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

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S *Supporting Information*

ABSTRACT: Silver nanowires (Ag-NW) assembled in interdigitated webs have shown an applicative potential as transparent and conducting electrodes. However, upon integration in practical device designs, the presence of silver oxide, which instantaneously forms on the Ag-NW surfaces in ambient conditions, is unwanted. Here, we report on the functionalization of Ag-NWs with 4-nitrophenyl moieties through A-C bonds using a versatile two step reduction process, i.e., ascorbate reduction combined electrografting. We show that 40% of the Ag atop sites were terminated and provide high surface stability toward oxidation for more than 2 months while keeping the same intrinsic conductivity as in bulk silver.

KEYWORDS: *silver nanowires, transparent electrodes, Ag−C bonds, electrografting, XPS, surface functionalization*
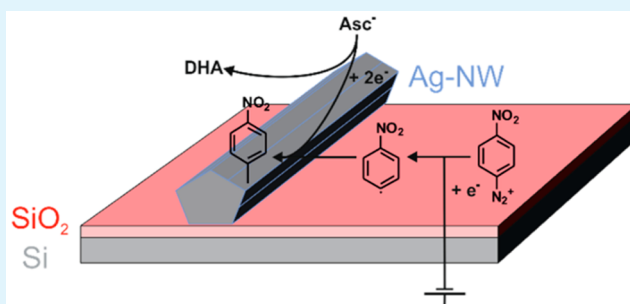
The successful application of transparent conducting films (TCF) such as indium tin oxide (ITO) or aluminum doped zinc oxide (AZO) in optoelectronic devices such as lasers, light-emitting diodes (LEDs), solar cells, or hand-held electronics has fueled a huge interest to further develop those TCFs using inexpensive, easy-to-process (ideally with low thermal budget) materials that are ideally earth abundant, unlike indium and nontoxic.[1] ITO is the most commonly used TCF and serves as a benchmark in terms of high optical transparency in the visible spectral range and at the same time good electrical conductivity.[1] Major disadvantages of ITO are brittleness and limited indium availability with a forecasted strategic reach of less than 10 years if usage continues as of today. AZO is an alternative TCF without rare components; however, the conductance of the layer at high transmission lacks behind the ITO performance. Extensive research goes now into the exploration of nanocomposite alternatives to ITO and AZO using, e.g., silver nanowires (Ag-NW) in interdigitated webs that form a flexible electrode which relies on easy, cost efficient, and low thermal budget synthesis based on simple beaker-type chemistries.[2,3] The major drawback of these Ag-NWs is that they oxidize substantially in ambient conditions at their large exposed surface area.[4] The unwanted immediate oxidation and the interface induced, increased

resistivity of the Ag-NW webs with time that need to be controlled and ideally hindered through surface functionalization. Moreover, attachment of functional groups to the Ag-NW surfaces is expected to permit precise work function engineering.[5,6] Through work function tuning, Ag-NW webs as an external electrode on a semiconductor device, can be adapted to optimize band alignment at the metals/semiconductor interface i.e. a so-called Schottky barrier forms.[7] Despite the fact that sulfur-terminated silver or gold surfaces are used successfully in contemporary electronic devices, little is known about the carbon-terminated Ag-NW surface chemistry through Ag−C bonds and the bond stability in ambient conditions.[8] Electrografting is an easy to perform wet chemical protocol to tailor the properties of an electrode surface, and can be applied to the functionalized Ag-NW web electrode as well.[9−13] In general, electrografting refers to the electrochemical reaction that permits organic layers to be attached to solid conducting substrates. This definition can be extended not only to reactions involving an electron transfer between the working substrate and the functional group, but also to examples where

a reducing or oxidizing reagent is added to produce the reactive species. These methods are interesting as they provide real covalent bonds (i.e., chemical bonds not physical adsorption) between the surface and the organic layer. We selected diazonium derivatives as coating agent, because they are easily accessible and highly reactive toward surface atoms after reduction. Our grafting process can be influenced by additives to the electrolyte, which help to control the formation of an organic functional layer at the surface of the Ag-NW electrode material.[14]

