Electronic Supplementary Material (ESI) for Nanoscale.

Nanobursa Mesh: Graded Electrospun Nanofiber Mesh with Metal Nanoparticles on Carbon Nanotubes

Semra Senturk-Ozer,[a] Tao Chen,[a] Nebahat Degirmenbasi,[a,b] Halil Gevgilili,[a] Simon G. Podkolzin[a] and Dilhan M. Kalyon[a]*

[a] Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, New Jersey 07030 USA.

[b]Gazi University, Department of Chemistry, 06500, Teknikokullar, Ankara, Turkey.

Electronic Supplementary Information: Experimental and Computational Methods

Pristine multi-walled carbon nanotubes (CNTs) had a density of 2100 kg/m^3, outside diameter of 30-50 nm, inside diameter of 5-10 nm, length of 10-20 µm, and aspect ratios of 200-670 (95 wt% purity, SKU #030106, C-Tubes, Inc., Brattleboro, VT). CNTs were composed of 15-20 concentric graphene layers (Figure 2f). All reagents in synthesis of metal nanoparticles were of the analytical grade (Sigma-Aldridge, St. Louis, MO) and used without further purification. The polycaprolactone (PCL) (Sigma-Aldridge, St. Louis, MO) had a number average molecular weight of 70,000-90,000, a melting point of 60 °C and density of 1.145 g/mL at 25 °C.

Prior to functionalization of CNTs with Pt, Ag and Co nanoparticles, CNTs were first surface treated with citric acid. CNTs were added at 0.47 vol% to 0.047 M aqueous solution of citric acid sonicated at 150 W for 15 min using a Misonix XL2020. The resulting paste was dried at 120 °C for 12 h and under vacuum at 200 °C for an additional 30 min. Prior to functionalization with Pd nanoparticles, CNTs were first treated with sodium dodecyl sulfate (SDS) surfactant in order to improve the nanoparticle dispersion.

Pt nanoparticles were deposited using a modified procedure of Poh et al.[7] 40 mg of acid-treated CNTs were added into 50 ml of ethylene glycol under sonication at 150 W, followed by mixing with 1 ml of 0.04 M $H_2PtCl_6 \cdot 6\ H_2O$. 0.5 ml of 0.8 M NaOH was added drop-wise under magnetic stirring for 2 min. The mixture was additionally kept under stirring at 160 °C for 10 min.

Co nanoparticles were deposited using a modified procedure of Zhang et al.[8] A solution of 0.05 M $CoCl_2$ in ethylene glycol was prepared under sonication at 150 W at 70 °C. 60 mg of acid-treated CNTs were added into a 100 ml $CoCl_2$/ethylene glycol solution and sonicated at 70 °C for 10 min followed by dissolution of 0.6 g of NaOH pellets in the $CoCl_2$/ethylene glycol solution at 70 °C for 60 s. At the same temperature of 70 °C, 2.65 g of Na_2CO_3 were added under sonication for 60 s, followed by an addition of 15 ml of hydrazine hydrate at 70 °C for 60 s. The sonication was continued for an additional 3 min, with the temperature held at 70 °C. The reaction was then run under magnetic stirring at 70 °C for an additional 60 min.

Ag nanoparticles were deposited using a modified procedure of Gao et al.[9] 100 mg of acid-treated CNTs were added into 140 mL of deionized water under sonication at 150 W for 20 min. 200 mL of 0.5 M aqueous solution of $AgNO_3$ were added drop wise under stirring. The mixture then was kept under stirring for an additional 72 h.

The resulting suspensions of Co, Pt, and Ag supported on CNTs were centrifuged at 4000 rpm for 15 min, and the pastes were separated and washed with ethanol and deionized water, dried under vacuum at 80 °C overnight and then stored in a desiccator.

