

ELECTRONIC SUPPLEMENTARY INFORMATION

Generation of Highly Porous Silver Nanowire Networks by Plasma Treatment and their Direct Application as Supercapacitor Electrodes

Vu H. Dao ^{*a} and Benjamin J. Mapleback ^a

Aerospace Division, Defence Science and Technology (DST) Group, Melbourne, VIC 3207, Australia; vu.dao@dst.defence.gov.au (V.D.); benjamin.mapleback@dst.defence.gov.au (B.M.)

Experimental Section

Synthesis of AgNWs

All chemicals employed in the synthesis process were purchased from Sigma-Aldrich and used as is without further purification, unless stated otherwise. The AgNWs were synthesised through a conventional one-pot polyol method. Since its first discovery in 2002 by Xia and coworkers, this process has been heavily modified in various studies in an effort to improve the aspect ratios of the AgNWs. In a typical experiment, a combination of PVP with average molecular weights of 360 kDa (PVP360) and 1,300 kDa (PVP1300; 95 %) was initially charged into a clean reaction flask at a ratio of 1:4 w/w, respectively. The PVP (0.09 M, calculated based on monomeric unit) was subsequently dissolved in 15 mL of ethylene glycol (EG; 99.8 %) at room temperature. Once dissolved, the temperature of the reaction mixture was increased and maintained at 130 °C for 1 hour. A solution of 22 mM copper (II) chloride (CuCl₂; 99 %) in EG was prepared separately, and 80 µL of this was then added into the reaction mixture. After 15 min, a 5 mL solution of 0.24 M silver nitrate (AgNO₃; 99.8 %) in EG was slowly added over a period of 1 hour, with the aid of a 74905-50 Infusion Syringe Pump (Cole-Parmer, US). A stirring rate of 50 rpm was applied throughout this addition, and stopped immediately afterward. The reaction was left standing at 130 °C for another 3 hours. AgNWs crude product was washed with copious amounts of ethanol (Chem-Supply, 99.5 %) to remove the PVP capping layer and other impurities. Between each wash, the AgNWs were separated from the supernatant via a sedimentation and decantation technique outlined elsewhere by Simonato and coworkers. The final AgNWs product was then redispersed in ethanol.

Plasma Treatment

The AgNWs sample was spin coated using a WS-650-23 Spin Processor (Laurell, US) onto either aluminium stubs or 15 mm diameter stainless steel discs prior to plasma treatment, for scanning electron microscopy (SEM) characterization or construction of supercapacitor electrodes, respectively. This coating technique was performed at 200 RPM to allow for an even distribution, without the excessive expulsion of materials off the surface of the substrate. The deposited AgNWs were dried in a vacuum oven at 25 °C. Plasma treatment was performed using an Evactron® 25 RF Plasma Cleaner and Decontaminator (XEI Scientific, US) using 13.56 MHz RF source at 20 W, with atmospheric air as the feeder gas. A modified vacuum chamber was employed to allow for 90° line-of-sight exposure angle between the sample and the plasma source, where the distance between the

two was approximately 20 cm. The pressure of the vacuum chamber was maintained at approximately 53 Pa for all treatments.

SEM Characterization

Silver nanowires were characterized using an Apreo S (ThermoFisher Scientific, AU) field emission SEM at 5 kV accelerating voltage with a working distance of approximately 2 mm, using optiplan and immersion mode with in-lens detectors. Plasma-treated SEM stub samples required no further preparation before imaging, however post-mortem supercapacitor electrode samples were removed from deconstructed coin-cells and washed several times with ethanol and then dried under atmospheric conditions. Recovered pieces of the AgNWs electrode were adhered to aluminium SEM stubs using conductive silver adhesive (ProSciTech, AU) and dried in an oven at 60 °C.

Coin Cells Preparation

Supercapacitor cathodes were made by lightly abrading a stainless steel disc before plasma treating the surface to promote AgNWs adhesion. The AgNWs were deposited and plasma-treated at various times as described above. Grade 1 cellulose filter paper, 180 µm thick (Fisherman, DE), is used as the separator and blank 15 mm diameter stainless steel disc was used as the cathodes. Aqueous 6 M potassium hydroxide (KOH) solution is used as the electrolyte and was applied in excess to the electrodes and separator. 2023 coin cells were used for assembly and were crimped with an electric coin cell crimper (MTI Corporation, US) in an argon filled glovebox (Vigor Tech, US).