Here, we report on the deposition of 4-nitrophenyl moieties on Ag-NWs as a model group for the electrografting process and their covalently bound nature. Covalent Ag−C bonds form on the Ag-NW surface as confirmed by X-ray photoelectron spectroscopy (XPS). In addition, we provide a pathway for subsequent functionalization using the aforementioned electrografting procedure. We demonstrate that the aforementioned chemical overlayer formation can impede the undesired oxidation/sulfidation of Ag-NWs in a variety of environments while maintaining surfaces of high electrical quality. Ag-NWs were synthesized using a method reported by Korte et al., which was modified to obtain a high yield of Ag-NWs with controlled length and diameters.[15] Briefly, $AgNO_3$ was dissolved in ethylene glycol and reduced in the presence of $CuCl_2$. Ethylene glycol was selected as mild reductant and "green" solvent.[15] The addition of $CuCl_2$ supplied a copper source for the formation of Cu(I), which scavenges oxygen at the silver surface. At the same time, chloride acts as a leveler, directing the growing nanocrystal into a long and thin shape. The Ag-NWs were stabilized with the polymer polyvinylpyrrolidone (PVP). The electron rich carbonyl groups (C=O) in the polymer stabilizes the formation of Ag-seeds via coordinative bonding toward the positively charged surfaces of the growing crystals. More information can be found in the Supporting Information. This synthesis procedure results in Ag-NWs with 100 ± 20 nm in diameter and 10 ± 2 μm in length as confirmed by scanning electron microscopy (SEM), an example of which is shown in Figure 1a, b.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) confirm that the Ag-NWs exhibit the well-known penta-twinned microstructure consisting of five Ag-fcc segments separated by {111} twin boundaries that meet at a common [110] direction parallel to the wire axis.[16,18] The strand like contrast in the bright-field TEM image (Figure 1c) originates from the different crystallographic orientations of the twin segments. The SAED pattern (Figure 1d) is depicted in correct relative orientation with respect to the bright-field TEM image and confirms that the long axis of the nanowire is [110] as prior discussed by Chen et al.[19] Because of the addition of $CuCl_2$ in the synthesis of the nanowires, the formation of bimetallic Ag−Cu, CuO, or Cu crystal domains is plausible, but could not be observed. Concerning the surface modification an important consequence of the penta-twinned microstructure is that all segments of the Ag-NWs are terminated by {001} surface facets. Streaking of some diffraction spots in the SAED pattern (as exemplarily marked with the black arrow in Figure 1d arises from the existence of planar faults (twin boundaries or stacking faults) and/or elastic strain present in the Ag-NWs.[16]

A total of 10 samples has been prepared to investigate the surface modification of Ag-NW by diazonium treatment. One set of samples (five samples) was modified by the addition of ascorbate while the other set was left without ascorbate. Every sample was prepared by the following protocol: 30 μL of the
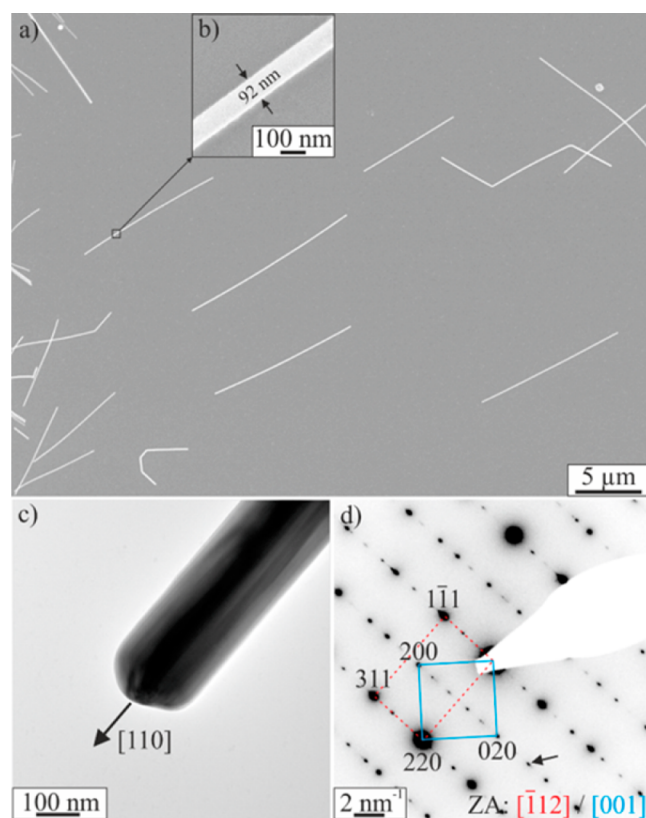

