

## Supporting Information

# Functionalization of Silver Nanowires Surface using Ag-C Bonds in a Sequential Reductive Method

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**Synthesis the cover layer: 4-Nitrobenzenediazonium without additive:** 4-Nitrobenzenediazonium was synthesized according to the protocol described by *Belanger in Ref 21*. Briefly, 138 mg (10 mmol, 1 eq.) of 4-nitrobenzenediazonium and 1.06 g (100 mmol) LiClO<sub>4</sub> were dissolved in acetonitrile at room temperature. To this mixture, 309 mg (30 mmol, 3 eq.) *tert*-butyl nitrite were added and the resulting mixture stirred for 10 minutes at room temperature.

**4-Nitrobenzenediazonium with additive:** the same above protocol was applied here as well. However, prior to the cyclic voltammetry experiments, the additive reagent Bu<sub>4</sub>NAsc, 42 mg (1 mmol) was mixed the 4-Nitrobenzenediazonium solution for 10 min at room temperature.

**Synthesis of Silver Nanowire:** Silver nanowires were synthesized similarly to the method reported by *Corte et. al.* as described in ref 15. The recipe is divided to short section as follows:

**Step 1: Ethylene-glycol solution:** 30 mL of ethylene glycol were placed in a 50 mL flask and heated to 150±1°C with a magnetic stirring bar at 260 rpm for 60 min.

**Step 2: CuCl<sub>2</sub> solution:** 6.8 mg of CuCl<sub>2</sub> (the additive reagent) was dissolved in 2mL of ethylene glycol.

**Step 3: Injection of CuCl<sub>2</sub> and polymer into the ethylene-glycol:** 40 µL of Cu-additive solution was injected into the heated ethylene-glycol solution and increased the stirring speed to 700 rpm. After 5min, 1.5 mL of PVP-stabilizer polymer was inserted.

**Step 4: Growing the Silver Nanowires: the Ag nanowires** were prepared by dissolving (160mg of AgNO<sub>3</sub> dissolved in 10ml of ethylene glycol) and added drop wise within 8 minutes (~11 drops in sec) to the ethylene-glycol (step 3) and kept for 60min. After 60 minutes, the reaction is stopped by submerging the glass vial into a petri dish filled with water.

**Notes:** the high-yield of Ag nanowires can be followed by color changes: in the very first seconds, the reaction mixture (step 4) turns into a bright yellow color indicating the initial reduction of silver to small nanoparticles. After ~2 minutes, the size of the nanoparticles increases and color gradually changes into red. 3 minutes later, the color becomes green with a silvery hue, the multi-twin-pounders are formed and the silver nanowires start to grow. The color

becomes more opaque and the silver color starts to dominate. The wispieness starts to show due to the nanowire stirring effect and the silver nanowires after 60 min are finally formed.

**Cleaning recipe:** The reaction mixture is transferred to a 15 mL centrifugation bottle and set at 2000 rpm for 5 minutes. After 5 minutes, adhered Ag-NWs can be seen and the supernatant is removed. 10 mL of fresh ethanol is used and the nanowires are re-dispersed by a sonication bath (several seconds) then centrifuged (300 rpm for 30min). The previous steps are repeated again 2-3 time and the silver nanowires mixture is purified.

**Electrografting of 4-nitrobenzenediazonium on Ag-NW surfaces:** Cyclic voltammetry was performed with a self-made electrolysis vessel equipped with a PAR263A potentiostat (Ametek, Berweyn, USA). WE: Ag-NWs deposited onto a diced piece (1.5x1.5 cm<sup>2</sup>) single side polished silicon, 1 cm diameter restricted by an EPDM sealing; CE: platinum wire; RE: Ag/0.1 M AgNO<sub>3</sub> in ACN.

