO NP agglomerate size in the ethanol dispersion prior to sedimentation. Notably, the mean agglomerate size in the concentrated dispersion increases with increasing measurement time from 504 ± 35 nm to 747 ± 64 nm (after 10 minutes). This effect can be attributed to the temperature instability of the dispersion directly after the ultrasonic treatment. Namely, the ultrasonic treatment increases the temperature of the solvent resulting in a lower viscosity and thus a higher Brownian motion, which both promote particle-particle interactions and agglomeration (and possibly sedimentation) during the first minutes of the DLS analysis (i.e. during temperature equilibration of the dispersion). Comparison of the photographs of the analyzed dispersions (see Fig. 1) illustrates the main limitation

for the DLS analysis of concentrated dispersions; i.e. these dispersions (or rather suspensions; see below) become very dark, which hinders an effective penetration depth of the laser light into the dispersion. Therefore, a concentration of 500 mg/L was used for further investigations of the mobility and agglomeration behavior of CuO NP aggregates, dispersed in organic solvents with different surfactants.

CuO NP dispersions in different organic solvents without surfactant

The effective mobility (i.e. the particle mobility under influence of an externally applied electric field) of CuO NP aggregates and/or agglomerates, as well as the conductivity of the different dispersions are reported in Table 1 (as obtained from Zeta-Potential measurements). The viscosity of the primary organic solvent increases with increasing hydrocarbon chain length from ethanol to hexanol. Accordingly, the (absolute) effective mobility of CuO NP aggregates and/or agglomerates, as well as the conductivity of the dispersions decrease with increasing viscosity (i.e. with increasing hydrocarbon chain length) from ethanol to hexanol.

Table 1 Mean size, effective mobility and conductivity obtained from Zeta-Potential measurements of CuO NP aggregates dispersed in different primary organic solvents (without surfactant). The viscosity and dielectric constant (ϵ) of the solvents are also given.^{49–51}

Solvent	Mean size (nm)	Mobility ($\mu\text{m}\cdot\text{cm}\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	Conductivity ($\times 10^{-4} \text{ mS}\cdot\text{cm}^{-1}$)	Viscosity (mPa·s)	Dielectric constant
Ethanol	180 ± 24 nm	-0.513 ± 0.031	17.30 ± 0.43	1.08	25.3
	580 ± 110 nm				
Propanol	1651 ± 422	-0.066 ± 0.008	7.368 ± 0.81	1.94	20.9
Butanol	832 ± 87	0.016 ± 0.005	5.501 ± 0.59	2.57	17.7
Pentanol	709 ± 75	< 10 ⁻³	3.302 ± 1.00	3.51	15.3
Hexanol	488 ± 43	< 10 ⁻³	3.572 ± 1.14	4.59	13.3

The mean size distributions of the CuO NP aggregates and/or agglomerates in different organic solvents (at a concentration of 500 mg/L without surfactant) were measured by time-resolved DLS for a

duration of 15 minutes, starting directly after the ultrasonic treatment (Figs. 2a-e). The agglomerate sizes are plotted as function of the DLS measurement time in Fig. 3a; the corresponding averaged values are given in Fig. 3b. As previously discussed (cf. Fig. 1b) and reflected in Fig. 2a, the CuO NP dispersion (500 mg/L) with ethanol solvent yields a bimodal size distribution through the ultrasonic treatment with mean size ranges of 180 ± 24 nm and 580 ± 110 nm. The initial aggregates (~ 180 nm) have a very high mobility in the pure ethanol dispersion due to its relatively low viscosity (see Table 1). Consequently, concentrated CuO NP dispersions in ethanol solvent exhibit very fast agglomeration of small aggregates. The low viscosity of ethanol allows the coagulation of large agglomerates into even larger ones, as indicated by the occasional occurrence of signal intensities at size > 1000 nm. In addition, the low viscosity of ethanol solvent enabled fast sedimentation of large agglomerates under the influence of gravity. The concurrent fast coagulation and sedimentation of large agglomerates (size > 1000 nm) results in correlated fluctuations of the measured bimodal DLS signal intensity with time. We conclude that the concentrated CuO NP dispersions in ethanol solvent are unstable without the addition of a surfactant and thus rather resemble suspensions.