Figure 1. SEM and TEM analysis of Ag-NW: (a) SEM micrograph of Ag-NW prepared on a Si wafer, (b) magnified region of one Ag-NW with a diameter of ~92 nm; (c) is a bright-field TEM image of a Ag-NW with the long axis in [110] direction; (d) is an inverted SAED pattern of the Ag-NW shown in c. The SAED pattern in d corresponds to overlapping of two zone axes: [$\bar{1}$12] (marked with the red dashed box) and [001] (marked with the blue solid box).

Ag-NWs dispersed in ethanol (0.094 M) were deposited via drop-casting onto a diced piece (1.5 × 1.5 cm^2) of a polished silicon wafer. Subsequently, the samples were dried in a N_2 gas flow. The density of the deposited Ag-NWs was extracted from the analysis of SEM micrographs and 10 NWs per 400 μm^2 could be found. Silicon (100) substrate wafers (1−5 Ωcm) with a native oxide (SiO_2 thickness: 1−2 nm) were used, because native SiO_2 is highly disfavored with respect to diazonium immobilization, whereas the silicon wafer of the given doping level supports the electron injection for the electrografting toward the Ag-NW.[20,21] The modification was carried out by 4-nitrobenzenediazonium (NBD) using cyclic voltammetry for one to ten cycles cycling between a potential of 0.1 to −1 V (vs Ag/Ag$^+$). NBD was employed because of its role as a "quasi-gold standard" for a diazonium surface chemistry.[9] The electrolyte consisted of a 0.1 M solution of $LiClO_4$ in acetonitrile (see Figure S1). The NBD (0.01 M) was prepared directly before each experiment by following a procedure reported by Belanger.[21] One set of samples was functionalized with tetrabutylammonium ascorbate (Bu_4NAsc, 1 mM) as additive. A typical cyclic voltammogram of 4-nitrobenzenediazonium on the prepared samples can be found in Figure S2 and S3. Compared to the grafting of NBD on Si−H-terminated silicon, the reduction of NBD is detected at more negative potential and the typically observed strong current decrease in the second grafting cycle was not found. This strongly emphasizes the low efficient grafting on native silicon oxide

