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Electroactive Triphenylamine-Based Polymer Films as Passivation Layers for Improving Electrochemical Oxidation Stability of Silver Nanowires

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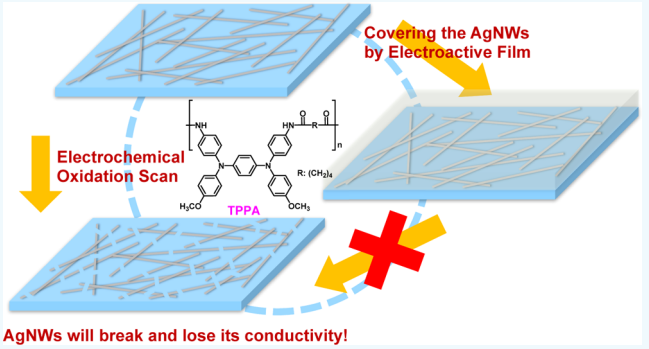
ABSTRACT: Silver nanowires (AgNWs) have emerged as a greater promising material for transparency-based electrodes compared to indium-tin-oxide (ITO) electrodes because of the tunable figures of merit, large-scale processability, and flexibility. However, they still suffered from a crucial problem of instability under the thermal condition, mechanical stimuli, and particularly sustained electrical currents, which is a challenge persisting to date. Here, we demonstrate the improved electrochemical stability of AgNWs by a simple cost-effective electroactive triphenylamine (TPA)-based polymer film as a passivation layer onto the AgNW networks. The AgNW/TPPA hybrid electrode could not only enhance the overall performance including electrical oxidation stability and adhesion to the substrates but also has little effect on transparency contrary to typical passivation films. Besides, the electrochromic behaviors of the obtained AgNW/TPPA hybrid electrode demonstrated obvious multicolor appearance changes during their two oxidation stages. Finally, the AgNW/TPPA hybrid was fabricated as an electrochromic device (ECD) according to the ambipolar conduction behavior. The fabricated ECDs were also used in cyclic and differential pulse voltammetry techniques at a wide-range applied potential for continuous 300 switching cycles, which signifies that our proposed method has long-term operational stability. Thus, our fabrication strategy platform should enable an improved pathway to the development of optoelectronic devices and offer considerable promise for addressing growing concerns of device stability.



KEYWORDS: *silver nanowire, passivation layer, stability, electrochromism, triphenylamine*

1. INTRODUCTION

The rapidly increasing advances in the field of science and technology, mainly, transparent conductive electrodes (TCEs) are indispensable elements in a plethora of flexible and transparent optoelectronic devices for applications including smart-touch screens, light-emitting diodes (LEDs), solar panels, and health monitoring technologies.[1−9] In this row, indium tin oxide (ITO) is an important ubiquitous TCE material widespread applied in the development of optoelectronic devices because it has exclusive optical transmittance with a minimum sheet resistivity. Although ITO shows excellent suitability for optoelectronics applications, there have been extensive research studies focused on the replacement of ITO in recent years because of its inherent properties with fragility, shortage of indium, and the expensive manufacturing process.[10,11] These concerns of ITO have limited its applications for next-generation electronic devices. To date, various alternative TCE materials including conductive polymers,[12,13] carbon nanotubes (CNTs),[14] graphenes,[15] and metallic nanowires[16,17] are sprung up like mushrooms. Within these candidates, silver nanowires (AgNWs) are apparently way ahead of the pack in this category due to their advantages such as an adjustable figure of merit (FoM), large-scale synthesis, cost-effectiveness, and flexible mechanical strength, and also can afford enough optical transparency and superior electrical and thermal conductivity in comparison to ITO. At the same time, there has been a growing trend in recent years toward emphasizing flexibility, chemical and thermal stabilities, and even electrical stability under mechanical stress (for example: stretching, twisting, and bending).[18−22] However, there was no report so far that focuses on the electrochemical oxidation stability of AgNW electrodes during the conduction current of the oxidation redox process. This is one of the most important

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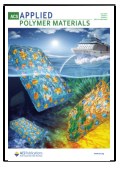

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factors that need to be concerned for evaluating AgNW-based TCEs in further industrial applications.

