Supporting Information:
Broad-spectrum Enhancement of Polymer Composite Dielectric Constant at Ultra-low Volume Fractions of Silica-supported Copper Nanoparticles

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Synthesis of Thiol-functionalized Mesoporous Silica Microspheres

Mesoporous silica microspheres were synthesised following a procedure reported by Nakamura *et al.*[1] The molar ratios of ingredients were as follows: 1 TMOS : 0.2 MPTMS : 0.85 CTMACl : 0.17 NaOH(1M) : 1707 H_2O : 959 MeOH

In a first step CTMACl, NaOH, distilled water and methanol were mixed under magnetic stirring until a clear stock solution was obtained. Subsequently, TMOS and MPTMS were mixed in a separate vial and added dropwise to the stock solution using a micro pipette. The process was carried out at room temperature. The solution became turbid after 10 min. Stirring was stopped after 24 h and the obtained opaque solution was left to age for 72 h. The synthesized silica microspheres were separated from the solution by filtering with a funnel and filter papers, then thoroughly washed three times with distilled water (without ultra sound or centrifugation). The solid wet product was dried in an exsiccator over silicagel at room temperature for 48 h. The structure directing agent (CT-MACl) was then removed by acid extraction. To this end, 3 g of the dried SiO_2 powder were mixed with 300 ml ethanol and 3 ml concentrated HCl solution in a flask. The mixture was stirred for 3 h at 60°C in a water bath. Following this, the solution was filtered with a vacuum funnel and filter papers followed by washing thoroughly with ethanol, before the wet residue was dried over silica gel in an exsiccator for 48 h.

Characterization of Silica Microspheres

SEM and TEM Analysis

For SEM analysis (JEOL 7401F, 4 kV acceleration voltage), sample powders were mounted on double-sided conducting carbon tape, with no further treatment (specifically, no gold was sputtered onto the samples). For TEM analysis (CM20 STWIN (FEI), 200 kV acceleration voltage), powders were placed in a mortar, and ground until the powder appeared finely distributed. This powder was placed on a finely masked carbon grid, with no further treatment.

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BET analysis

BET analysis (Quantachrome Autosorb-1-C) was used to determine the density of the SiO_2-spheres. The specific pore volume V_p of the spheres was measured to be 0.73 cm^3/g (N_2). With V_p and the bulk density of quartz crystals of 2.6 cm^3/g, the resulting SiO_2-sphere density ρ_{SiO_2} can be calculated using (assuming that the density of the cavities is negligible):

$$\rho_{SiO_2} = \frac{1}{\frac{1}{\rho_{quartz}} + V_p} \qquad (1)$$

With this, the density of silica microspheres is determined to be ρ_{SiO_2}=0.89 g/cm^3.

Cu-loading Process of Silica Microspheres

Preparation of Regular and Highly Loaded Silica Microspheres

In the following, the procedure for loading the silica microspheres with Cu nanoparticles is described. Also, to facilitate subsequent analysis, a preparation was made in which an elevated content of Cu was used, mainly to determine optimal oxidation and reduction temperatures.

Preparation P1 (Regular Cu-loading)

The dried silica microspheres were mixed with an aqueous copper acetate monohydrate (Sigma Aldrich) solution (conc. 0.05 g/ml) in a ratio of 1:30 and stirred for 24 h. The surplus solution was decanted and the particles dried on filter paper. The copper acetate treated silica microspheres were placed in a tube furnace and exposed to air at 450°C (N_2:O_2, 80:20), to convert all Cu ions into CuO and to remove the thiol groups. This process leads to small residues of $CuSO_4$, while all CuS should be removed.[2] The particles were then reduced in a diluted hydrogen flow at 230°C (H_2:Ar, 5:95), resulting in three Cu phases: Cu, CuO and $CuSO_4$.

Preparation P2 (High Cu-loading)

XRD analysis required an increased Cu loading in order to distinguish Cu-related information from the signal background. Since such high loading was not achieved using acetate as Cu precursor, silica microspheres were loaded with aqueous copper nitrate solution (2.0 g/ml $Cu(NO_3)_2 \cdot 2.5H_2O$). A Cu content of 27%$_{wt}$ (ICP-OES) was obtained.