Figure 2. Contour plots of the size distributions of the CuO NP aggregates and agglomerates dispersed in the different organic solvents without addition of a surfactant. The data was obtained by time-resolved DLS directly after ultrasonic treatment. The color-coded scale bar indicates the corresponding particle size distribution scale.

Figure 3. (a) Mean agglomerate size of the concentrated CuO NP dispersions in the different organic solvents versus DLS measurement time. (b) Mean agglomerate size plus standard deviation (over the DLS measurement time of 5 to 15 minutes) for the different organic solvents without surfactant. All data were extracted from the contour plots in Fig. 2.

The viscosity of propanol is roughly doubled compared to ethanol (see Table 1), which drastically reduces the Brownian motion of smaller aggregates and, particularly, of larger agglomerates in the dispersion. Consequently, a distinct bimodal size distribution as observed with ethanol is no longer evident for the CuO NPs dispersed in propanol (Fig 2b). Although we still find evidence for the presence of initial CuO NP aggregates in propanol by occasional signal intensities around ~180 nm, their signal is much less pronounced. Instead a broadening of the signal intensity of the larger agglomerates is observed, indicating coagulation of smaller aggregates and agglomerates into larger agglomerates of irregular size and shape. Interestingly, the higher viscosity of propanol does not only suppress the mobility of larger agglomerates, but also reduces their sedimentation rate (compared to ethanol). Consequently, the mean agglomerate size of 1651 ± 422 nm is significantly larger in propanol than in

ethanol solvent and hence the formation of very large agglomerates with sizes in the range of 4000-5000 nm was occasionally detected (Fig. 2b).

With the stepwise increase of the carbon chain length to butanol, the solvent viscosity further increases (see Table 1). Therefore, the agglomeration kinetics were further reduced compared to propanol and, particularly, ethanol. While agglomeration of the smallest aggregates still occurred, the coagulation of large agglomerates further into larger ones is kinetically hindered, resulting in a relatively intense and narrow size distribution and a relatively small mean agglomerate size of $\sim 832 \pm 87$ nm.

The viscosity of the solvent further increases from pentanol to hexanol (Table 1); the corresponding DLS analyses are shown in Figs. 2d and 2e, respectively. DLS yielded mean agglomerate sizes of 709 ± 75 nm and 488 ± 43 nm for pentanol and hexanol respectively. With the increase in viscosity of the solvent, the size distributions show even less variance indicating a homogenous dispersion of stable agglomerates. Notably, the smaller size mode detected at ~ 180 nm (characteristic for the initial aggregate size in the powder) is only occasionally detected in the organic solvents with higher viscosities, which can be rationalized as follows. First, the disruption of weakly linked aggregates in the original nanopowder by the ultrasonic treatment is less effective for organic solvents with a higher viscosity. Secondly, with increasing viscosity of the solvent, larger agglomerates become more stable and thus more prominent, eventually dominating the DLS signal intensity.

SLS is a complementary technique to DLS, since it measures the average particle size by integrating the intensity of the scattered light at several angles over time. SLS analysis was applied to investigate the long-term stability of the CuO NP dispersions in the different organic solvents without surfactant. Prior to the ageing process, the concentrated dispersions were freshly prepared and ultrasonicated. Afterwards the dispersions were rested for 24 h under laboratory conditions and subsequently measured by SLS. Fig. 4 shows the thus-obtained volume size distributions of the CuO NP agglomerates in the different solvents. The volume percentage of agglomerates with sizes smaller than 1000 nm was most pronounced, especially in ethanol. Hence, the aged dispersions still maintain stable agglomerates with sizes of up to about 1 μ m, despite progressive aggregation, agglomeration and sedimentation during 24 hours of aging.

Figure 4. The mean sizes and volume size distributions (by multi modal peak analysis) of the CuO NP agglomerates in the different dispersions (without surfactants) after aging for 24 hours. The color-coded scale bar denotes the volume percentage for the different size ranges. The average agglomerate size is indicated by the red line.