Despite these excellent properties of AgNWs, they are not broadly recognized for commercialization purposes due to their poor durability. Moreover, AgNW electrodes are well known to be vulnerable to oxygen, a sulfur-containing compound,[23,24] elevated temperatures,[25] humidity,[26] ultraviolet irradiation,[27] and sustained electrical currents.[28] Owing to these potential problems, the pristine AgNWs may deteriorate and lose their conductivity during the time of production and/or utilization of devices. As a consequence, researchers have devoted themselves to focus studies on improving the lifetime and the stability issues of AgNWs. After realizing the easy degradation mechanisms of AgNWs, various passivation layers have been developed to protect AgNWs for decades, such as graphene oxide (GO)-treated AgNW electrodes via a dip coating method to avoid the increase in the sheet resistance under ultraviolet irradiation and thermal treatment.[27] The oxidation stability of AgNW-based TCEs under the thermal and chemical conditions was also improved by growing monolayer graphene onto the pristine AgNWs using the chemical vapor deposition (CVD) method.[29] Besides, metal or metal oxide deposited on AgNW electrodes by an atomic layer deposition (ALD) method is another way to enhance the electrical conductivity and thermal oxidation stability.[30−35] Apart from coating passivation layers onto the AgNW electrodes, functionalizing the AgNWs with strongly bound ligands could enhance their stabilities.[36−38] However, the aforementioned approaches are relatively technical, have a high cost, and make sacrifices of optoelectrical performance to some extent, which would hinder their adoption for commercial applications.

Since 2015, our research group has been interested in the fabrication of AgNW electrodes.[39−42] Besides, substrates such as polyimide (PI) and poly(dimethylsiloxane) (PDMS) for the fabrication of foldable and elastomeric devices and defogging and electrochromic devices (ECDs) have been applied with the incorporation of AgNWs. Nevertheless, these AgNW-based TCEs were usually used as a cathode in electrochemical devices to avoid losing conductivity caused by oxidation. Even though these stretchable AgNW electrodes could be fabricated into ECDs, the lifetime of electrodes decreased rapidly at higher oxidation potentials. Hence, for solving the critical stability issue of AgNW-based TCEs, a promising potential avenue for electrode fabrication that is both simple in terms of manufacturability and high stability under conduction current is proposed. By introducing electroactive TPA-based polymer films as the passivation layers into this system, we expect that the electrochemical oxidation stability of AgNWs can be significantly improved. Consequently, ECD could be successfully fabricated using AgNW/TPPA hybrid electrodes as both a cathode and an anode at the same time. Thus, not only could this facile strategy of adopting an electroactive TPPA material as the passivation protect layer enhance the overall performance of AgNWs but it plays the role of anodic EC behavior. This judicious and innovative approach may be used to develop integrated fields since triphenylamine (TPA)-based polymer films also demonstrate excellent thermal oxidation stability and flexible mechanical strength in addition to the optoelectronic characteristics.

2. RESULTS AND DISCUSSION

2.1. Electrical Stability of Pristine AgNW Electrodes. To investigate the electrochemical stability of AgNWs covered by TPPA polyamide, before that we have the responsibility to discuss the stability of pristine AgNW electrodes. According to the previous reports,[22−27] AgNWs have some disadvantages of easy oxidation, weak adhesion, and poor stability under the conduction current. Especially, pristine AgNW electrodes easily resulted in oxidation and corrosion of Ag under positive potentials in any electrolyte solution.[43] The electrical stability of pristine AgNW electrodes was conducted in a conventional electrochemical cell containing a pristine AgNW-coated glass substrate as a working electrode, a slice of platinum (Pt) as a counter electrode, Ag/AgCl as a reference electrode (0.3 M KCl), and 0.1 M $TBABF_4$/MeCN as a supporting electrolyte. The result shown in Figure 1 implies that the oxidation

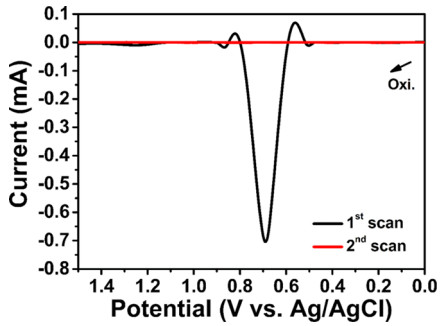

Figure 1. DPV diagram of first and second scans of the pristine AgNW electrode in 0.1 M $TBABF_4$/MeCN with a scan rate of 2 mV/s, pulse amplitude: 50 mV, pulse width: 25 ms, and pulse period: 0.2 s (working electrode area: 3 cm × 0.7 cm and sheet resistance: 15 Ω/sq).

stability of the pristine AgNW electrode has been observed to be extremely unstable and at its second sweep becomes completely flattened. This result shows that the AgNW electrode has greatly suffered without the presence of passivation layers due to the damage of electrical conductivity, which restricts its further practical application. To overcome this difficulty, the electroactive material TPPA polyamide as a passivation layer was introduced to improve stability, and it could maintain the electrical conductivity of AgNWs to prevent the short-circuit against the oxidation during the electrochromic operation.