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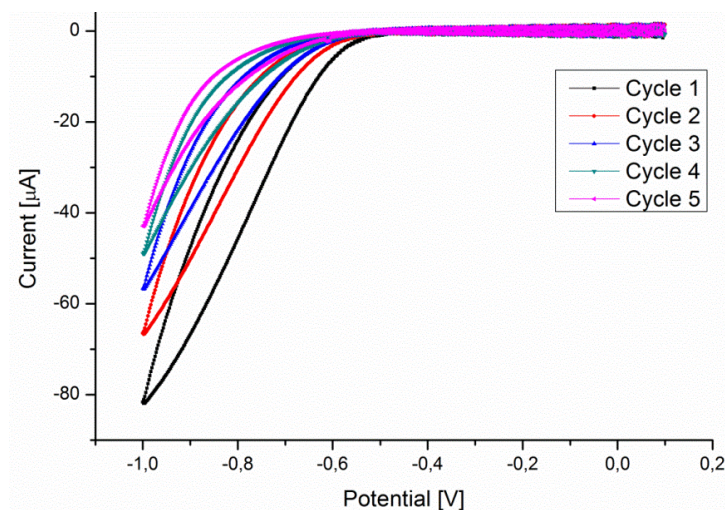
- (1) Glass joints for the RE and CE.
- (2) Glass vessel
- (3) Flange to seal the electrolysis cell
- (4) Contact pin for the working electrode
- (5) Insulating Teflon block



**Figure S1:** Self-made electrolysis vessel for the surface modification of Ag-NWs.

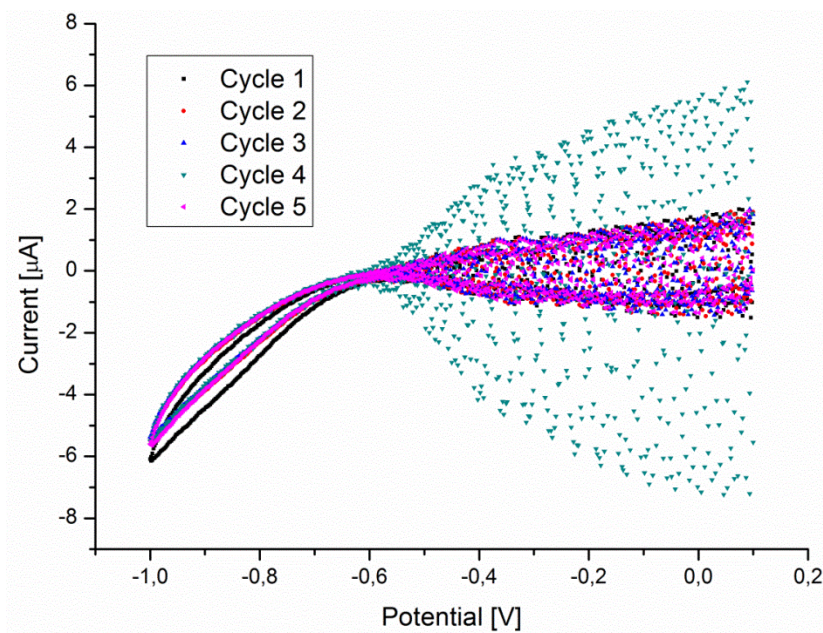
## Exemplary cyclo-voltammograms

### (a) Without the addition of $\text{Bu}_4\text{NAsc}$ :



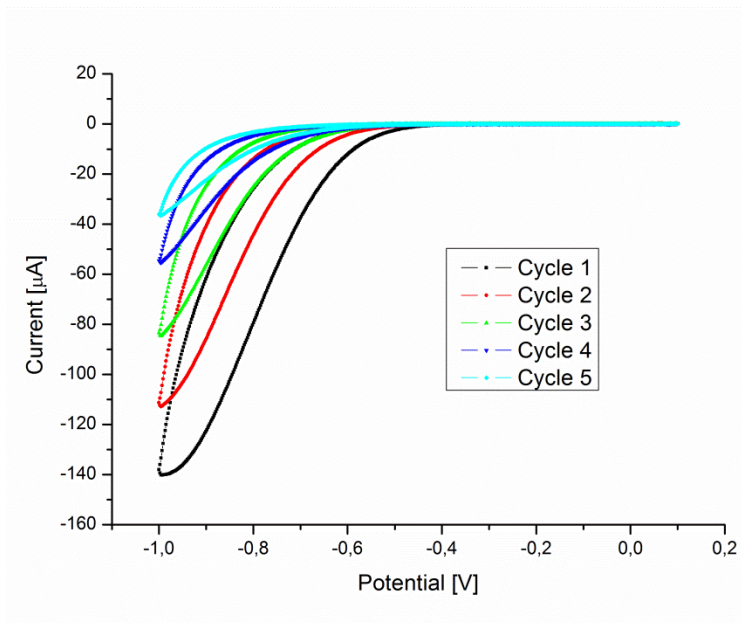
**Figure S2:** Cyclic voltammogram for the electrografting of NBD without the addition of  $\text{Bu}_4\text{NAsc}$ . The figure is representative for all the electrografting experiments with NBD.