Characterization of Cu-loaded Silica Microspheres

ICP-OES Analysis

Sample P1 was decomposed in HF and analyzed using ICP-OES (optical emission spectroscopy enabled by inductively coupled plasma) to determine the amount of Cu in the loaded silica microspheres. This analysis determined a copper content of 8.0%$_{wt}$.

XPS Analysis

XPS analysis of copper-loaded silica microspheres (C) was performed (VG ESCALAB 220 iXL). The powder was mounted on two-sided carbon tape, ensuring complete coverage, and excited with an 1253.6 eV x-ray source (Mg K$_\alpha$). From the observed binding energies, the phases can be assigned to $CuSO_4$, CuO and metallic Cu (Figure 1). The determined relative amounts of Cu in the three phases were 0.195 %$_{at}$ for metallic Cu, 0.075 %$_{at}$ for CuO and 0.071 %$_{at}$ for $CuSO_4$. Hence, out of the total amount of copper present, the fraction of copper in the metallic state is 57.2%.

XRD Analysis

Crystalline phases in un-loaded, as well as in Cu-loaded silica microspheres with low (P1) and increased (P2) content of Cu were investigated by powder XRD (STOE STADI P). Samples derived from P1 did not produce distinguishable reflections after oxidation, nor after reduction. In contrast, samples derived from P2 show a crystalline CuO phase after oxidation, and a transition from
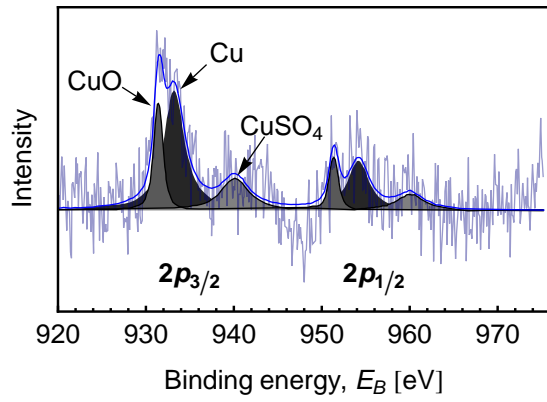
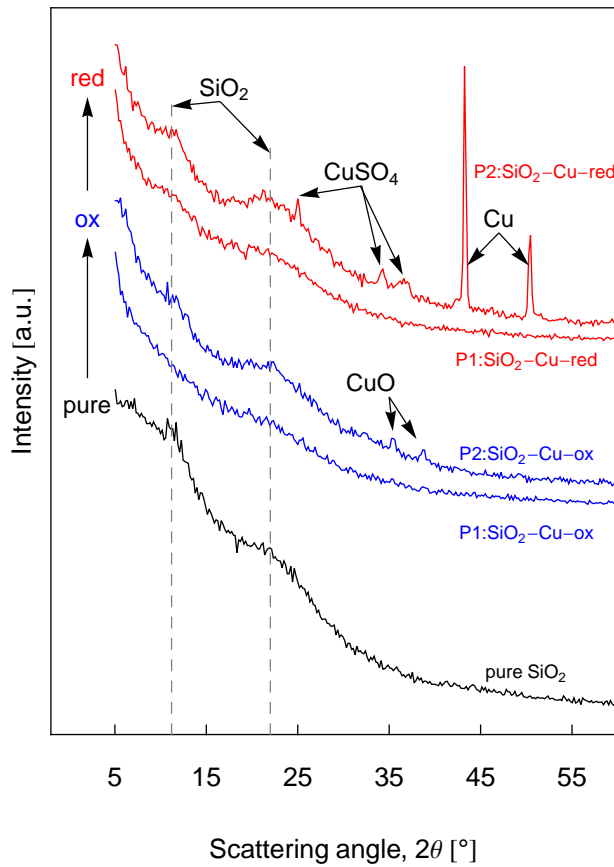Figure 1: XPS analysis of the Cu-loaded silica microspheres (P1) – three different Cu phases were detected.

Figure 2: XRD intensity (arbitrary units) of pure silica microspheres and Cu-loaded SiO_2-microspheres of low (P1) and high (P2) Cu content. Curves for SiO_2-Cu samples P1 and P2 are shown after oxidation (blue) and after reduction (red).