2.2. Optical and Electrochemical Properties of AgNW/TPPA Hybrid Electrodes. *2.2.1. Electrochemical Properties.* In recent years, various types of materials were introduced as passivation layers to improve the cycle life of AgNW electrodes. Although hybridizing AgNWs with ZnO,[29−31] Ni,[44] and TiO_2,[45] through thermal evaporation and chemical vapor deposition, and graphene[46] is an effective way to slow AgNW electrodes from degradation. However, these approaches are relatively technical, time-consuming, and even reduce the transparency of electrodes. To overcome these issues, herein, we newly modified the surface of AgNW networks of the electrode with inexpensive and simple TPPA polyamide as a suitable passivation layer for improving thermal stability, transparency, and mechanical flexibility. The electrochemical properties of the obtained AgNW/TPPA hybrid electrodes were thoroughly examined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques.

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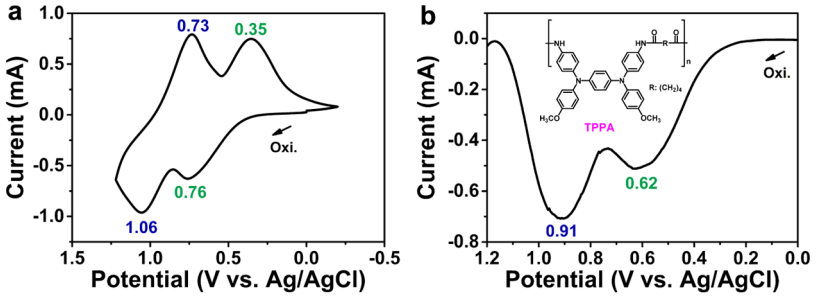

Figure 2. (a) CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of the AgNW/TPPA hybrid electrode measured in 0.1 M $TBABF_4$/MeCN (working electrode area: 3 cm × 0.7 cm and sheet resistance: 15 Ω/sq).

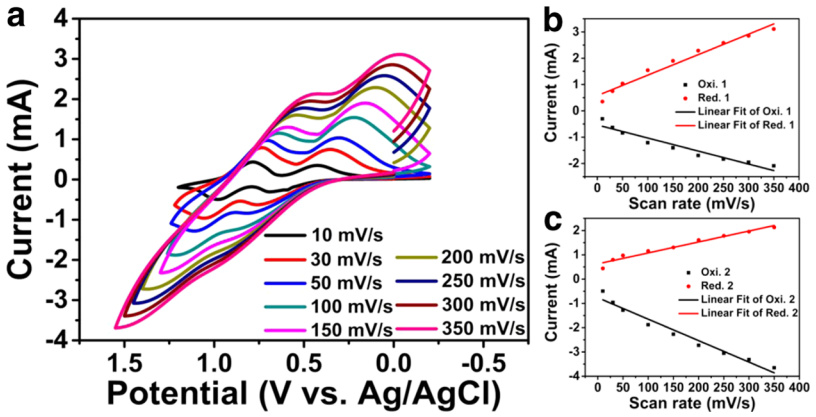

Figure 3. (a) CV diagram of the AgNW/TPPA hybrid electrode measured at different scan rates between 10 and 350 mV/s and scan rate dependence on the peak current for the AgNW/TPPA hybrid electrode at (b) first oxidation and reduction states and (c) second oxidation and reduction states in 0.1 M $TBABF_4$/MeCN.