and the possibility to use this characteristic to direct the grafting process (see Figures S4 and S5).[20,21] After the functionalization, the samples were rinsed with acetonitrile and dried in an Ar gas flow. The composition of the Ag-NW after the electrografting procedure was confirmed by energy dispersive X-ray spectroscopy (EDX) in an SEM (cf. Figures S6 and S7). The electronic properties of the coated samples were obtained by high-resolution X-ray photoelectron spectroscopy (XPS) (see the Supporting Information). XP spectra prior and after the functionalization (which is in fact a passivation against Ag-NW oxidation/sulfidation) confirm the covalent bond formation (i.e., Ag−C) of the 4-nitrophenyl groups at the Ag-NW surfaces. The XP spectrum of bare Ag-NWs shows two peaks at 368.32 ± 0.03 eV and 374.32 ± 0.03 eV that are related to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively (Figure 2). Compared to Ag−Cu bimetallic nanocrystals, no shift to higher binding energies can be observed.[22]
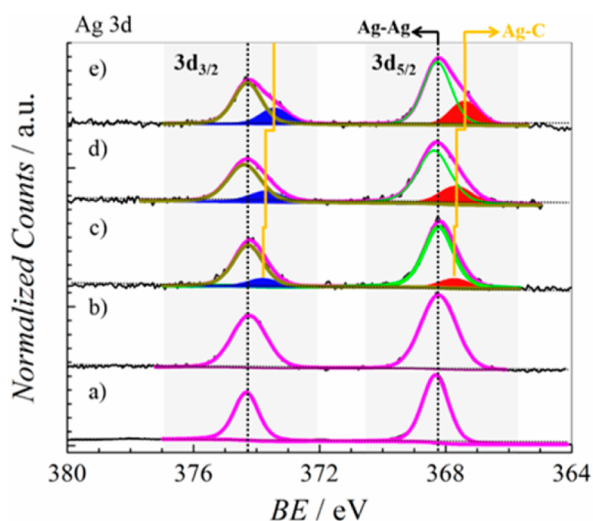

Figure 2. High-resolution XP spectra of the Ag-NW in the Ag 3d region of the XP spectrum (a) prior to and (b−d) after electrografting. In all spectra, the spin−orbit doublets of silver, namely Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks, assume a 3:2 ratio as expected with an energy separation of 6.04 eV. Red and blue lines indicate the new signals that appear after electrografting due to the coating with 4-nitrophenyl groups. Green lines represent Ag−Ag bonds and dark-yellow lines represent Ag−C covalent bonds. XP spectra of (a) pristine Ag-NWs before electrografting, (b) electrografting without the ascorbate. (c−e) Electrografting with ascorbate: (c) one cycle, (d) three cycles, (d) five cycles.

Upon electrografting, without using Bu$_4$NAsc as additive, the XP survey spectrum did not show a emission at lower binding energy (0.7 eV) indicating that this procedure did not lead to an interaction with the Ag-NW surfaces even after 10 grafting cycles (see Figure.S7 in the SI) so that no passivation took place and no Ag−C bonds formed. However, after applying the same protocol with Bu$_4$NAsc, the high resolution XP spectra (resolution of ~20 meV) revealed next to the Ag 3d peak an additional peak located at ~300 meV lower binding energy (Figure 2). The position and intensity is consistent with the formation of Ag$^+$ ions in a polarized Ag−C bond. The position and the intensity of the peak represents the chemical functionalization of the Ag-NWs with Ag−C bond formation and the intensity in particular is a measure for the surface coverage with those Ag−C bonds. Consequently, the more

electrografting cycles have been applied the more pronounced this Ag−C peak is. The varying position with electrografting cycles is due to partial electron transfer from Ag to C. This shifts the peak position to lower energy values: after 3 grafting cycles the original peak position is lowered by 40 ± 10 meV and after 5 grafting cycles it is lowered by 300 ± 10 meV relative to the position after only one grafting cycle. NOTE: neither Ag$^+$ ions of oxidized nor peaks related to Ag−O bonds as they occur in Ag$_2$O or AgO appear in the XP spectrum which confirms that the native oxide on the Ag-NW is being removed during the electrografting procedure. The full width at half-maximum (fwhm) of the Ag 3d core levels (after grafting) also confirms the covalent attachment (i.e., Ag−C bond formation) of carbon atoms to the Ag surface. The Ag 3d XPS scan of the passivated Ag-NWs show larger (0.34 ± 0.04 eV) fwhm's of their respective peaks rather than for pure Ag-NWs. These fwhm differences in the Ag 3d core-level peaks can be attributed to the nonsymmetrical passivation of the 4-nitrophenyl groups on the Ag NW surface, i.e., pinholes between the groups do exist.[23,24]

