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Supporting Information

Assembly of Ultrasmall Cu_3N Nanoparticles into Three-Dimensional Porous Monolithic Aerogels

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Chemicals. Copper(II) methoxide [$Cu(OCH_3)_2$, 97%], chloroform (≥99.8%), acetonitrile (≥99.8%) and pentane (≥99%) were purchased from Sigma-Aldrich. Benzylamine (≥99%) was purchased from Fluka-Chemie AG. Acetophenone (98%) and *N*-Methyl-2-pyrrolidone (99%) was purchased from Acros Organics. Liquid carbon dioxide (CO_2, ≥99%) was supplied by PanGas AG, Switzerland. All chemicals were used as received without further purification.

Synthesis of Cu_3N Nanoparticles.

The synthesis of Cu_3N nanoparticles was performed according to our previously reported procedure.[1] In a glovebox under argon atmosphere ($O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm), 250 mg of $Cu(OCH_3)_2$ and 25 mL of benzylamine were mixed in a 40 mL glass vial. The vial was sealed with a Teflon cap and taken out of the glovebox. The reaction vial was transferred into a preheated oil bath set at 140 ^oC and held at that temperature for 30 min under vigorous magnetic stirring. During heating, the color of the reaction solution changed from dark blue to red. Afterwards, the reaction mixture was cooled down to room temperature and the product was precipitated by adding 40 mL pentane and collected by centrifuging at 4000 rpm for 15 min. The product was washed two more times using 40 mL of pentane.

Preparation of Cu_3N Gel and Aerogel.

To obtain stable colloidal dispersion, the wet Cu_3N nanoparticles were dispersed in 1 mL acetophenone using ultrasonication for 15 min at 37 kHz. The nanoparticle dispersion was transferred into the open end of a vertically placed syringe (the upper end of the syringe was cut off) and closed with a Teflon lid. The gelation was induced by destabilizing the nanoparticle dispersion by heating in an oven at 60 ^oC for 1 h. To prevent the gel from drying out during heat treatment a saturated acetophenone atmosphere was generated inside a sealed glass bottle. Subsequently, the gel was transferred to pure acetophenone. Before supercritical drying, the gel liquid was thoroughly exchanged with acetonitrile, which is miscible with liquid CO_2, without disturbing the gel network. The solvent exchange was performed in steps of 10 vol%, until the gel liquid was thoroughly exchanged to acetonitrile. Subsequently, the gel was placed in the pressure chamber of the critical point dryer (Critical Point Dryer 13200JE-AB from SPI), which was filled with acetonitrile. The acetonitrile was exchanged to liquid CO_2, in intervals of 30 min, over 3 h. For supercritical drying, the chamber was half filled with liquid CO_2 followed by gradual temperature increase from 10 ^oC to 40 ^oC, which results in pressure increase from 60 to 95 bar. The supercritical state is reached at 31 ^oC and 74 bar and the chamber was kept in the supercritical state for 30 min followed by controlled pressure release through a needle valve to obtain the monolithic aerogel.

The redox reactions involved during Cu_3N formation. In a previous work, we elucidated the formation mechanism of Cu_3N nanoparticles.[1] Here we briefly explain the redox reactions responsible for Cu_3N formation. The reaction between $Cu(OCH_3)_2$ and benzylamine at 140 ^oC proceeds via the reduction of the Cu(II) to Cu(I). We proposed that dehydrogenative oxidation of benzyl amine to benzenemethanimine is responsible for reducing the Cu(II) center. As a mater of fact, *N*-benzylidenebenzylamine, the condensation product of benzenemethanimine and benzylamine, was detected in considerable amount in the final reaction solution by gas chromatography-mass spectrometry analysis. Ammonia, the other condensation product formed in situ immediately reacts with $CuOCH_3$ to form Cu_3N and methanol.

Characterization Techniques. X-ray powder diffraction (XRD) patterns were recorded on an X'Pert Pro (PANalytical B.V., Netherlands) powder diffractometer operating in reflection mode, equipped with a diffracted beam curved graphite crystal monochromator, with Cu K_α radiation (45 kV, 40 mA). The dried samples were ground in a mortar and deposited on silicon sample holder with zero background. SEM characterization was performed on a Hitachi SU-70 instrument. For SEM imaging, the aerogel samples were fixed to a flat aluminium sample holder using silver paste. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and scanning TEM (STEM) images were recorded on a FEI Talos F200X operated at 200 kV. The samples for TEM imaging were dispersed in chloroform and dropcasted onto a carbon coated copper grid. Nitrogen physisorption isotherms were measured at 77 K on a Quantachrome Autosorb iQ. Previous to gas sorption measurements, the samples were outgassed overnight at 50 ^oC under vacuum. The surface area was determined by applying the Brunauer-Emmet-Teller (BET) model and the pore size and pore volume were determined by density functional theory (DFT) analysis using a Non Local DFT calculation model for nitogen at 77 K based on silica cylindrical pores.[2]