The schematic diagram of setting CV and UV−vis measurements is illustrated in Figure S1. As a result, Figure 2a displays the CV scan of the simultaneous first and second oxidation states of the AgNW/TPPA hybrid electrode at the peak potentials of +0.76 and +1.06 V (vs Ag/AgCl), while the DPV scan in Figure 2b shows the peaks at potentials of +0.62 and +0.91 V (vs Ag/AgCl), respectively, reflecting the most favorable kinetic process in the highly sensitive DPV technique. These obtained results are also consistent with our previously reported ones.[47]

To get more insights into the AgNW/TPPA hybrid electrode, different scan rates between 10 and 350 mV/s in a 0.1 M $TBABF_4$/MeCN electrolyte solution were measured (Figure 3a). Indeed, a linear dynamic behavior related to the electrode reaction mechanism was found from the correlated relationship between the obtained peak current intensities and their functions of the scan rate. As shown in Figure 3b,c, the obtained anodic (oxidation) and cathodic (reduction) peak current intensities versus the scan rate as a function, respectively, are well fitted with the linear relationship, indicating that the reversible electrochemical kinetic process is not under the diffusion-controlled reaction even at high scan rates. Meanwhile, the peak current intensities are shown linear to the scan rates, suggesting that the polymer film as a passivation layer for improving the drawbacks of AgNW networks should be electroactive and adhere well to the electrode.[48]

2.2.2. Spectroelectrochemical Properties. The spectroelectrochemical behavior of the AgNW/TPPA hybrid electrode shown in Figure 4 at different applied potentials demonstrated

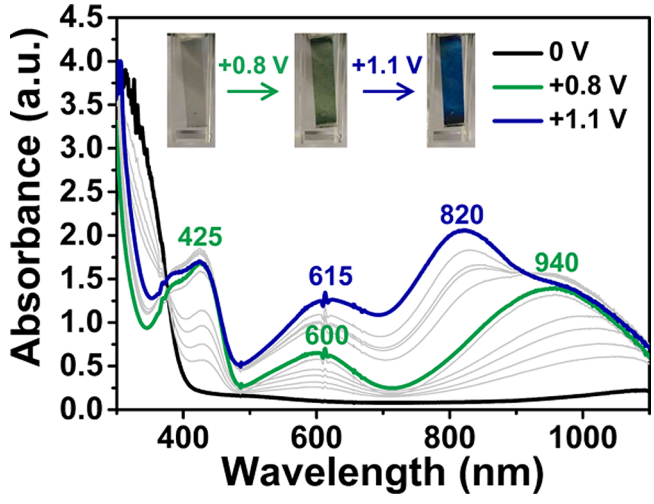

Figure 4. Spectroelectrochemical property of the AgNW/TPPA hybrid electrode. The absorbance spectrum change of the AgNW/TPPA hybrid electrode measured in 0.1 M $TBABF_4$/MeCN at different applied potentials between 0 and 1.1 V (vs Ag/AgCl), and the inset shows the corresponding color change.

that electroactive TPPA polyamide is transparent and very colorless at the neutral state. During the oxidation from 0.0 to +0.8 V (vs Ag/AgCl), the increasing characteristic absorption peaks of the first oxidation state were observed at 425, 600, and 940 nm over the visible−near-IR regions associated with the appearance of a green color. On increasing the applied potential to the second oxidation state, the characteristic

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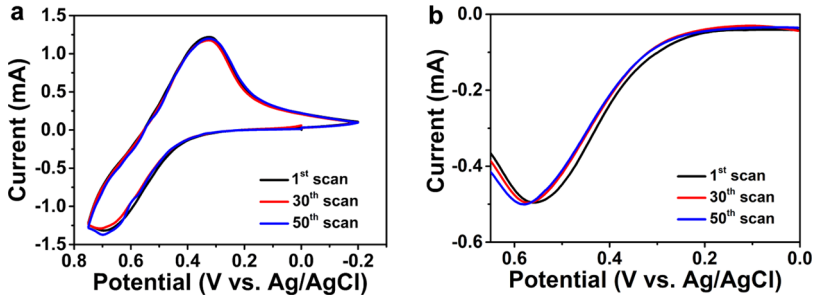

Figure 5. Electrochemical stability of the AgNW/TPPA hybrid electrode at the first oxidation potential. (a) Repetitive CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of the AgNW/TPPA hybrid electrode after 50 cycles in 0.1 M $TBABF_4$/MeCN.