### (b) With the addition $\text{Bu}_4\text{NAsc}$ :



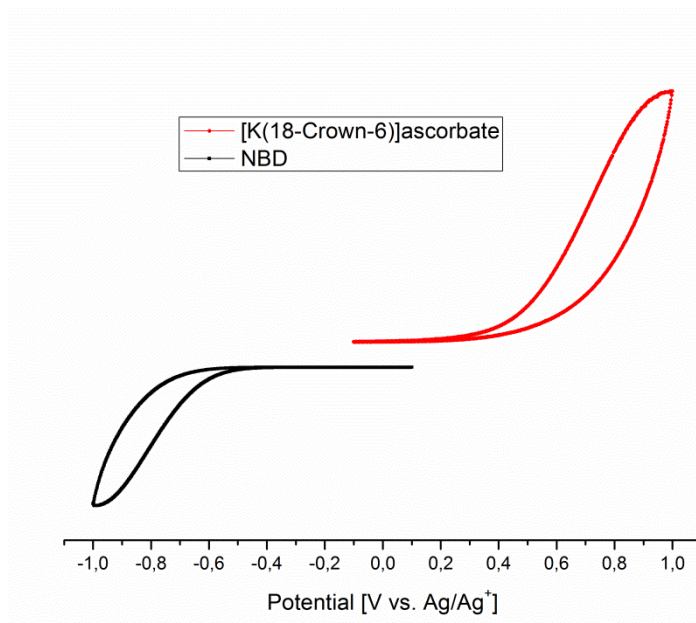
**Figure S3:** Cyclic voltammogram for the electrografting of NBD with the addition of  $\text{Bu}_4\text{NAscH}$ . The figure is representative for all the electrografting experiments with NBD and  $\text{Bu}_4\text{NAscH}$ . The large noise at the beginning of each cycle results from aggregation at the surface. The peak current is expected to be lower, due to the aggregation at the surface.

**(c) On bare silicon substrate**



**Figure S4:** Cyclic voltammogram for the electrografting of NBD without any additives on a bare silicon substrate. In contrast to the grafting of NBD on carbon modifications, no strong current decrease in the second grafting cycle can be observed.

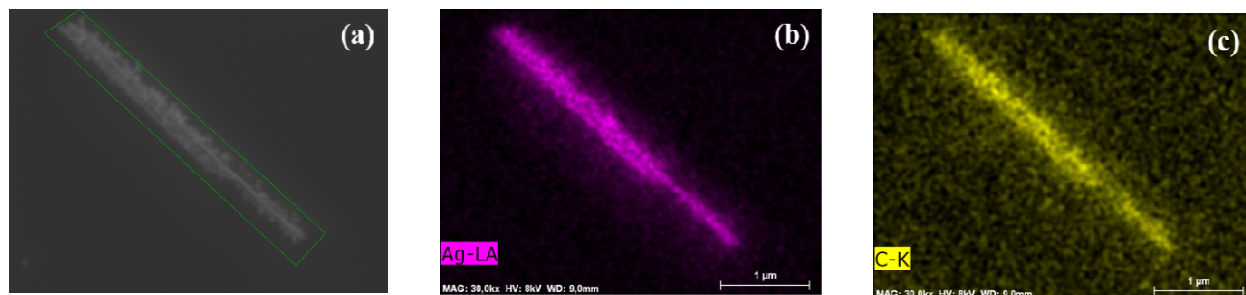
**(d) With and without NBD on bare silicon**



**Figure S5:** Comparison of the cyclic voltammogram for the electrografting of NBD on bare silicon (first cycle, black graph) without any additives and the cyclic voltammogram of the acetonitrile-soluble [K(18-crown-6)] ascorbate salt (red graph). A different ascorbate salt was selected for this study, due to the higher solubility in acetonitrile.