CuO to Cu and $CuSO_4$ in the reduction step (Figure 2).

The peak width in the diffractograms is related to the crystallite size of the Cu particles by the Scherrer equation:

$$L = \frac{K\lambda_{Cu}}{\beta \cos(\theta)} \quad (2)$$

where L is the average size of the crystallites, K is the shape factor (0.89 for spheres, 0.94 for cubes), $\lambda_{Cu} = 154$ pm is the wavelength of the x-ray light, β is the FWHM of the peak (rad), and θ is the position of the peak maximum. The absence of any Cu-related reflections for low-loaded sample P1 can be explained by the small size of the Cu particles (5 nm, from TEM), which broadens the corresponding peaks ($\Delta\theta_{FWHM} \stackrel{\wedge}{=} 2.18°$) as well as the low content of Cu, making the peaks indistinguishable from the background. Employing Eq. (2), the width of the metallic Cu peak of sample P2 corresponds to Cu crystallites of roughly 30-40 nm, which is in agreement with the SEM images of this sample (Figure 3). The SEM images of high-loaded sample P2 indicate the presence of large Cu particles on the outer surface of the silica microspheres featuring diameters of roughly 40 nm, and a wide size distribution. Since Cu particles on sample P2 with high Cu-loading did not show a defined or controlled morphology and distribution, the sample was not incorporated into SEBS-composites nor used for DRS investigations. Sample P2 demonstrates only in principle that metallic Cu can be obtained under the synthesis conditions employed in the present study.
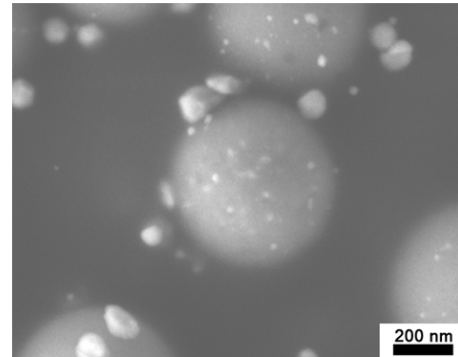

Figure 3: SEM image of P2 (silica microsphere with elevated Cu loading). Larger Cu particles outside the silica microspheres are clearly visible as bright objects on the darker silica background.

Calculation of Metallic Cu Content in Silica Microspheres

Based on the above mentioned BET analysis, the density of the silica microspheres was determined to be ρ_{SiO_2}=0.89 g/cm^3. The ICP-OES analysis of the Cu-loaded silical microspheres, sample P1, indicated a copper content of 8.0%$_{wt}$, without indication of the chemical phase. The XPS analysis showed the relative amount of copper in the metallic state as 57.2% relative to all present copper. The bulk density of metallic copper is 8.94 g/cm^3. With these values, the volume percentage of metallic copper of the total volume of the porous silica microspheres (including voids) is calculated as 0.46%$_{vol}$.

Preparation of Composite Polymer Films

DRS measurements require the composite of SEBS and filer material to be shaped in the geometry of a parallel plate capacitor. Sample capacitors from compositions A (SEBS), B (SEBS-SiO$_2$) and C (SEBS-SiO$_2$-Cu) were prepared as follows: the elastomer (Dryflex SEBS500120S, VTC Elastoteknik), was dissolved in toluene with a concentration of 40 g/l. The corresponding filler particles were mixed with the polymer solution, then sonicated using an ultrasound tip (Bioblock Vibracell 75041) for 5 min at 20%power and subsequently placed in an ultrasound bath for 1 h, resulting in a homogeneous suspension. Each suspension was dropcast on glass substrates with previously prepared evaporated aluminium electrode ($d = 20$ mm). The samples were dried at room temperature under a cap to control the evaporation rate. The resulting film thickness was measured with a profilometer (DekTak^{3}ST). A gold electrode was sputtered on the top of the films, ensuring good electrical contact between both DRS electrodes and the film surfaces.
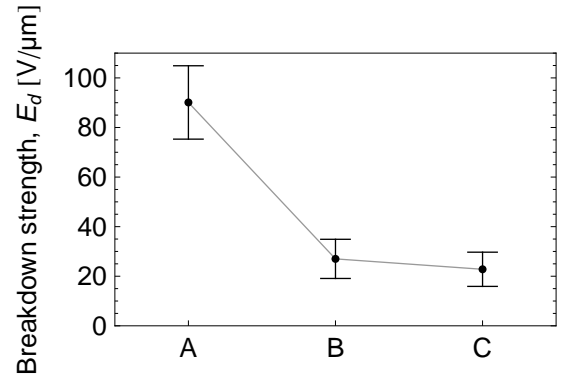

Figure 4: Electrical breakdown field measured on samples A (SEBS), B (SEBS-SiO$_2$) and C (SEBS-SiO$_2$-Cu).