In conclusion, the CuO NP powder dispersed in a primary organic solvent is predominantly stabilized by physical effects, e.g. by the viscosity of the used dispersant. Time-resolved DLS analyses showed that the agglomeration rate of smaller CuO NP aggregates and, especially of larger agglomerates, is successively reduced with increasing viscosity (i.e. with an increasing carbon chain length) of the organic solvent from ethanol to hexanol. The resulting mean agglomerate size decreased with increasing solvent viscosity from propanol to hexanol (see Fig. 3b). Ethanol is an exception to this rule, since larger agglomerates still have sufficient mobility to coagulate into even larger agglomerates, which quickly sediment from the dispersion.

Previous research on surface charging mechanisms of oxides in pure primary alcohols with an intermediate dielectric constant ($10 < \epsilon < 30$) indeed showed that the decrease in particle mobility with increasing hydrocarbon-chain length is mainly due to the difference in viscosity^{52,53}. The electrophoretic mobility and aggregation behaviors of oxide particles in colloidal dispersions is also governed by their surface charge. In the present study, all the alcohol solvents have the same functional OH-group and it can thus be assumed that the basic particle-solvent charging mechanism is identical for all organic solvents (without surfactant).^{52,54} It was shown that the aggregation behavior of CuO nanoparticles in

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3 *aqueous* solutions can be controlled by tailoring its surface charge by controlling the pH.⁵⁵ In the pH
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5 range of 6-11 the electrostatic repulsive forces no longer prevent the particles from aggregating.⁵⁶ In
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7 this regard, it is noted that none of the solvents were dried in the present study. Consequently, in
8
9 particular the ethanol solvent will absorb humidity and thus have a higher water content than the other
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11 organic solvents. By absorption of humidity, a polar medium (water, $\epsilon = 80$) is passively added, which
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13 leads to an increase of the effective surface charge of CuO particles that interact with dissolved water
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15 molecules (accordance to the Nernst equation⁵⁷). This may also partially rationalize the much enhanced
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17 mobility and aggregation/agglomerates of the CuO particles in ethanol solvent (without surfactant).
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23 **CuO NP dispersion in ethanol solvent with different surfactants**

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26 The relatively high mobility of larger CuO NP agglomerates in ethanol solvent is a key criteria for the
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28 development of a suitable EPD process. Moreover, ethanol is the most volatile solvent, which facilitates
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30 removal of carbon contamination (solvent) residues from the deposited coating after the EPD step. As a
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32 next step, we investigated if the stability of the CuO NP dispersion with ethanol solvent could be
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34 improved by addition of a suitable surfactant, while assuring a high mobility and narrow size distribution
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36 of the dispersed CuO NP aggregates and/or agglomerates.
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40 To this end, CuO NP dispersions with ethanol solvent and 0.5 wt.% of AcAc, SDS, PEG-1450, PEG-
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42 4000, PVP-K12 or PVP-K15 surfactant were prepared, as described earlier. The different surfactants were
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44 selected based on their chemical nature: i.e. AcAc as a bidental aprotic ligand; SDS as an aprotic polar,
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46 ionic ligand; PEG-1450 & PEG-4000 as a short and longer polar, protic polymers; PEG-4000 as a longer
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48 chained protic polymer; PVP-K12 & PVP-K15 as short and long aprotic polymers. The effective mobility
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50 and conductivity of the dispersions, as obtained from Zeta-Potential measurements, are given in Table
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52 2 (the mean average agglomerate size by DLS is also listed).
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56 Exemplary results of the agglomerate size distribution and mean agglomerate size with time
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58 (directly after ultrasonification) are depicted for AcAc, SDS and PEG-1450 in Fig. 5a (as measured by
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60 time-resolved DLS). The corresponding data for pure ethanol solvent (EtOH; without surfactant is again

given as a reference. The corresponding mean agglomerate size (plus standard deviation; as averaged over the DLS measurement time from 5 to 15 minutes) for each surfactant is given in Fig. 5b. The mean sizes and volume size distributions of the CuO NP agglomerates in the dispersions after aging for 24 hours are plotted in Fig. 5c (as determined by SLS).

Table 2 Effective mobility and conductivity for the CuO NP dispersions in ethanol solvent with 0.5 wt.% addition of various surfactants, as obtained from Zeta-Potential measurements.