Electrochemical Testing

The assembled coin cells were then tested at ambient temperatures with a VMP3 galvanostat/potentiostat (BioLogic, FR). Electrochemical impedance spectroscopy (EIS) is performed using a single sign wave method with 10 mV amplitude and 100 mHz to 1 MHz range with 10 sampling points per decade. Cyclic voltammetry (CV) is performed for three cycles between -0.6 V to 1.2 V at the following rates; 10, 20, 50, 100, 500 and 1000 $\text{mV}\cdot\text{s}^{-1}$, with the third cycle plotted to allow for steady cycling. Chronopotentiometry (CP) is used to test electrochemical rate performance where cells are cycled between -0.6 V and 1.2 V once at the following specific currents, standardized to the AgNWs loading mass, from 0.2 to 2 $\text{A}\cdot\text{g}^{-1}$ with 0.2 $\text{A}\cdot\text{g}^{-1}$ intervals. Additionally CP is used to assess the high powered cycling stability of the plasma-treated AgNWs supercapacitors by conducting 5000 cycles from -0.6 V to 1.2 V at 1 $\text{A}\cdot\text{g}^{-1}$. The following standard test sequence is applied to all cells to avoid variations to cell conditioning; EIS, CV, EIS, CP rate performance, EIS, CP long term high-power cycling performance, EIS.

Sheet Resistance Measurement

To evaluate the conductivity of the plasma treated AgNW networks, thin films were deposited onto 1 inch (25.4 mm) diameter quartz wafers using a spin coater a WS-650-23 Spin Processor (Laurell, US) at 150 RPM with a total mass of 3 mg. These films were dried in vacuo at room temperature and then plasma treated for 0.5, 1, 5, 10, 30 and 60 min for subsequent resistivity testing. Sheet resistance of the films were measured using a linear four-point probe system (Ossila, UK) with 1.27 mm probe spacing's and 0.48 mm diameter probes typically with 150 mA probe current with multiple positions probed for each sample.

Energy Dispersive X-ray Spectroscopy (EDS)

The progressive increase in silver oxidation is demonstrated using SEM EDS captured at 5 keV accelerating voltage and is shown in Figure S1. The following Ag L peaks are identified (Figure S1a): L_I (2.6 keV), L_α (3.0 keV), L_β1 (3.2 keV), L_β2 (3.4 keV) and L_γ1(3.5 keV) with other peaks of interest including the C K_α (0.3 keV), O K_α (0.5 keV) and Al K_α (1.5 keV) peaks which is attributed to the aluminium SEM stub used. Figure S1b shows the normalized and aligned O K_α peaks showing no oxidation of the untreated and no detections of oxidation in the 30 s plasma treatment time due to detection limits of the instrument, even though some oxidation is seen in Figure 1c in the main manuscript.