Electrical Characterization of Polymer Composites

Electrical Breakdown

The materials were prepared as for DRS (see above), . For breakdown field testing, a spherical electrode (radius of curvature 100 mm) was pressed with a small force (50 mN) into the sample surface. A ramp voltage (100 V/s) was applied between the electrodes until electrical failure. The measurement could be repeated at different locations on the same sample more than 20 times, leading to adequately significant statistics.

The measurement results are presented in Figure 4. The difference in electrical breakdown strength between B and C is not statistically significant. It is found that the breakdown field drops when adding the un-loaded silica microspheres, from approximately 90.1±14.8 to 27.0±7.9 V/μm, which is almost identical to pure silica. The breakdown field when using copper-loaded silica microspheres is approximately 22.8±6.9 V/μm, within experimental error the same value as for un-loaded microspheres.

DRS Analysis of Humid and Dried Composites

The presence of water in the composite sample B (SEBS-SiO$_2$) has an enormous impact on the dielectric spectra. Figure 5 shows DRS measurements on a thoroughly dried (exsiccator, 2 days) sample B (right), and a sample B which has been

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stored under ambient laboratory conditions for 1 week (left). The features of the dried sample can be summarized as a plateau in the real part at higher temperatures and frequencies. A distinct increase in the real permittivity appears at low frequencies and high temperatures is also observed, which is typical for polymer composites.

The only difference between the two sets of spectra is found in an additional relaxation peak, with temperature varying relaxation times. The relaxation times of this peak can be used to extract activation energy of the relaxation process using Arrhenius' Law,

$$\tau(T) = A_0 e^{-\frac{E_A}{k_B T}} \tag{3}$$

where A_0 is an Amplitude, E_A is the activation energy of the relaxation process, k_B is the Boltzmann constant and T the temperature. To extract the relaxation time, the Havriliak-Negami relaxation[3] was fitted

$$\varepsilon = \frac{\Delta\varepsilon}{\left(1 + (i\omega\tau)^\alpha\right)^\beta} \tag{4}$$

where ε is the complex permittivity, $\Delta\varepsilon$ is the relaxation strength, τ is the relaxation time, ω is the circular frequency, i the complex unit and α as well as β are fit parameters. For the sample stored under ambient laboratory conditions, the relaxation times have been plotted in Figure 6, and the straight lines are fits of Arrhenius' Law.

From Figure 6 it is seen that the activation energy of the relaxation process changes at $0°C$, and for temperatures higher than $100°C$, the peak disappears entirely (Figure 5). Clearly, this peak is due to the presence of water. The disappearance of this peak upon drying (Figure 5, right) shows that the influence of water can be avoided entirely by drying the composite films in an exsiccator for several days.

References

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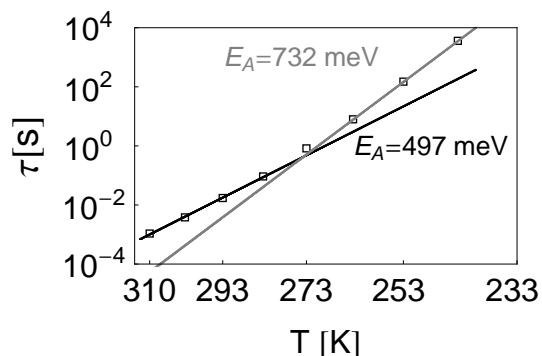
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Figure 6: Relaxation times of the humid sample. The activation energy is indicated by Arrhenius fits, showing an abrupt change from 497 meV to 732 meV around $0°C$, which is related to the presence of water.

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3. Havriliak, S.; Negami, S. A Complex Plane Representation of Dielectric and Mechanical Relaxation Processes in Some Polymers. *Polymer* **1967**, *8*, 161–210.