Dispersion composition	Average size (nm)	Mobility ($\mu\text{m}\cdot\text{cm}\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	Conductivity ($\times 10^{-4} \text{ mS}\cdot\text{cm}^{-1}$)
pure ethanol	225 $\pm$ 103	-0.513 $\pm$ 0.031	17.3 $\pm$ 0.43
	650 $\pm$ 198		
+ acetylacetone	819 $\pm$ 155	0.221 $\pm$ 0.060	26.7 $\pm$ 1.2
+ SDS	1440 $\pm$ 286	0.477 $\pm$ 0.029	2945 $\pm$ 5.0
+ PEG 1450	236 $\pm$ 45	-0.784 $\pm$ 0.033	41.9 $\pm$ 1.0
	1048 $\pm$ 298		
+ PVP K12	247 $\pm$ 90	-0.596 $\pm$ 0.038	22.6 $\pm$ 0.6
	1295 $\pm$ 259		
+ PEG 4000	211 $\pm$ 75	-0.530 $\pm$ 0.061	24.1 $\pm$ 0.3
	1240 $\pm$ 287		
+ PVP K15	232 $\pm$ 97	-0.603 $\pm$ 0.029	20.8 $\pm$ 1.0
	1057 $\pm$ 181

Figure 5. (a) Exemplary results of the size distribution for the concentrated CuO NP dispersions in ethanol solvent with 0.5 wt.% of AcAc, SDS or PEG-1450 surfactant. The corresponding data for pure ethanol solvent (EtOH; without surfactant) is also given as a reference. (b) The mean agglomerate size (plus standard deviation; as averaged over a measurement time from 5 to 15 minutes) in ethanol solvent with the given surfactant. (c) Mean particle sizes and volume size distributions of the dispersions in pure ethanol solvent with different surfactants after aging for 24 hours (as determined by SLS).

As follows from Fig. 5a, addition of AcAc or SDS to the concentrated CuO NP dispersion resulted in a more intense and narrower agglomerate size distribution. Fluctuations of the size distribution were only observed during the first few minutes, which can be attributed to a temperature equilibration of the freshly ultrasonicated dispersion. The mean agglomerate size with AcAc (as averaged over a measurement time from 5 to 15 minutes) was 819 ± 155 nm. The agglomerates in the SDS dispersion were larger than with AcAc, having a mean size of 1440 ± 286 nm. Zeta-potential measurements (Table 2) indicate that the addition of AcAc or SDS changes the sign of the surface charge of the dispersed CuO NP agglomerates from negative to positive, which appears to be crucial for an effective stabilization of

the ethanol dispersion. Addition of surfactants to the dispersions introduces additional ions, which can adhere to the initially negatively charged surface of the dispersed CuO nanoparticle aggregates. The addition of SDS is associated with the adsorption of sodium ions onto the oxide surface, which explains the observed surface charge reversal. AcAc coexist as keto and enol tautomers in solution. The enol form is a weak acid, which changes the pH of the dispersion. In addition, its interaction with the negative surface charge of the oxide particles apparently also results in a positive surface charge. Similar phenomena were previously observed for SiO₂, MgO and TiO₂ particles in methanol when stabilized by aerosol OT.⁵² The agglomerate mobility is only slightly higher with SDS, whereas the conductivity of the dispersion is increased by a factor 10³ for SDS (both as compared to AcAc; see Table 2). Notably, as prior discussed, a too high conductivity of the dispersion is problematic for the EPD process, which favors the use of AcAC over that of SDS.

The use of PEG-1450, PEG-4000, PVP-K12 or PVP-K15 does not change the sign of the surface charge of the dispersed CuO NP agglomerates (as compared to pure ethanol). Consequently, the agglomerate mobilities and dispersion conductivities in the presence of PEG-4000, PVP-K12 and PVP-K15 are very similar compared to ethanol; only PEG-1450 gives a slightly higher mobility and conductivity (see Table 2). Accordingly, time-resolved DLS also detected a fluctuating bimodal size distribution for the dispersions with PEG-1450, PEG-4000, PVP-K12 and PVP-K15 as surfactants: cf. Fig. 5a for PEG-1450. Notably, the fluctuating bimodal size distribution in the case of PEG-1450 was more distinct and indicated larger agglomerate sizes compared to the pure ethanol dispersion, which suggests that the agglomeration rates are slightly enhanced in the presence of PEG-1450. The usage of PEG 4000, PVP K12 or PVP K15 surfactant yielded fluctuating bimodal size distributions that were similar to plain ethanol; i.e. the formation of very large agglomerates (as for PEG-1450) was not observed. While the smaller size distribution around ~180 nm originated from the initial aggregates in the original nanopowder, the larger agglomerates are roughly two times larger compared to pure ethanol solvent (i.e. in the size range of 1050 -1300 nm). Hence it is concluded that the use of the long-chained polymer surfactants PEG-1450, PEG-4000, PVP-K12 or PVP-K15 does not improve the intrinsically poor stability of the CuO NP dispersions in ethanol solvent. An improved stability of the CuO NP dispersions in ethanol