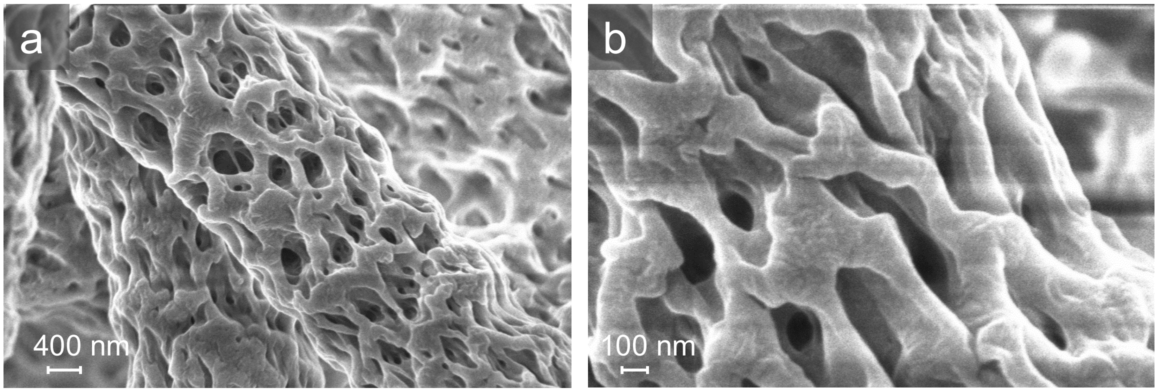

Fig. S1 Hollow electrospun fibers with open-cell type porosity: (a) Low magnification, (b) High magnification.

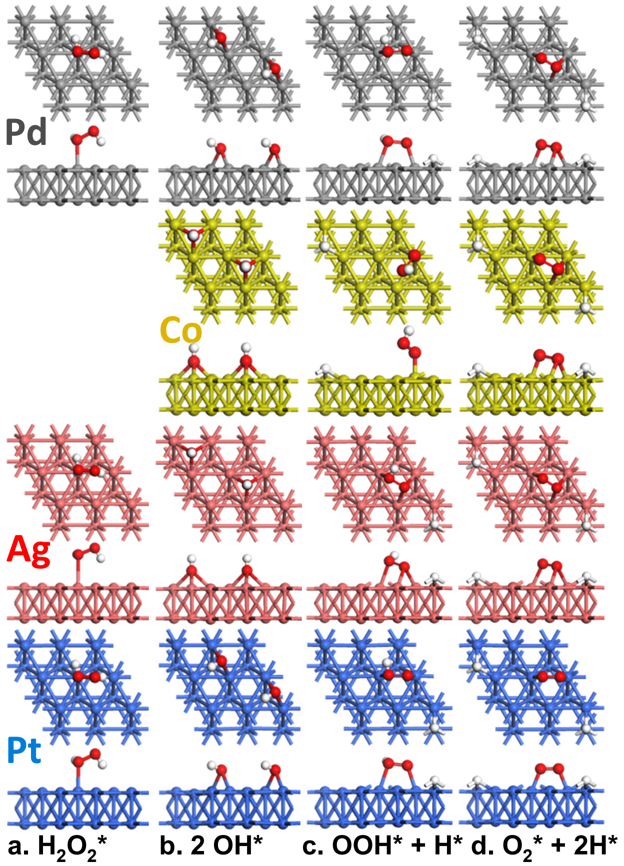

Fig. S2 Optimized geometries of surface species: (a) H_2O_2*, (b) 2 OH*, (c) OOH* and H*, and (d) O_2* and 2 H* on Pd, Co, Ag, and Pt surfaces obtained with DFT calculations. Top row for each metal shows a top view and lower row – a side view. Only two metal surface layers out of total five in the computational models are shown for clarity.

Pd nanoparticles were deposited using a modified procedure of Karousis et al.[10] 5 mg of untreated CNTs were added into 10 ml of 0.05 M aqueous SDS solution. The suspension was sonicated at 150 W for 20 min. 10 mg of $Pd(COOH)_2$ were added into the CNT/SDS suspension at 100 °C. The solution vapor was cooled and recycled back into the reaction vessel using a reflux setup for 6 h. After cooling to room temperature, the reaction mixture was filtered through a Millipore GTTP 0.2 μm filter paper, the filtrate was washed with deionized water three times and twice with ethanol to remove any excess surfactant. The Pd/CNT paste was dried under vacuum at 80 °C overnight and then stored in a desiccator.