The evaluation of all XPS measurements suggests the following mechanism of passivation through Ag−C bonds against oxidation/sulfurization (cf. Figure 3) to take place.
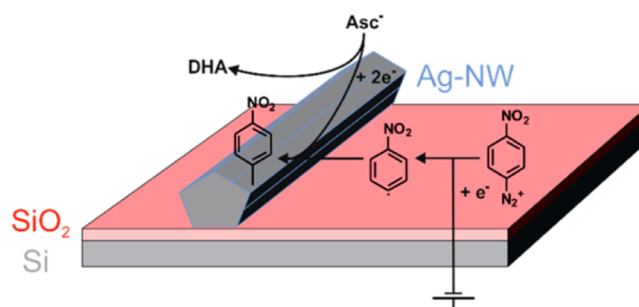

Figure 3. Immobilization of nitrophenyl moieties on Ag-NW surfaces by electrochemical reduction of nitrobenzenediazonium in the presence of Bu$_4$NAsc. Ascorbate is oxidized to dehydroascorbic acid (DHA).

Here, in particular the role of ascorbate as a reducing add-on is elucidated for the understanding of the silver surface passivation. Upon exposure to air Ag−O bonds can form at Ag surface atoms after the Ag-NW synthesis. These sites cannot take part in functionalization with the diazonium chemistry. By adding ascorbate as a mild reducing agent, the oxidized silver ions were reduced activating the surface again for successful diazonium functionalization. In the meantime, nitrophenyl radicals are produced and locally confined at the substrate surface in close vicinity to the Ag-NWs. In a subsequent reaction, the radicals recombine with the freshly prepared Ag-NW surface, immobilizing the nitrophenyl moiety on the NW surface. After the first layer of Ag−C bonds through nitrophenyl moieties is deposited, overgrafting takes place resulting in multilayer formation. Becaise pf diffusion limitation of the organic layer and the presence of ascorbate, the galvanic displacement reaction (GDR) is limited to the close vicinity of the Ag-NWs. At a certain point, the organic layer reaches a critical density, stabilizing the surface and inhibiting GDR.[25]

The chemical and photoelectron spectroscopy data described herein are therefore, entirely consistent with the desired Ag−C bond formation at the Ag-NW surface. The Ag surface chemistry by diazonium functionalization supports the results

of Mangeney et al. obtained for Au nanorod surfaces.[26] The coverage of the coated Ag-NW surfaces with Ag−C bonds can be quantified by evaluating the areas under the Ag−C and Ag−Ag peaks in relation of C−Ag/Ag−Ag. This coverage increased monotonically with an increasing number of the electrografting cycles reaching saturation upon five cycles. As depicted in the Figures 2 and 3, the more reductive cycles the more molecules passivate the Ag-NW surface: $12 \pm 2\%$, $29 \pm 1\%$, and $36 \pm 1\%$ of the Ag-NW surface area were passivated after one cycle, three cycles and five cycles, respectively. The maximum coverage obtained after five cathodic cycles can be explained by using arguments similar to those for molecular-packing on NWs or 2D surfaces.[23,24] Modeling indicated that steric effects based on van der Waals diameter of the phenyl moiety seem to play a critical role in determining the coverage obtained. For example, the van der Waals diameter (28 Å) of the phenyl substituent is larger than the internuclear distances between adjacent Ag atoms (2.5 Å) and, thus, the packing density was claimed to be, at maximum, 40% of a monolayer of Ag-NW surface sites, which explains the highest coverage after five cycles. This installed overlayer exhibits a high stability on the Ag-NW surface in ambient conditions. To demonstrate the molecular integrity of the grafted Ag-NWs, such freshly prepared Ag-NWs having maximum coverage (after 5 cycles) were exposed to ambient air for several hundreds of hours (Figure 4).
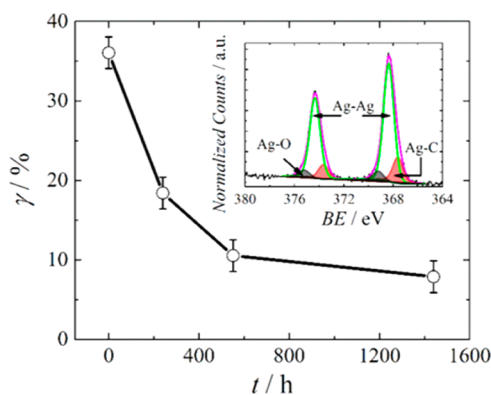