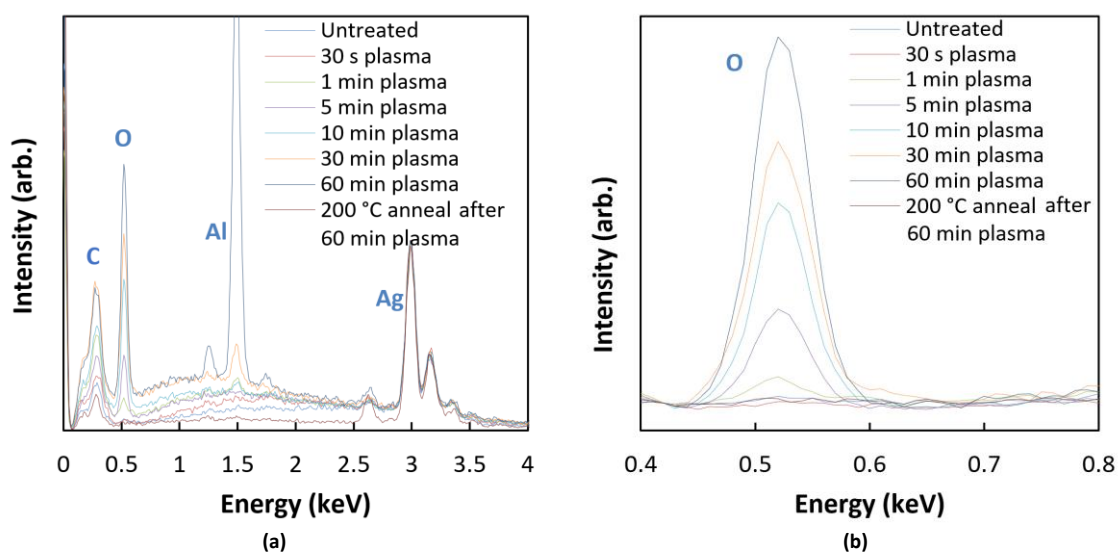


Figure S1. EDS spectra of the plasma-treated AgNWs on aluminium SEM stubs acquired at 5 kV accelerating voltage, showing clearly defined Ag L_α peaks, from 2.6 keV to 3.5 keV, and increasing oxygen K_α peak, at 0.5 keV, with increasing plasma treatment times. Here, (a) and (b) have been normalized to the peak height of the primary Ag L peak at 3.0 keV and in (b) all plots are additionally shifted to 0 at 0.4 keV for height and shape comparison.

Reduction of AgNW/Ag₂O Network

A control test was performed on plasma-treated AgNWs to reduce the silver oxide species back to silver. This was performed in vacuo at 200 °C. The SEM micrographs of the resultant silver product are shown in Figure S2.

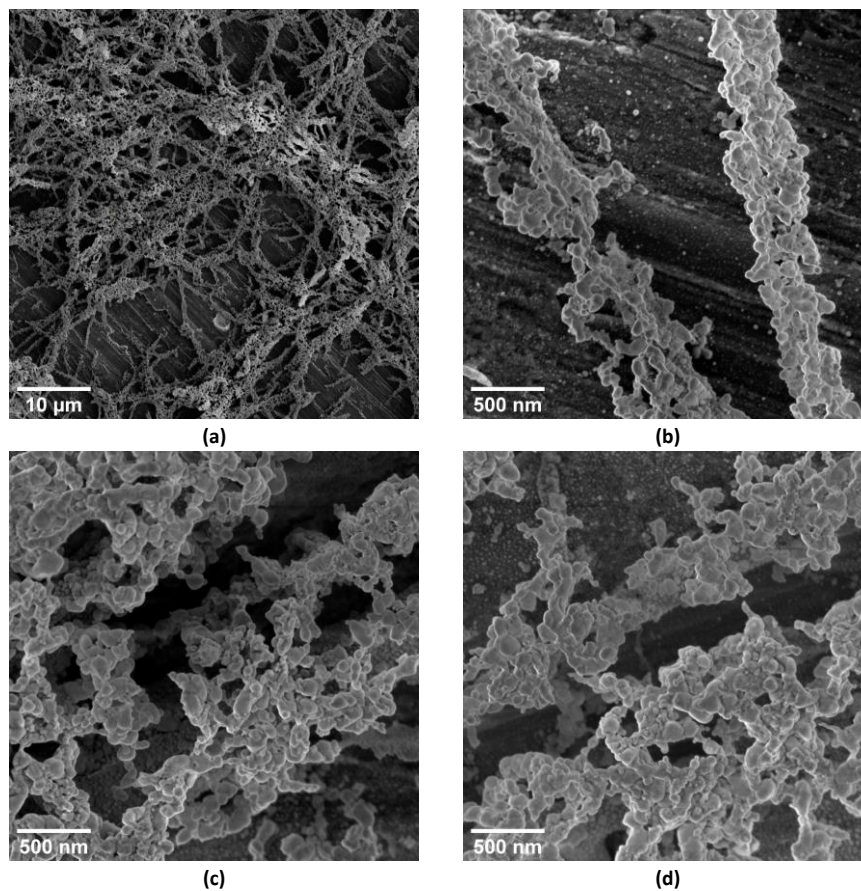


Figure S2. SEM micrograph of AgNWs showing plasma treatment of 60 min which is then reduced in a vacuum oven at 200 °C showing (a) retention of high surface area, (b)-(d) degradation of flakes into balls but increasing connectivity.