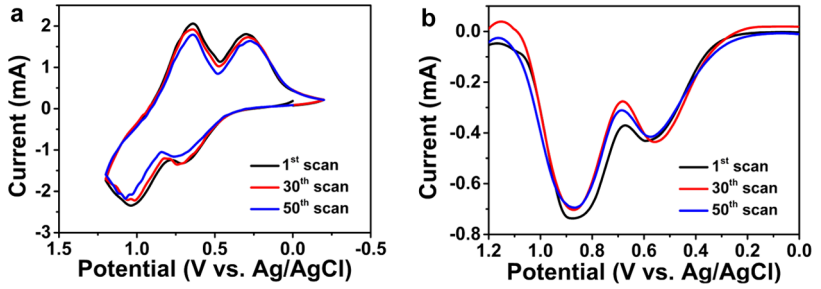

Figure 6. Electrochemical stability of the AgNW/TPPA hybrid electrode at the first and second oxidation potentials. (a) Repetitive CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of the AgNW/TPPA hybrid electrode after 50 cycles in 0.1 M $TBABF_4$/MeCN.

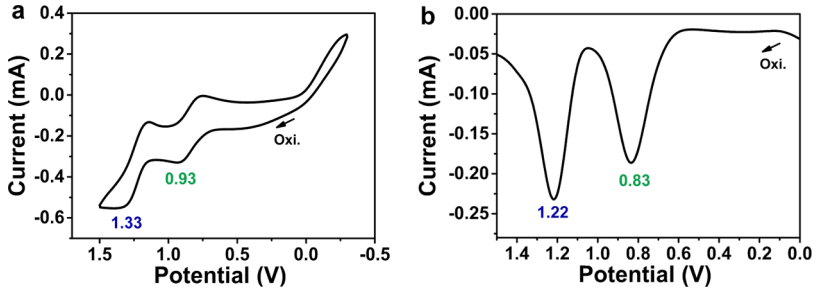

Figure 7. Electrochemical properties of ECD based on AgNW/TPPA hybrid electrodes. (a) CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of ECD based on AgNW/TPPA hybrid electrodes with 0.015 M HV and 0.1 M $TBABF_4$ in 0.05 mL propylene carbonate (PC), (working electrode area: 2 cm × 2 cm and sheet resistance: 15 Ω/sq).

absorption peaks transferred to 615 and 820 nm, and the color changed from green to blue owing to the formation of $TPPA^{2+}$. Furthermore, the electrochromic device (ECD) containing a AgNW/TPPA hybrid as an anode and a cathode electrode was also successfully fabricated to confirm the feasibility for practical applications.

2.2.3. Cycle Stability Tests. The electrochemical stability of the AgNW/TPPA hybrid electrode was assessed in 0.1 M $TBABF_4$/MeCN using the CV and DPV methods. Initially, the AgNW/TPPA hybrid electrode was subjected to the first oxidation state (between +0.75 and −0.2 V) and the second oxidation state (between +1.2 and −0.2 V), respectively, to verify its stability on the positive scan (oxidation) and reverse scan (reduction). According to the abovementioned results and discussion, the pristine AgNW electrodes exhibited very poor stability and lost conductivity at the second scan. While, upon continuous CV and DPV scanning for 50 cycles (Figure 5a,b), the electrical stability of the AgNW/TPPA hybrid electrode revealed less variation in the curves, ascribed to the effect of suppressing the dislocation of silver atoms over a nanowire surface by TPPA, resulting in strongly enhanced electrochemical oxidation stability of AgNW even at the sustained current flow condition without a network interval compared to the pristine AgNW electrode. Consequently, even after continuous 50 oxidation redox cycles over the first and second oxidation states of the AgNW/TPPA hybrid electrode (Figure 6), it exhibited less decay in the curves, indicating the significantly improved electrochemical stability of the AgNW/TPPA hybrid electrode, corresponding to the first and second oxidation states. These successful results suggest that the TPPA polyamide film onto AgNWs could effectively protect from the loss of AgNW network conductivity and maintain the most favorable electrochemical oxidation stability.

