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Electrophoretic silica-coating process on a nano-structured copper electrode

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A method for silica-coating at the nanoscale by electrophoretic deposition is presented here, using raw or grafted silica dispersions.

Advances in nanotechnology have given birth to new classes of materials such as activated carbons, zeolites, carbon nanotubes or porous metals and oxides with three-dimensional architecture at the nanoscale. As these nano-architectures provide a high surface area, they have great potential to be used in various applications such as energy storage and conversion, catalysis and sensors.¹⁻⁵ However, one of their drawbacks is certainly the difficulty encountered in modifying their surfaces due to their small dimensions. A widely used technique for coating nano-structures is electrolytic deposition (ELD)⁶ from soluble precursors. However, this technique is limited to specific compounds exhibiting redox potentials within the electrolyte voltage stability window.

A promising way to overcome these difficulties is to make a coating using electrophoretic deposition (EPD) techniques.^{6,7} The interest of EPD is two-fold: first, a wide variety of compounds can be deposited using this technique, assuming that stable colloidal dispersions can be prepared, and secondly, it allows the deposition of very small particles, small enough to enter a 3D nano-structure.

As a first approach to demonstrate the feasibility of such a nanoscale coating, we have chosen to prepare a coating from silica nanoparticles dispersed in isopropanol (*i*PrOH) as a model compound. EPD of silica is an easy process because unmodified-silica suspensions are characterized by a high negative ζ potential, providing good stability of the dispersion and efficient migration.⁸⁻¹¹

The results obtained with silica could be applied to several other oxides that show similar suspension properties.

Another reason for choosing silica is its usefulness in the field of sensors; as silica surface can be functionalized with various organic molecules, it can be given new properties that improve the performance of biosensors, analytical chemistry detectors¹²⁻¹⁶ or photovoltaic devices.¹⁷ Another advantage of this graftability is that surface charge (ζ potential) can be modified by the ligand. For example, aminopropyl ligands are known to provide positive ζ potentials.^{18,19} Such tailor-made

silica allows deposition on the anode instead of the cathode, thus protecting the electrode from corrosion.

Here we report a process to coat a nano-structured copper surface, consisting of well-aligned nanopillars with a diameter of 200 nm, with silica nanoparticles using a simple electrophoretic deposition. We demonstrate the feasibility of this deposition on Cu anodes and cathodes, using 10 nm silica nanoparticles, pure or grafted with aminopropyltrimethoxysilane (APTMS). This technique can open new paths in various fields such Li-ion batteries or sensors.

Nano-structured copper electrodes (ns-Cu) were prepared according to previous work from Taberna *et al.*²⁰ Roughly, electrolytic deposition of copper pillars in the pores of a commercial membrane was achieved through a double step galvanostatic method.

A commercial dispersion of silica nanoparticles (10 nm) in isopropanol (ABCR) was used. This dispersion was diluted ten times with isopropanol (Sigma), leading to a concentration of about 1.5 g L⁻¹, and sonicated for 20 min. No other dispersants were added. Functionalization of silica was achieved by adapting a protocol proposed by Cousinie *et al.*¹² Namely, 50 ml of the diluted suspension of SiO₂ was placed in a flask and vigorously stirred. APTMS was added dropwise (0.19 ml of APTMS). The mixture was placed in a thermostatic bath at 20 °C under stirring for a day. After grafting, a part of the dispersion was centrifuged and the solid was washed with ethanol and dried for characterization while the other was used as-prepared for EPD.

For the electrodeposition of pure SiO₂, a Pt grid (4 cm²) was used as the negative electrode and ns-Cu as the positive one (1.5 cm²), since pure silica particles have negative charge. The suspension was sonicated for 20 min and an electric field of 100 V cm⁻¹ was applied for 5 min (potentiostatic deposition, 2 cm spacing).

For the electrodeposition of APTMS-grafted SiO₂, 2 ml of an I₂-acetone mixture⁷ was added to the as-prepared suspension and the dispersion was sonicated for 20 min. Here, because we expect APTMS to give a positive charge to the particles, the electrode polarities were reversed; the Pt grid was the positive electrode and the ns-Cu was the negative one. An electric field of 100 V cm⁻¹ was applied for 3 and 5 min.