CNTs with deposited metal nanoparticles were dispersed in dichloromethane (DCM) at 0.21 g/100 mL under sonication at 150 W at 20 °C. PCL was also dissolved in DCM (10.6 g of PCL/100 mL of DCM) and then mixed with the CNTs/DCM suspension under light agitation overnight, followed by sonication at 150 W in order to generate a CNT concentration of 0.15 wt %, i.e., a volume fraction of φ = 0.0009.

The hybrid twin-screw extrusion/electrospinning process is shown in Figure 1. The process consists of a specially designed and fabricated twin-screw extruder front end with fully intermeshing and co-rotating twin screws of 7.5 mm diameter and a spinneret die with three parallel nozzles. The extruder has a capability to control temperatures over three separate heat transfer zones. The extruder was specially designed and fabricated so that the drive and the barrel/die units of the extruder are electrically insulated to allow the application of a high voltage to the electrospinning head. A special screw design with three mixing zones and with kneading disks for dispersive mixing incorporated into the screw configuration ensures good mixing through the application of high shearing stresses.

Three parallel nozzles/needles with an inner diameter of 300 μm were connected to a 15 kV DC power supply. The separation distance between the needle tips and the collecting surface was kept constant at 20 cm. Functionalized CNTs were sonicated and dispersed in DCM. Then, PCL was dissolved in a CNT and DCM mixture, and this gel suspension was fed into the second mixing zone of the extruder via a syringe pump at a rate of 33 μL/min, where it was continued to be mixed until flowing into the spinneret.

To generate graded meshes, suspensions of PCL with nanotubes functionalized with Pt, Ag, Co and Pd nanoparticles were sequentially fed into the twin-screw extruder without interruption. This process generated contiguous meshes consisting of consecutive layers of nanotubes with Pt, Ag, Co and Pd nanoparticles incorporated into polymer nanofibers. A typical feeding duration for each metal suspension was 45 min. The total duration of the experiment for generating a graded mesh sample with four different metal layers with an overall thickness of 2.5 mm and a surface area of 34.5 cm^2 was 4.5 h. The combined process of the hybrid twin-screw extrusion and electrospinning, thus, demonstrated the potential of an industrially relevant throughput. The porosity of the nanofibers can be custom-tailored via changes in the solvent concentration (dichloromethane, DCM) and the use of a blend of PCL and polyethylene oxide, PEO, (POLYOX AWSR 205 mw 600,000 available from Union Carbide Inc.). The procedure involved the blending of the PCL with PEO at a typical PCL/PEO concentration ratio of 2:1, For the fabrication of the hollow fibers of Fig. S1 5% of PCL was mixed with 2.5% of PEO and 92.5% of DCM. The electrospinning conditions involved a distance of separation between the nozzle tips and the collecting plate of 0.2m and a voltage of 20kV. Upon electrospinning the fibers were dried overnight in a vacuum oven at 50C followed by the dissolution of the PEO in deionized water. The electrospinning rate could be increased by increasing the number of nozzles of the spinneret.

TEM micrographs were obtained with a Philips FEI CM-20 transmission electron microscope. The maximum accelerating voltage and the lateral resolution of the instrument were 200 kV and 0.27 nm (point), 0.14 nm (line), respectively. CNTs with metal nanoparticles were placed in ethanol using a micro tip sonication horn at 90 W and then dropped onto a Cu TEM grid. The excess ethanol was evaporated. TEM images of electrospun meshes were obtained using a Zeiss Auriga Small Dual-Beam FIB-SEM scanning electron microscope with a resolution of 1.0 nm at 15 kV.