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solvent is only achieved by the addition of AcAc or SDS due to the associated modification of the oxide surface charge.

For our targeted application in the field of CuO-based nanothermites, it is essential to reduce the carbon contamination in the EPD coatings to a minimum. Therefore, we tested if CuO NP agglomerates in ethanol solvent can also be stabilized by lower SDS and AcAC concentrations (0.05 wt.% and 0.25 wt.%, see Table S4 and Fig. S2). Although the addition of AcAc and SDS in lower concentrations clearly stabilizes the CuO NP agglomerates (most evident for SDS) in the ethanol dispersions, it also lead to the appearance of not previously detected agglomerate sizes in the dispersion (i.e. initial aggregates and their agglomerates, as well as very large agglomerates), which is unwanted in the present work. Apparently, AcAc or SDS surfactant concentrations of 0.25 wt.% are too low to stabilize a single agglomerate size. A stable dispersion with a mono-modal size distribution can be obtained for AcAc and SDS surfactant concentrations of 0.50 wt.% (see Figs. 5b and 5c), which we therefore applied for the EPD step.

The investigation of the effective mobility with different surfactant concentrations (Table S4 and Fig. S2) gives additional insights on the underlying mechanisms for the observed dispersion stabilization using SDS or AcAc. For SDS, the effective mobility and hence the surface charge increases with increasing SDS concentration, which supports the above statement that the particles are being electrostatically stabilized through the adsorption of positive sodium ions on the aggregate surface. For AcAc, the effective mobility and thus the surface charge increases with increasing surfactant concentration from 0.05 wt.% up to 0.25 wt.%, but is again lower for even higher concentrations of 0.5 wt.% (see Table S4 and Fig. S2). This observation suggests that the majority of AcAc-related ions are adsorbed on the particle surfaces up to 0.25 wt.%, which prevents a change in acidity of the dispersion by still dissolved AcAc ions. For higher AcAc surfactant concentrations >0.25 wt.%, the AcAc anion concentration in the dispersion rises, which results in a reduced acidity of the dispersion, as accompanied by a lowering of the effective surface charge.

Electrophoretic deposition from tuned CuO NP dispersion

Concentrated CuO NP dispersions are required to realize fast formation of micrometer thick coatings by EPD. Therefore, CuO NP concentrations of 5000 mg/L in ethanol solvent were used for the EPD step using a surfactant concentration to 0.5wt%. We increased the particle concentration to ensure a sufficiently high particle concentration for fast deposition of micrometer-thick coatings. Comparison of the DLS investigations for different particle and surfactant concentrations showed that the increased agglomeration behavior for these concentrated CuO NP dispersions has no significant effect on the maximum agglomerate size (see Fig. 1) prior to sedimentation and thus results in comparable aggregate/agglomerate size distributions.

Electrophoretic deposition was performed on Ti-covered glass substrates, according to the procedure described above. A planar SEM micrograph of the nanoporous CuO coating surface, as obtained after four EPD cycles from the dispersion with 0.5wt% AcAC, is shown in Fig. 6a. A corresponding cross-sectional SEM micrograph of the same sample is shown in Fig. 7. The original substrate could be fully covered with CuO NP agglomerates from the dispersion. Analysis using a profilometer yielded an average coating thickness in the range of 20 - 30 μm , after 480 s deposition time, as confirmed by cross-sectional SEM (Fig. 7). Image analysis of the cross-sectional SEM micrograph resulted in an estimated coating porosity of 43 % $\pm$ 2 %. Of course, the resulting coating porosity mainly depends on the mean size and shape of the initial aggregates in the selected CuO nanopowder. This implies that the nanoporosity of the coatings can easily be varied by choosing a finer or coarser CuO nanopowder.