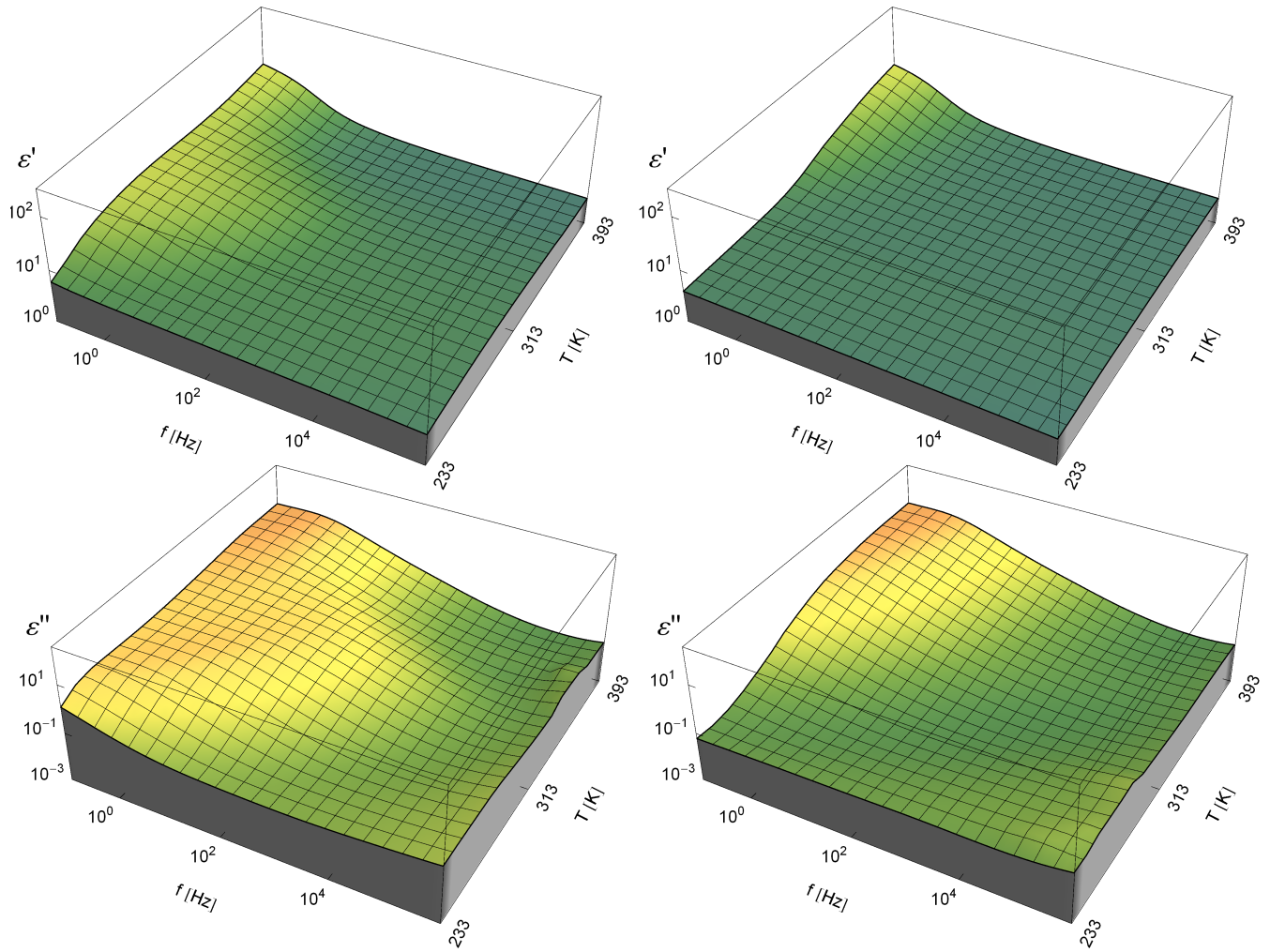This information is available free of charge via the Internet at http: //pubs.acs.org.

Figure 5: Dielectric relaxation spectroscopy of a sample of composite B (Left: exposed to ambient humidity for several days, Right: dried in exsiccator for several days).