Sheet Resistance Measurements

The AgNWs were spin coated onto a 1" diameter quartz wafers and subsequently plasma treated accordingly to allow for resistivity measurements conducted using a four point probe. These results are shown in Figure 2 of the main article, and the photographs of the untreated and treated AgNW films are shown in Figure S3.

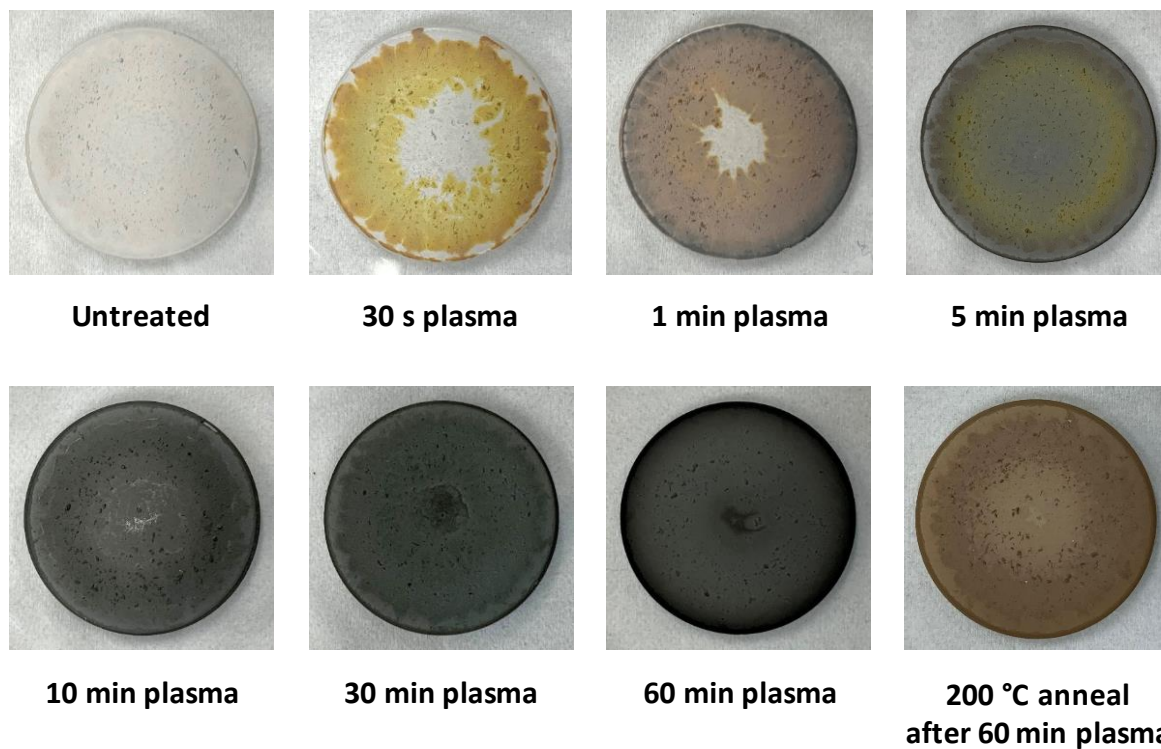


Figure S3. Photographs of the untreated and plasma-treated AgNW films on 1" quartz wafers prior to resistivity measurements.

Components of the Coin Cells

Figure S4a shows a conventional coin cell assembly layout with one spacer used as a counter electrode and the other used as the working electrode once coated with AgNWs and subsequently plasma treatment. The oxidation of the AgNW is visible in Figure S4b, where the 30 s plasma-treated sample showed little color change, the 1 min sample changes to a yellow color before changing to an increasingly darker grey with increasing oxidation.