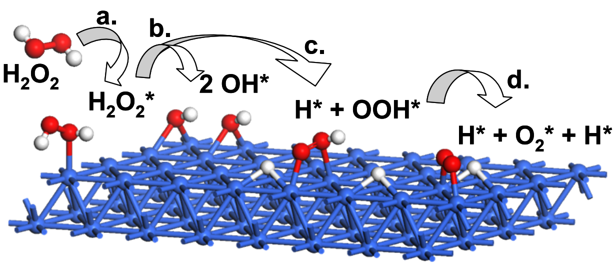

Fig. S3 H_2O_2 reactions on catalytic metal surfaces: (a) Adsorption, (b) Decomposition to 2 OH* surface species, (c) Decomposition to OOH* and H* and then to (d) O_2* and 2 H* surface species.

The energetics of H_2O_2 adsorption and reactions on Pd, Co, Ag, and Pt surfaces were evaluated with DFT calculations using a consistent set of computational parameters in order to provide guidance on the compositional grading of nanobursa meshes. Gradient-corrected periodic DFT calculations were performed with the DMol^3 code in Materials Studio 4.0 program by Accelrys Software, Inc. The calculations used the DNP basis set and the GGA PW91 functional. Tightly bound core electrons for metals were represented with semicore pseudopotentials. Reciprocal-space integration over the Brillouin zone was approximated through k-point sampling with a separation of 0.4 nm^{-1} using the Monkhorst-Pack grid: (3×3×1). Convergence with respect to the number of k-points was tested by increasing their number for representative structures. The density mixing fraction of 0.1 with direct inversion in the iterative subspace (DIIS) and orbital occupancy with smearing of 0.002 Ha (0.02 for Co) were used. The orbital cutoff distance was set at 0.4 nm for all atoms.

All surfaces were modeled using infinite slabs constructed with 3×3×5 periodic unit cells: a 3×3 surface with 5 layers (a total of 45 metal atoms). The following optimized metal lattice constants were used: 0.40012 nm for Pt (1.97% deviation from experimental), 0.39759 for Pd (2.19% deviation), 0.41891 nm for Ag (2.53% deviation) and a=b=0.25103 (0.13% deviation) and c= 0.40360 nm (-0.81% deviation) for Co. Surfaces were generated from the bulk crystal with a vacuum spacing of 3 nm between the slabs in the c direction.

The three top surface layers were optimized with adsorbate species during geometry optimizations, simulating surface relaxation upon adsorption. The two bottom layers were constrained at the corresponding bulk crystal positions, simulating multilayer nanoparticles. Adsorption energies were calculated at 0 K without zero-energy corrections using as a reference the sum of energies for the appropriate clean surface and H_2O_2 calculated separately. Reaction energies were calculated similarly as a difference between product and reactant configurations shown in Figure S2. This figure shows periodic unit cells with only two top metal layers out of total five for clarity. No stable geometry for molecular H_2O_2 was identified on the Co surface after evaluation of all possible adsorption sites: atop, bridge, and three-fold. As a result, the reaction energies for H_2O_2 decomposition for Co in Table 1 were calculated using not adsorbed, but isolated molecular H_2O_2. On other surfaces, as shown in Figure S2a, H_2O_2 preferentially adsorbs on a single metal atom (atop site) through an oxygen atom. OH groups preferentially adsorb on two metal atoms (bridge site) on Pt and Pd surfaces, and on three metal atoms (three-fold site) on Ag and Co (Figure S2b). Similarly, OOH species preferentially adsorb on bridge sites on Pt and Pd surfaces, and on three-fold sites on Ag (Figure S2c). On Co, a configuration with OOH species on an atop site (Figure S2c) was identified as the only stable geometry. Molecular oxygen preferentially adsorbs through both O atoms with the O-O bond parallel to the surface (Figure S2d).

Figure S3 shows schematically that the catalytic decomposition of H_2O_2 in the presence of H_2 can proceed through two pathways: (1) O-O bond cleavage (Figure S3b) or (2) O-H bond cleavage (Figure S3c,d). The calculated reaction energies for each step are summarized in Table 1.