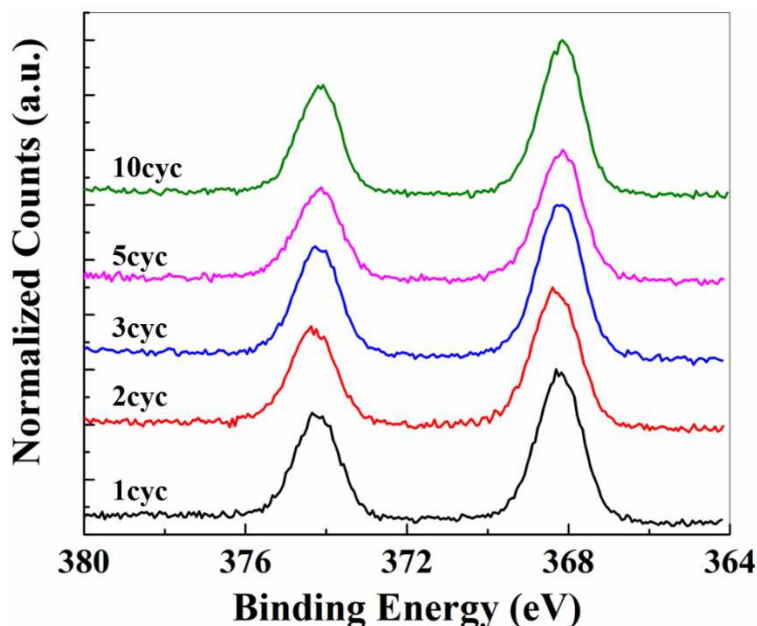
**EDX after the surface modification:** The SEM images of the deposited particles were obtained with field emission scanning electron microscope FE-SEM (Zeiss Merlin). Images were recorded at 8 kV acceleration voltage in secondary electron detection mode with standard Everhart-Thornley detector. Helium ion microscopy images were obtained in helium ion microscope (Zeiss Orion) at 35 kV acceleration voltage in secondary electron detection mode with standard Everhart-Thornley detector. The energy dispersive X-Ray Spectroscopy software of Bruker was used to analyze roughly the chemical composition of the silver nanowire after electrografting.



**Figure S6:** Energy-dispersive X-ray spectroscopy map of a single Ag-NW after five cycles of electrografting. (a) SEM image of individual Ag-NW, (b) silver EDx diffraction on the Ag-NW shown in (a), and (c) carbon EDx diffraction on the Ag-NW shown in (a).

**X-Ray Photoelectron Spectroscopy (XPS):** Core level and valence band photoelectron spectra were excited by monochromatic Al K radiation (1487 eV) and minimize the effect of X-ray damage due to the sample collected with an adjustable overall resolution between 0.8 and 1.2 eV. Photoelectrons were picked up at a takeoff angle of 35° enhancing the surface sensitivity of the technique to about ~20 Å depth. Samples were first scanned from 0 to 800 eV to monitor signals for C, O and Ag. The C1s at 282.0-287.0 eV, O1s at 525-550 eV and Ag3d 360-380 eV were investigated in detail. Scan times of up to ~4h were employed for all data collections. Data analysis was performed using the Sigma Probe Advantage software. Precise binding energy positions and intensities were calculated by peak fitting using software package (XPSPEAK version 4.1). Peak fitting solutions were sought for  $\chi^2 < 1$ , where  $\chi^2$  stands for the standard deviation. The pristine Ag sample, prior to surface modification was deconvoluted to two spin orbit-doublets with an energy splitting of  $6.03 \pm 0.04$  eV: Ag3d<sub>5/2</sub> at  $368.31 \pm 0.02$  eV and Ag3d<sub>3/2</sub> at  $374.34 \pm 0.02$  eV. The observed binding energy of the Ag 3d<sub>5/2</sub> bulk signal allows determining the Fermi level.