2.3. Optical and Electrochemical Properties of ECDs Based on AgNW/TPPA Hybrid Electrodes. For the practical application, AgNW/TPPA hybrid electrodes were further constructed to fabricate the electrochromic devices (ECDs), and the related electrochemical properties were

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established. The devices with a 120 μm gap and a 4 cm^2 active area were prepared from two AgNW/TPPA hybrid electrodes as the cathode and the anode, respectively. At the same time, heptyl viologen (HV) was used to fabricate ECD with an ambipolar system. HV can provide lower working voltage and enhanced EC performance in a two-electrode system, which is attributed to the role of HV, i.e., HV^{2+} readily accepts electrons from TPPA during the oxidation process. Meanwhile, HV^{1+} gives the electron back to the cation radicals of $TPPA^{+\bullet}$ in the reduction process. The CV and DPV diagrams of ECDs derived from AgNW/TPPA hybrid electrodes are shown in Figure 7a,b. The obvious peaks of the first and second oxidation states from the AgNW/TPPA hybrid electrode in the ECD could be observed, which is consistent with the three-electrode system results, indicating the excellent feasibility of the fabricated ECD using AgNW/TPPA hybrid electrodes.

The spectroelectrochemical spectra of ECD derived from AgNW/TPPA hybrid electrodes with 0.015 M (0.75 μmol) HV as a cathodic EC material and 0.1 M (5 μmol) $TBABF_4$/PC as a supporting electrolyte under oxidation potential is depicted in Figure 8. The obvious characteristic absorption

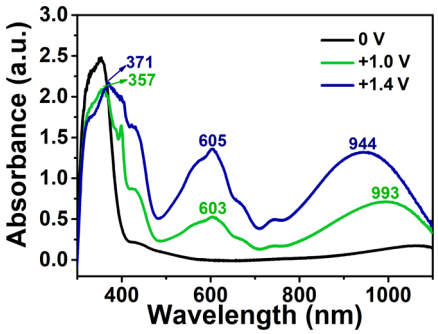

Figure 8. Spectroelectrochemical spectra of the ECD derived from AgNW/TPPA hybrid electrodes. Absorption spectra of ECD based on AgNW/TPPA hybrid electrodes with 0.015 M HV and 0.1 M $TBABF_4$ in 0.05 mL PC at various applied potentials between 0 and 1.4 V.

peaks that appeared at 603 and 605 nm are attributed to the typical HV oxidation stage. The characteristic absorption peaks from the TPPA polyamide film at 357 and 993 nm are ascribed to the colorless to the green color appearance during their first oxidation stage. The two strong characteristic absorption peaks at 371 and 944 nm correspond to the change of the green color into the blue color at the second oxidation stage. The obtained results indicate that the first and second oxidation states at around +1.0 and +1.4 V, respectively, are synchronized with the CV measurements shown in Figure 7. Therefore, it suggests that the ECD derived from AgNW/TPPA hybrid electrodes could reveal excellent spectroelectrochemical behaviors. Furthermore, it is important to evaluate the electrochemical stability of ECD based on AgNW/TPPA hybrid electrodes to ensure the use in practical optoelectronic applications.

The cyclic stability of ECDs during the first and second oxidation states was evaluated using CV and DPV techniques, as shown in Figures 9a,b and 10a,b, respectively. The ECDs show less decay in curves even after 300 cycles of the first oxidation state and simultaneous of first and second oxidation states, demonstrating that the electrochemical oxidation stability of ECD could be efficiently improved through an electroactive TPPA polyamide film as a passivation layer. These obtained performances of ECDs indicate that the introduction of TPPA polyimide as a passivation layer could substantially improve the operational stability of ECDs because of the strong protection from deterioration and loss of conductivity of the AgNW network compared to without the passivation layer. That is momentous progress so far for the AgNW-based TCE with such enhanced cyclic stability using TPPA polyamide films as passivation layers.

3. CONCLUSIONS

In summary, we reported a simple and effective approach to passivate the AgNW networks through an electroactive TPA-based polymer, which significantly enhanced the electrical stability of pristine AgNWs. The AgNW/TPPA electrode exhibited excellent redox activity and optoelectronic properties that could be confirmed by CV and DPV scanning measurements, and the AgNW/TPPA hybrid electrodes revealed much enhanced electrochemical stability over continuous 50 oxidation redox cycles than the pristine AgNW electrodes. Importantly, the ECDs derived from AgNW/TPPA hybrids electrodes displayed excellent oxidation stability for continuous 300 switching cycles and optoelectronic behaviors. Thus, our newly developed ECDs using the AgNW/TPPA hybrids as an anode electrode to replace the ITO-based electrode could overcome the unsustainable dilemma that is a breakthrough in comparison to the previously reported literature. These obtained results certify that the developed AgNW/TPPA hybrid-based electrodes could be a very successful ideology for the stability of various next-generation applications by replacing the rigid glass substrates with other flexible or even stretchable substrates in the upcoming future technologies.