Figure 6. Secondary electron micrograph of the sample surface after electrophoretic deposition from the concentrated CuO NP dispersions (5000 mg/L) in ethanol solvent on flat Ti-coated glass substrates. (a) with 0.5 wt.% AcAc surfactant (b) without any surfactant.

Figure 7. Secondary electron micrograph of a cross-sectioned sample after electrophoretic deposition from the concentrated CuO NP dispersions (5000 mg/L) in ethanol solvent with 0.5 wt% AcAc surfactant on flat Ti-coated glass substrates.

For comparison, we prepared a planar SEM micrograph of the sample surface after four EPD cycles from the dispersion without surfactant (Fig. 6b). It follows that the same EPD step (under identical conditions) from a dispersion without surfactant does not result in a micrometer-thick nanoporous CuO coating. Instead, the sample surface after the EPD step is only partially covered with CuO NP agglomerates; the loosely-packed patches of deposited CuO NP agglomerates have a thickness of up to 4 μm , which is well below the coating thickness achieved for the dispersion with AcAc surfactant. These results indicate that the addition of AcAc surfactant does not only promote the formation of stable agglomerates in the CuO NP dispersion, but is also needed to promote layer formation during subsequent electrophoretic deposition of the same agglomerates. This suggests that the addition of AcAc surfactant to the dispersion not only shield the effective repulsive forces between the CuO NP aggregates and agglomerates in the dispersion and hence promoting attraction between them, but also results in a net attractive interaction between neighboring agglomerates deposited on the substrate surface during the EPD step, thus promoting laterally homogeneous layer formation. In the absence of AcAc surfactant, the attractive interactions between neighboring agglomerates on the substrate surface are too weak (or likely even repelling), thus preventing layer formation.

Noteworthy, the EPD step was also performed for the same dispersions with 0.5 wt.% SDS surfactant. However, this EPD process failed to produce adequate layers due to the very high conductivity of the dispersions, which resulted in the solution heating up very fast and boiling when the default parameters were applied in the EPD step. While such fast heating of the dispersion could be counteracted by active cooling during the EPD step, it would be technically challenging to ensure accurate control and homogenous distribution of the temperature (and thus the viscosity).

The nanoporous CuO coatings as produced by EPD from the concentrated CuO NP dispersions with ethanol solvent and AcAc surfactant can obviously be envisioned for applications in the field of

catalysis.^{58,59} In our present research, the obtained nanoporous CuO coatings will instead be used as a nanoporous scaffold for the production of Al/CuO nanocomposite thermite coatings by infiltration with Al metal, as will be presented in an upcoming paper. Such high energetic material systems with nano-sized components show promising application in the fields of combustion, propellants and joining.^{25,60–}

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Conclusions

The particle mobility, size distribution and agglomeration behavior of diluted to concentrated (50 up to 5000 mg/L), non-aqueous CuO NP dispersions were investigated and tuned to achieve fast electrophoretic deposition (EPD) of micrometer-thick, nanoporous CuO films.

Ultrasonic treatment of the freshly-prepared CuO NP dispersions was essential to disrupt weakly-bounded aggregates and agglomerates in the original nanopowder, which was particularly effective in ethanol solvent due to its low viscosity. However, the concentrated CuO NP dispersions (50 to 5000 mg/L) in ethanol solvent were unstable without the addition of a surfactant and rather resembled a suspension with a bimodal size distribution (with mean particle sizes of 180 ± 24 nm and 580 ± 110 nm). The smallest CuO NP aggregates (~180 nm) in ethanol solvent were composed of roughly 27 fused primary CuO nanocrystallites and reflected the average initial aggregate size in the nanopowder. The effective mobilities of CuO NP aggregates and/or agglomerates, as well as the conductivity of the dispersions, both decreased with increasing viscosity (i.e. with increasing hydrocarbon chain length) from ethanol to hexanol. Consequently, the rates of coagulation of initial aggregates and smaller agglomerates into larger agglomerates also decreased with increasing solvent viscosity.