SEM observations were conducted on a JEOL JSM 6700-F microscope. Raman measurements were performed using LAB-RAM HR800 from Perkin-Elmer. MALAVERN ZETASIZER was used for ζ potential measurements.

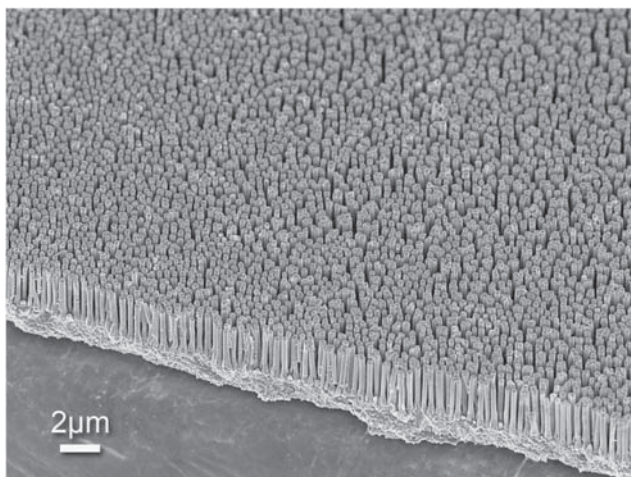


Fig. 1 SEM image of the Cu nano-structure.

Fig. 1 shows the as-prepared Cu nano-structure. The deposit consists of arrays of Cu rods, normal to the Cu foil surface. Measurements showed that the diameters of these rods are about 200 nm, which is consistent with the pore size of the membrane. The length of the rod is measured to be about 2 μm and the average inter-rod distance is 150 nm. The developed surface of this nano-structure was calculated to be about 7.5 cm² per cm².

The efficiency of the grafting process was checked by elementary analysis and TGA-TDA of the grafted SiO₂ powders after drying. Both experiments indicate the presence of ligand and the grafting ratio was calculated to be about 0.4 (±0.05) mmol g⁻¹ SiO₂.

ζ potential measurements were conducted on both suspensions before EPD: the silica nanoparticles present a ζ potential of -30 mV (±10) in *i*PrOH (neutral pH). APTMS-grafted SiO₂ shows a ζ potential of +15 mV. This value confirms the charging effect of the ligand, switching the surface charge from negative to positive, as described in the literature.²¹

After the EPD of non-grafted SiO₂ (for 5 min), a white layer covers the ns-Cu electrode thus confirming that the deposition

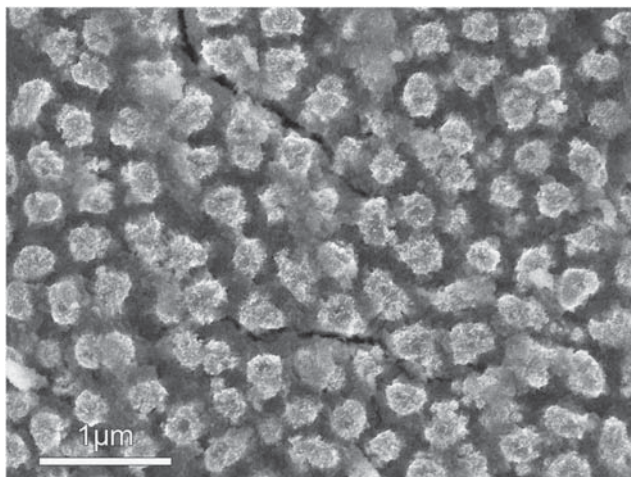


Fig. 2 SEM image of the Cu nano-structure coated with SiO₂ nanoparticles.