Figure 4. Normalized of the maximum coverage of grafted Ag-NW as a function of exposure time in ambient conditions. Inset is an example of the Ag-3d deconvolution after minor oxidation ($5 \pm 1\%$). The Ag_2O obtained at higher binding energy than Ag−C.

The degree of stability for the grafted molecules was tracked by the normalized coverage as a function of time, i.e., $(C-Ag/Ag\ 3d)_{t>0}$. As measured by the Ag 3d region of the XP spectra of the grafted Ag-NW surface, two regions can be distinguished: (i) 0−500 h and (ii) 500−1440 h (∼4 weeks). In the first regime; the molecule detachment occurred almost linearly with time until finally reaching 10% of the initial coverage (i.e., the Ag−C bond density decreased by ∼75%). However, in the second regime almost no further decreasing of Ag−C bond density was observed. Only 2% of Ag−C bonds were additionally removed even after exposing to air for >1440 h (Ag−C bond density reduction from 10 to 7.8%). It is worth to note that the Ag-NWs show marginal oxidation (only $5 \pm 1\%$) even upon the loss of organic coating a statement that was derived from deconvolution of the Ag 3d peak in the XP spectra (Figure 4). As a result, constant Ag_2O-related XP emissions can be found (inset Figure 4). This result is

significant because gradual oxidation of pristine Ag-NWs degrades the electronic properties of the surface and thus of the surface-dominated Ag-NW itself. This is in sharp contrast with the situation in silicon nanowires, where oxidation of wires indicated by an increasing SiO_x signal in XP spectra goes in parallel to the detachment of organic functional molecules.[27] This may indicate that after detaching of the functional molecule from the Ag-NW surface, the Ag^+ ion is reduced to form Ag^0. It may be speculated that two attached phenyl moieties recombine toward a biphenyl leaving an open coordination space to make this conformation happen. The electrical properties of the electrode webs were evaluated in a two terminal contact arrangement. Finally, the $I-V$ curves, which are a measure of the quality of the webs and impact of the passivation, were similar for the intrinsic bulk silver and fresh Ag-NWs. (cf. Figures S9 and 10).

In summary, the successful functionalization and thus the passivation against unwanted oxidation/sulfidation of Ag-NW surfaces with phenyl moieties using electrografting in combination with an additional electron donor represents a simple and easy to perform approach that opens new options toward the successful and technologically viable realization of a Ag-NW web-based electrode with long-term stability. This procedure permits the formation of chemisorbed carbon functionalities on Ag-NW complementary to existing methods (e.g., thiol passivation) and thus worth further exploring. Our results confirm that Ag-NW passivation against oxidation/sulfidation can be achieved without compromising its electrical characteristics using diazonium chemistry. Extension of scope for this promising approach will be conducted in due course. In particular, precise contact engineering with respect to the particular band structure of the underlying semiconductor and stabilization of the same by choosing the appropriate diazonium precursor and deposition potential is now readily available.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06830.

> Experimental procedures, synthesis of silver nanowires, details on electrografting recipe, cyclo-voltammograms for the deposition of NBD on Ag-NWs, cyclic voltammogram for the electrografting of NBD with and without the addition of Bu_4NAscH, comparison of the cyclic voltammogram for the electrografting of NBD on bare silicon, XPS details, HR-XPS spectra for Ag-NWs modified without using ascorbate, XPS of bare Ag NW, EDX after the surface modification, TEM details, and conductivity of Ag-NW webs (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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