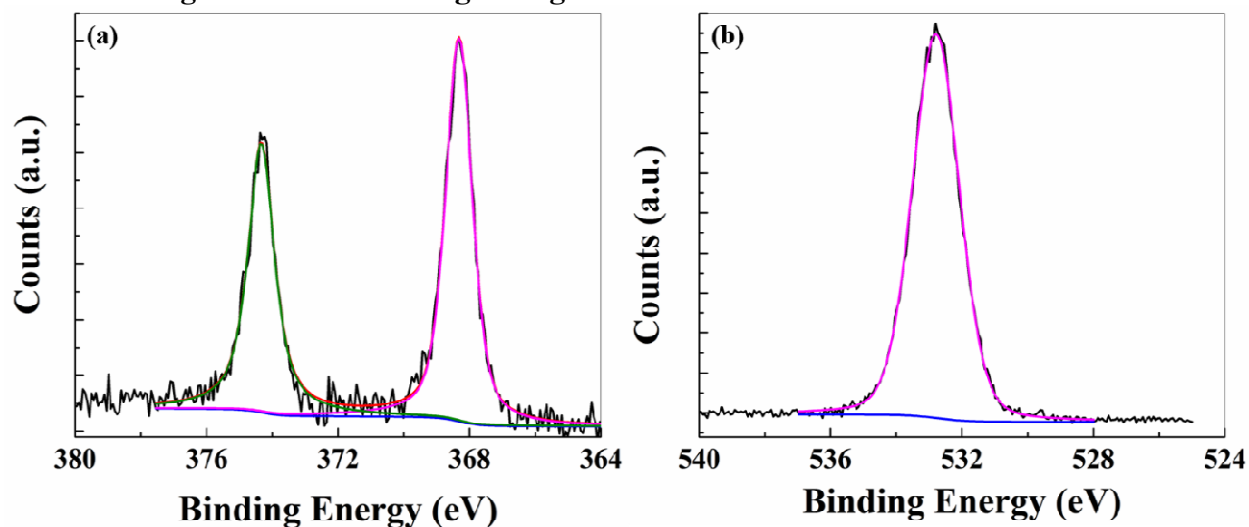
### HR-XPS spectra for Ag-NWs modified without using ascorbate



**Figure S7:** High-resolution XP spectra of the Ag 3d region of the Ag NW surfaces without using the electron transfer agent as function of cycling.

The integral areas under specific peaks of the XPS spectra were normalized to the integral under the Ag 3d (sum of  $3d_{3/2}$  and  $3d_{5/2}$ ) and adjusted with respect to scan time. For the passivated Ag-NW, we fitted the each of the spin orbit doublet with two peaks: C-Ag at  $367.5 \pm 0.2$  eV and Ag-Ag  $368.2 \pm 0.02$  eV. The XPS data from the Ag $3d_{5/2}$  emission region of the molecule-terminated Ag-NWs, fitted to two peaks: C-Ag at  $367.5 \pm 0.2$  eV and Ag-Ag  $368.2 \pm 0.02$  eV. The peaks were typically adjusted to produce fits that minimized the difference between the full widths at half-maximum (fwhm). The center-to-center distances were fixed at  $0.70 \pm 0.02$  eV between the C-Ag and the Ag-Ag emissions and then allowed flowing. For a specific sample, the integrated area under the C-Ag peak was compared to the one under the Ag $3d_{5/2}$  peak and normalized by scan time.

