Supporting Information for

Ultrahigh Surface-Area Metallic Electrodes by Templated Electroless Deposition on Functionalized Carbon Nanofiber Scaffolds

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Details of experimental procedure for functionalization and electroless deposition:

Vertically aligned carbon nanofibers (VACNF) were functionalized with carboxylic acid groups via a two-step procedure in which a methyl ester is first linked to the surface, and the ester protecting group is then removed to leave behind free carboxylic acid groups.[1,2] VACNF samples on their growth support were used. A small droplet of the methyl ester of undecylenic acid was placed on the sample. The sample was then covered with a fused silica coverslip, placed in a Teflon reaction vessel purged with N_2, and then illuminated with 254 nm light from a low-pressure mercury grid lamp (UV Products) for 16-18 hours. This procedure links the molecule to the surface via the alkene (C=C) group. The methyl ester was deprotected by immersion in a slurry of 250 mg potassium tert-butoxide in 10 mL dimethylsulfoxide. Following deprotection the samples were washed in 0.1 M HCl and then immersed in methanol.

Electroless deposition was performed using slight variations of established methods[3-5] The carboxylic acid terminated carbon nanofibers were sensitized with tin by immersion in a tin bath consisting of 0.026 M $SnCl_2$ and 0.07 M trifluoroacetic acid in 50:50 methanol: deionized water for 45 minutes at room temperature. This step leaves tin ions chelated to the carboxylic acid groups on the surface. The samples were then rinsed in methanol for at least 5 minutes. Activation of the surface by the reduction of sliver ions was achieved by placing the samples in sliver baths consisting of 0.03 M ammonical silver nitrate for 15 minutes at room temperature. The ammonical silver nitrate was prepared by creating a 0.03 M $AgNO_3$ solution and then titrating with ammonia hydroxide. The ammonia hydroxide was added drop wise to the silver nitrate solution with stirring. The solution initially turned turbid and dark brown and slowly became clear and colorless; at this point the addition of ammonia hydroxide was stopped. The samples were, again, rinsed in methanol for at least 5 minutes. Electroless gold deposition was carried out by placing the sliver activated nanofiber samples in individual gold baths in a refrigerator at 6˚C for 1 to 22 hours. The gold baths were prepared in advance with enough time to allow for cooling and consist of 0.127 M Na_2SO_3, 0.025 M $NaHCO_3$, 0.625 M formaldehyde and 8 mM $Na_3Au(SO_3)_2$ (Technic Oromerse Part B gold solution). They are prepared by making a stock solution that contains everything except the $Na_3Au(SO_3)_2$, and adjusting the pH to 10 using 1 M H_2SO_4. The gold is then added and the pH is adjusted to 10 again using 0.5 M H_2SO_4. The samples were removed from the gold bath, rinsed thoroughly with methanol and dried in an oven.

Differences in gold deposition as a result of molecular functionalization:

A number of studies have shown that intrinsic carbon based nanomaterials lack significant amounts of oxidized sites.[6-10] In order to create oxidized sites, carbon based nanomaterials are generally oxidized under rather harsh conditions before they are modified. However, common oxidizers such as nitric acid and sulfuric acid are incompatible with the metal under layers of our electrodes. Thus, to create reproducible oxidized carbon nanofibers we have attached carboxylic acid groups as described above. Figure S.1 shows a comparison of the structures observed on bare fibers (S.1a) and fibers that have been photochemical functionalized with the molecular monolayer (S.1b) to produce a carboxylic acid – terminated surface. In Fig. S.1a, there is some nucleation of gold, but not sufficient to form a continuous layer. In contrast, the functionalized fibers (S.1b) already show a complete, continuous film that is already

developing the highly textured surface described in the main paper. Thus, the covalent functionalization leads to a pronounced enhancement in the development of the nantextured gold surface.

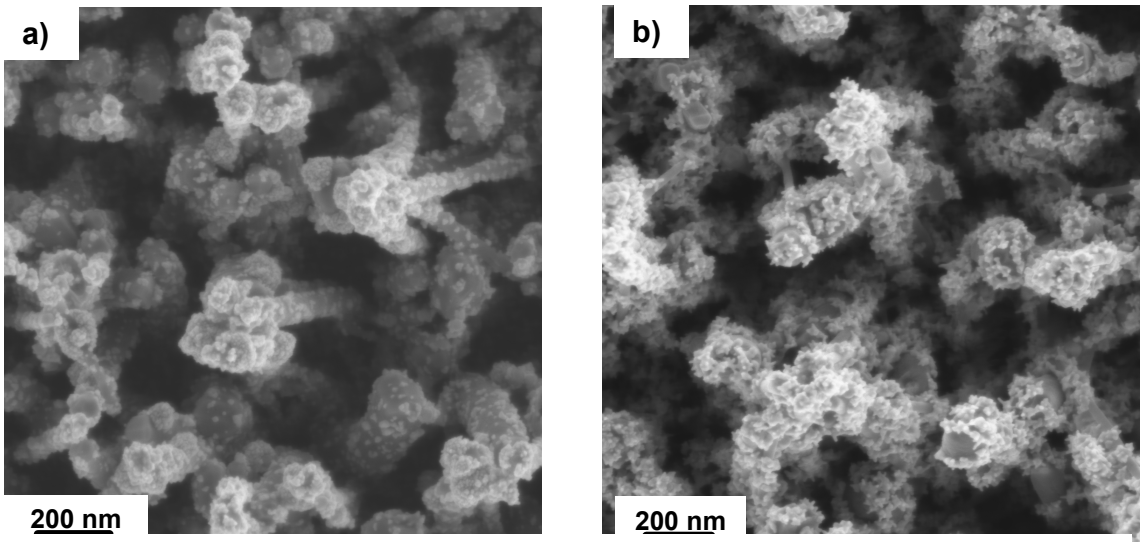

Figure S.1 a) Carbon nanofibers, without covalent modification, after 3.5h of gold deposition,
S.1 b) Covalently modified carbon nanofibers after 3.5h of gold deposition

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