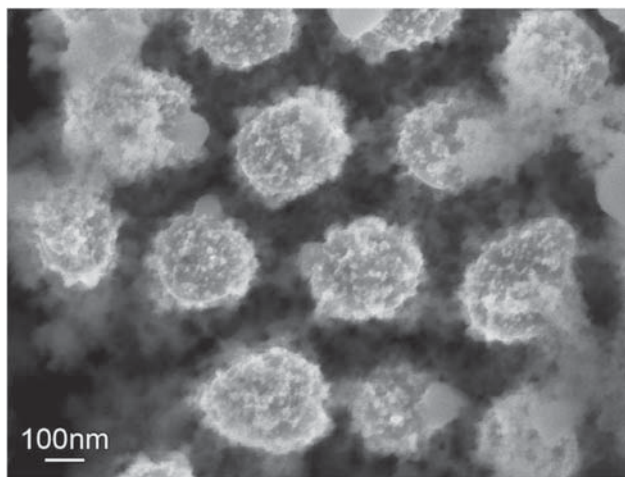


Fig. 3 SEM image of the Cu nano-structure coated with APTMS-grafted SiO₂ nanoparticles.

occurred at the anode. This layer is removed from the electrode surface using air-blow then prepared for SEM observation. The result is shown on Fig. 2. The silica particles appear to cover the all copper rods as well as the inter-pillar space. The silica particles are measured to be 10 nm, that indicates that there is no particle agglomeration in the dispersion. In the case of EPD of APTMS-grafted SiO₂, the ns-Cu electrode (cathode) is covered with a white layer, removed as previously described. SEM observations are shown in Fig. 3. Again, we obtained a good coverage of the rods with 10 nm particles, even if some cracks may be present.

Infrared spectroscopy was performed on both samples but only weak peaks were observed. At the same time, Raman spectroscopy led to better results, as shown in Fig. 4. The small peak ($\nu = 450 \text{ cm}^{-1}$) on both samples can be attributed to Si-O stretching vibrations; the peaks at $\nu = 2940 \text{ cm}^{-1}$ and $\nu = 680 \text{ cm}^{-1}$ on functionalized samples correspond to C-H (stretching CH₂) and Si-C (Si-CH₂ rocking vib),

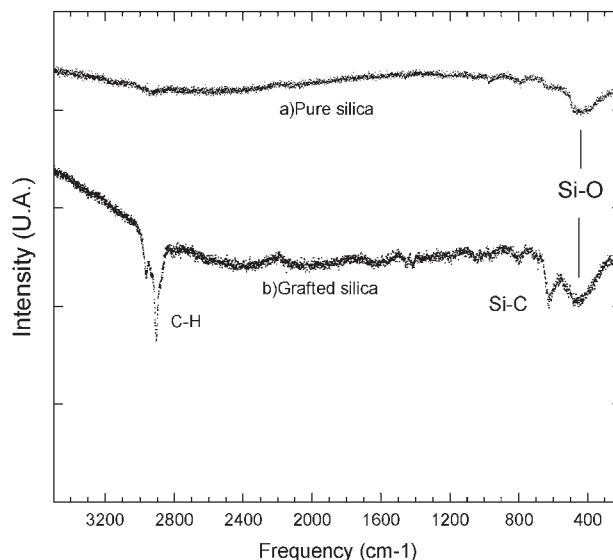


Fig. 4 Raman spectra of the SiO₂-coated Cu nano-structure (a) pure silica, (b) grafted silica.

respectively.²² This indicates that the ligand is still grafted on the silica nanoparticles' surface, undamaged by the electro-deposition process.

We have presented here a novel method to prepare a nano-structured silica deposit on copper, using the EPD technique. This method leads to a thin, well-covering deposit of pure silica nanoparticles on the anode. The interest in the chemical modification of silica is to reverse its surface charge. When APTMS is grafted on its surface, the deposition occurs now on cathode, without modification of the organic moieties.

These results open a new path in field sensors applications where new modified-silica electrodes could be prepared with this technique. Lower detection limits (due to the large surface area) and faster response times (due to the high organization and accessibility of the electrode) could be expected using such nano-structured devices. These results could be successfully applied in the Li-ion battery field, where several oxide coatings could be achieved by this method.

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