### XPS of the Ag NW before electrografting



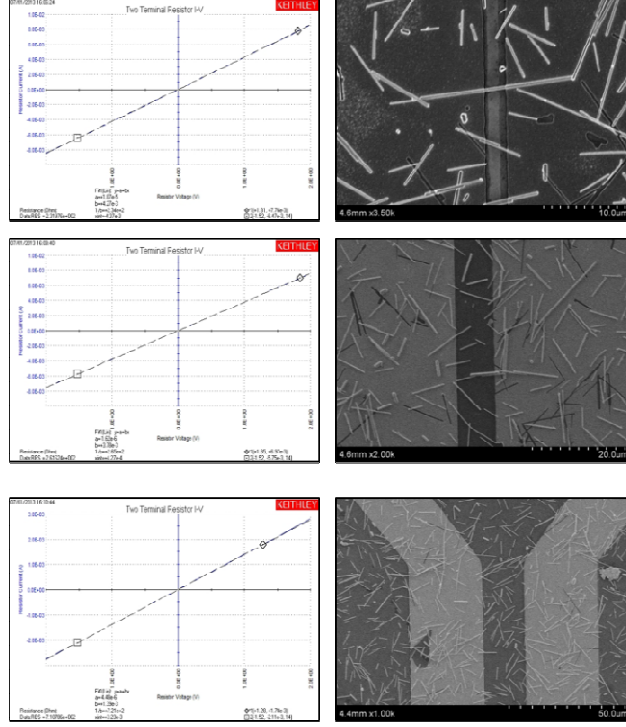
**Figure S8:** High-resolution XP spectra of (a) Ag 3d region and (b) O1s of the pristine Ag-NW surfaces prior electrografting.

**Transmission electron microscopy:** Transmission electron microscopy (TEM) was performed by using a Philips CM300 UltraTWIN equipped with a LaB<sub>6</sub> filament and operated at 300 kV acceleration voltage. TEM images and electron diffraction pattern were recorded by using a charged coupled device camera from TVIPS (Germany) with an image size of 2048 x 2048 pixels. The software JEMS (version 3.5505U2012) and the crystal data from the inorganic crystal structure database (ICSD) were used for the evaluation of the electron diffraction patterns. The TEM samples were prepared by drop-casting the solution (Ag-NW/EtOH) on commonly used copper TEM grids coated with a continuous carbon film.

### Conductivity of Ag-NWs webs:

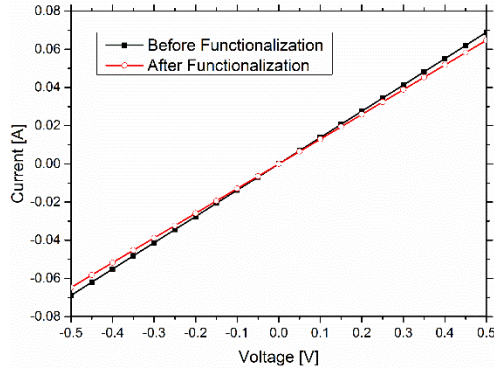
The conductivity of as synthesized silver nanowires used in the seed mediated polyol method were measured by a 2-contact electrode technique and proved conductive for single wires and an array of networks of silver nanowires. Additionally, it was compared to silver nanowires synthesized from industry. The nanowires were deposited on sputtered electrodes of different distances ranging from 2-20  $\mu\text{m}$  (Figure 6S).





**Figure S9:** Two terminal contacts at different gaps.

To check the impact of the modified Ag-NW, condense layer of Ag-NW was used. As shown from Figure S11, the conductivity of the bare and the functionalized Ag-NW are almost the same (1% of difference). The conductive of the bare Ag-NW webs (freshly prepared) is the same as for the bulk silver.



**Figure S10:** Conductivity of the bare and functionalized Ag-NW layer.

The specific conductance can be calculated as the following:

$$\rho = R \frac{A}{l}$$

When;  $\rho$  is the specific resistivity,  $R$  is the electrical resistance ( $\Omega$ ),  $L$  is the length of the nanowire (nm) and  $A$  is the cross-sectional area of the specimen i.e. the diameter of the nanowire (measured in square nano meters,  $\text{nm}^2$ ). The specific conductive would be:

$$\sigma = \frac{1}{\rho}$$

When ( $L = 20\mu\text{m}$ ,  $d = 92\text{nm}$ ), the specific conductivity for bare and functionalized Ag NW is  $3.17\Omega\text{nm}$  and  $3.32\Omega\text{nm}$  respectively. Note that specific conductivity of bulk silver is  $1.59\Omega\text{nm}$ . The minor change between the conductivity of the nanowires webs can be raised due to the non-perfect contact points between the linked nanowires. Nevertheless, the conductivity of bare and functionalized nanowires are almost the same which represent that the capping layer plays low role in terms of conductivity.