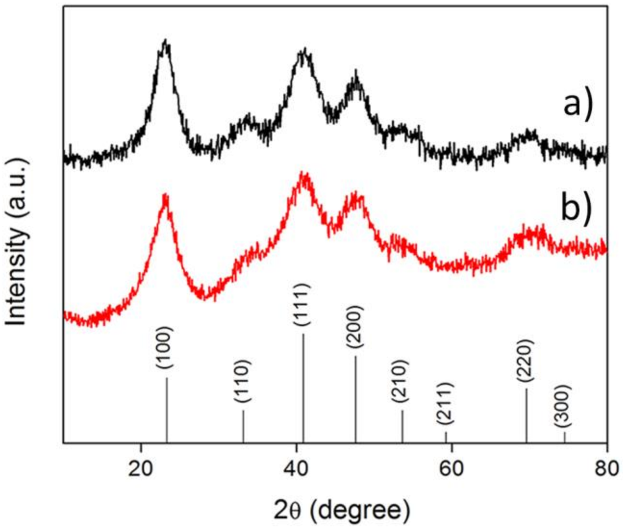

Figure S1. XRD patterns of a) as-synthesized Cu_3N nanoparticles and b) Cu_3N aerogel, with standard diffraction pattern as vertical lines (JCPDS No. 47-1088).

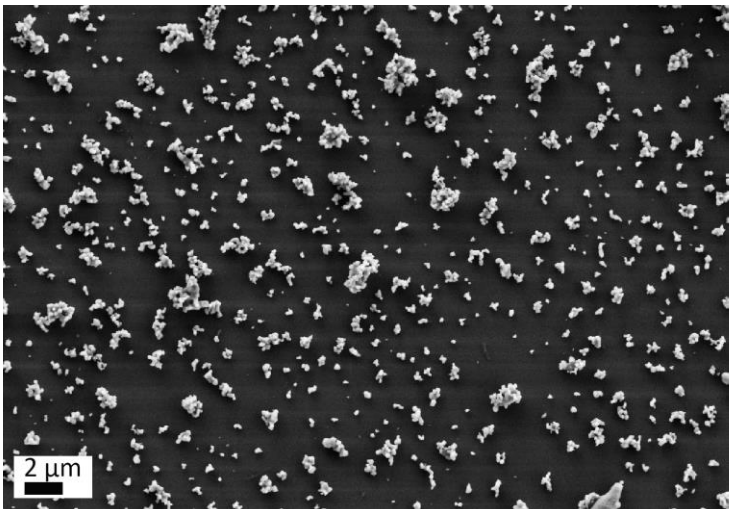

Figure S2. SEM image of the dry Cu_3N powder.

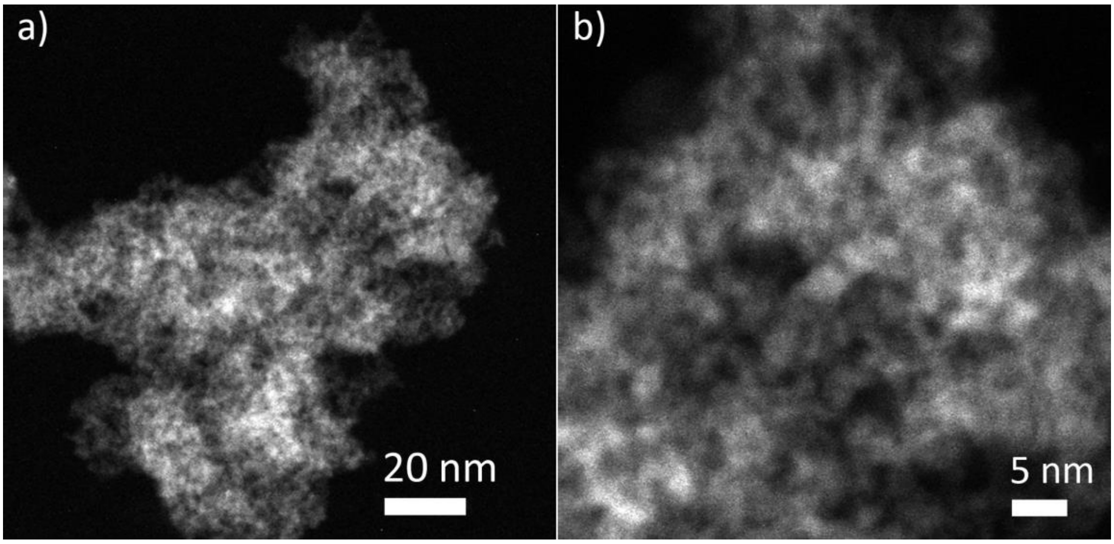

Figure S3. (a,b) STEM images of the Cu_3N aerogel.

References

1. R. Deshmukh, G. Zeng, E. Tervoort, M. Staniuk, D. Wood and M. Niederberger, *Chem Mater*, 2015, **27**, 8282-8288.
2. J. Landers, G. Y. Gor and A. V. Neimark, *Colloid Surface A*, 2013, **437**, 3-32.