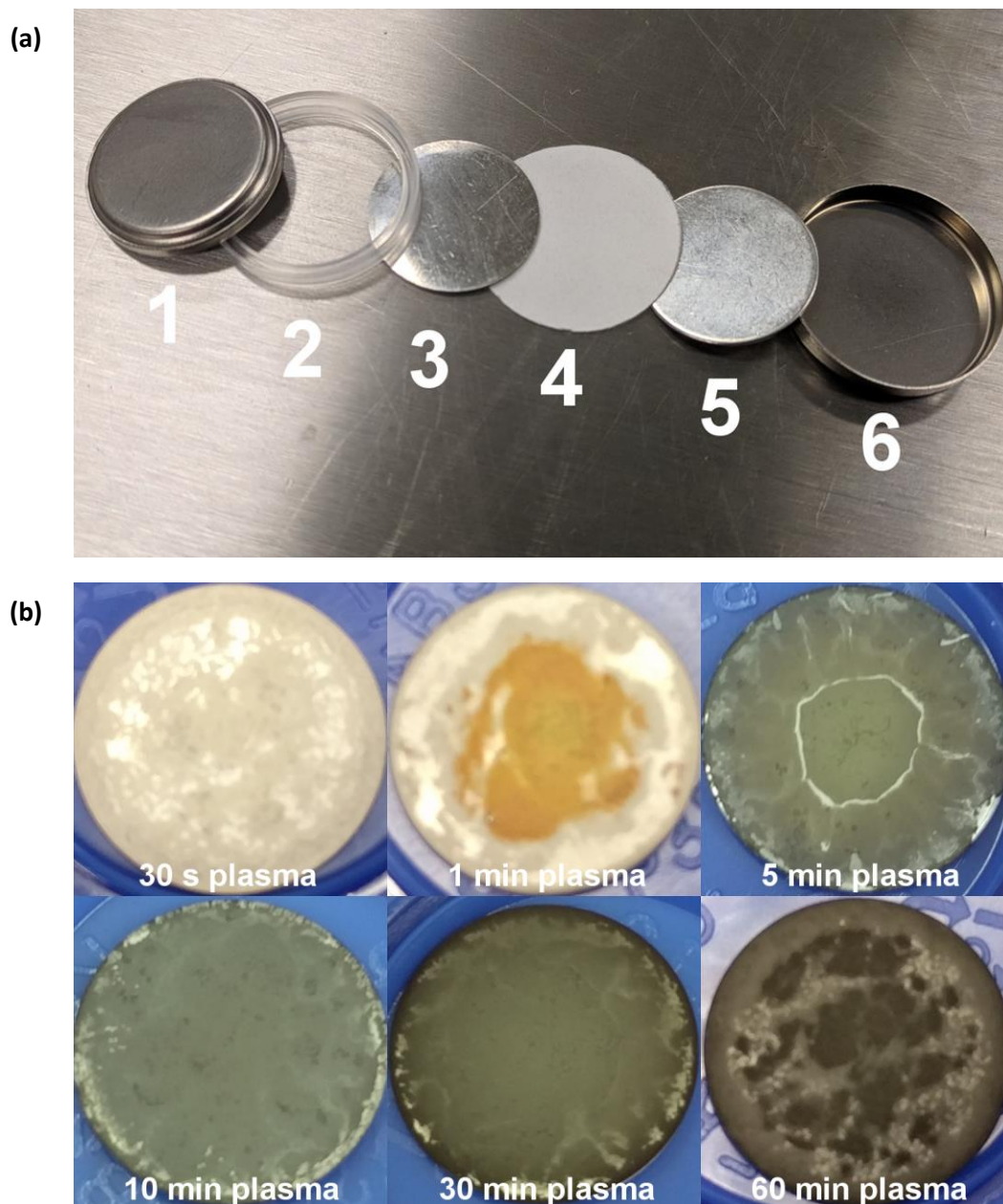


Figure S4. (a) Typical coin cell component layout with labels: **1** bottom cap, **2** seal, **3** stainless steel counter electrode, **4** cellulose separator, **5** cathode with deposited AgNWs, **6** top cap, and (b) plasma treated supercapacitor working electrodes before assembly.