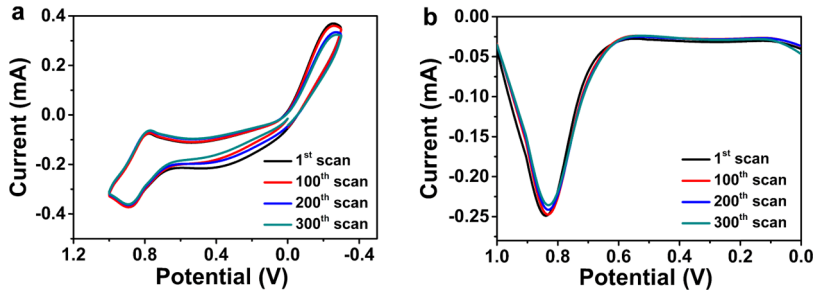

Figure 9. Stability of ECD based on AgNW/TPPA hybrid electrodes at the first oxidation potential. (a) Repetitive CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of ECD based on AgNW/TPPA hybrid electrodes with 0.015 M HV and 0.1 M $TBABF_4$ in 0.05 mL PC after 300 cycles.

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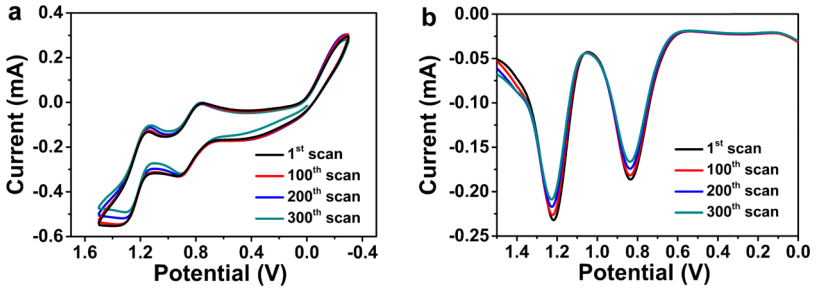

Figure 10. Stability of ECD based on AgNW/TPPA hybrid electrodes at the first and second oxidation potential. (a) Repetitive CV diagram (scan rate of 50 mV/s) and (b) DPV diagram (scan rate: 4 mV/s, pulse amplitude: 50 mV, pulse width: 50 ms, and pulse period: 0.5 s) of ECD based on AgNW/TPPA hybrid electrodes with 0.015 M HV and 0.1 M $TBABF_4$ in 0.05 mL PC after 300 cycles.

4. EXPERIMENTAL SECTION

4.1. Synthesis and Preparation of AgNW/TPPA Hybrid Electrodes. The materials used for the synthesis are commercially purchased. The high aspect ratio of AgNWs was exactly prepared via one-pot polyol synthesis according to our previously reported literature studies.[42,51,52] The photographic images of AgNWs' color changes from transparent to grayish-green are depicted in Figure S2. The morphology images of as-prepared AgNWs using a scanning electron microscope (SEM) are also shown in Figure S3. *N,N′*-Bis(4-aminophenyl)-*N,N′*-di(4-methoxyphenyl)-1,4-phenylenediamine (TPPA) (mp: 194−197 °C) followed by TPPA-polyamide with adipic acid (by replacing 4,4′-oxydibenzoic acid) were synthesized according to the methods described in our previous reports.[49] The cathodic EC material, heptyl viologen tetrafluoroborate $HV(BF_4)_2$, and the electrolyte tetrabutylammonium tetrafluoroborate ($TBABF_4$) was prepared as our previous report.[50] The preparation of AgNW/TPPA hybrid electrodes is similar to our previous reports, as shown in Figure S4, with a film thickness of about 200 nm.[18,53] The fabrication of ECDs based on AgNW/TPPA hybrid electrodes was according to our previous report.[47] Finally, the fabricated ECDs were used for the experiment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c00124.

Measurements, schematic diagrams of setting CV and UV−vis measurements, images of AgNWs, the schematic diagram of the formation of AgNWs, SEM images of AgNWs, and the schematic diagram of the manufacturing process for TCEs based on AgNWs (PDF)

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Author Contributions

This manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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