The addition of AcAc or SDS as a surfactant changed the sign of the surface charge of the CuO NP agglomerates in ethanol solvent from negative to positive and effectively stabilized the dispersion. The addition of 0.5 wt.% PEG-1450, PEG-4000, PVP-K12 or PVP-K15 surfactant did not change the sign of the surface charge of the dispersed CuO NP agglomerates in ethanol solvent and, consequently, the corresponding agglomerate mobilities and dispersion conductivities were similar to pure ethanol.

Electrophoretic deposition from concentrated CuO NP dispersions (5000 mg/L) in ethanol solvent with 0.5 wt.% AcAc surfactant was successfully applied for synthesizing micrometer-thick nanoporous CuO coatings, which can serve as scaffolds for the production of Al/CuO nanocomposite thermite coatings or as high-specific-surface-area catalysts. The addition of AcAc surfactant was a requisite to promote layer formation during the EPD step. In the absence of AcAc surfactant, the attractive interactions between neighboring agglomerates deposited on the substrate were too weak (or likely even repelling) to induce laterally homogeneous layer formation.

Supporting Information

Used chemicals with purity and distributor (Table S1), dispersion compositions for different organic solvents without (Table S2) and with (Table S3) surfactant, TEM micrographs of CuO nanoparticle aggregates dispersed in ethanol (Fig. S1), Contour plots of the size distributions of the CuO NP aggregates and agglomerates dispersed in ethanol with different surfactant concentrations (Fig. S2), Effective mobilities and conductivities for the CuO NP dispersions in ethanol solvent with different surfactant types and concentrations (Table. S4).

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Contour plots of the time-resolved CuO NP size distributions in ethanol (without surfactant), as measured by time-resolved DLS, for different CuO NP concentrations of: (a) 50 mg/L (diluted), (b) 500 mg/L (weakly concentrated) and (c) 5000 mg/L (concentrated). The color-coded scale bar indicates the corresponding particle size distribution scale. Photographs of the corresponding dispersions are also shown on the left.

149x109mm (800 x 800 DPI)

Contour plots of the size distributions of the CuO NP aggregates and agglomerates dispersed in the different organic solvents without addition of a surfactant. The data was obtained by time-resolved DLS directly after ultrasonic treatment, as described in Sec 3.1. The color-coded scale bar indicates the corresponding particle size distribution scale.

149x95mm (800 x 800 DPI)

(a) Mean agglomerate size of the concentrated CuO NP dispersions in the different organic solvents versus DLS measurement time. (b) Mean agglomerate size plus standard deviation (over the DLS measurement time of 5 to 15 minutes) for the different organic solvents without surfactant. All data were extracted from the contour plots in Fig. 2.

149x56mm (800 x 800 DPI)

The mean sizes and volume size distributions (by multi modal peak analysis) of the CuO NP agglomerates in the different dispersions (without surfactants) after aging for 24 hours. The color-coded scale bare denotes the volume percentage for the different size ranges. The average agglomerate size is indicated by the red line.

80x55mm (800 x 800 DPI)

(a) Exemplary results of the size distribution for the concentrated CuO NP dispersions in ethanol solvent with 0.5 wt.% of AcAc, SDS or PEG-1450 surfactant. The corresponding data for pure ethanol solvent (EtOH; without surfactant; see Sec. 3.2) is also given as a reference. (b) The mean agglomerate size (plus standard deviation; as averaged over a measurement time from 5 to 15 minutes) in ethanol solvent with the given surfactant. (c) Mean particle sizes and volume size distributions of the dispersions in pure ethanol solvent with different surfactants after aging for 24 hours (as determined by SLS).

149x114mm (800 x 800 DPI)

Secondary electron micrograph of the sample surface after electrophoretic deposition from the highly-concentrated CuO NP dispersions (5000 mg/L) in ethanol solvent on flat Ti-coated glass substrates. (a) with 0.5 wt.% AcAc surfactant (b) without any surfactant.

149x147mm (800 x 800 DPI)

Secondary electron micrograph of a cross-sectioned sample after electrophoretic deposition from the highly-concentrated CuO NP dispersions (5000 mg/L) in ethanol solvent with 0.5 wt% AcAc surfactant on flat Ti-coated glass substrates.

80x59mm (600 x 600 DPI)