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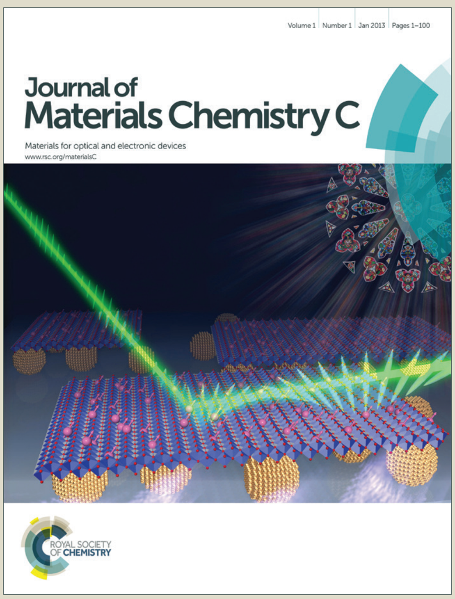

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ARTICLE

Highly Transparent and Flexible Polyimide/AgNWs Hybrid Electrodes with Excellent Thermal Stability for the Applications of Electrochromic and Defogging Devices†

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In this study, highly transparent and flexible electrodes with the highest thermal stability were successfully prepared from silver nanowires (AgNWs)/polyimide (PI) hybrid solutions by a facile solution casting on insoluble polyimide substrates without any trouble transferring process. The prepared highly flexible AgNWs/PI electrodes exhibit low resistance of 25 Ω sq^{-1} and high transmittance up to 86 % at 550 nm of wavelength. Thus, by introducing high performance polyimide as binder, the obtained colorless AgNWs electrodes not only could improve adhesion property between AgNWs and substrates effectively but also reveal excellent thermal stability and high glass transition temperature (T_g) above 300 ^oC. Furthermore, the resulted AgNWs/PI hybrid colorless electrodes could maintain the conductivity even after folding for more than 1000 times. Thus, these optically transparent AgNWs/PI hybrids electrodes have extremely high potential to operate at high temperature working environment or post processing.

1. Introduction

With advances in technology, the products of computers, communications and consumer electronics sprang up like mushrooms over the last two decades. The advances in materials are essential to enhance the performance of both high conductivity and transmittance. This important research topic has attracted great attention by using carbon nanotube (CNTs),[1] graphene,[2] metal oxide, and metallic nanowires.[3,4] Though indium tin oxide (ITO) has excellent properties in both electricity and optics, there are some serious problems faced with, such as high cost of indium and brittle property of ITO. Thus, some strategies adopted to obtain new hybrid materials for preparing flexible and transparent electrodes. For example, CNTs have been studied since 1991, and the electrodes made by CNTs showed sheet resistance of 200 Ω sq^{-1} and transmittance of 80 % at 550 nm.[5] However, such performances are still not enough to the commercial requirements. Another member of carbon family, graphene, also attracted a great deal of attentions since the discovery of graphene awarded the Nobel Prize of physics in 2010. Nevertheless, single layer and few layers graphene, that satisfy the requirements of transparent conductive electrodes, could only be prepared by chemical vapor deposition method (CVD), but the CVD method requires very high temperature and vacuum degree, and additional process of transferring is necessary for CVD graphene. Therefore, silver nanowires (AgNWs) have been considered as the most potential candidate to replace the ITO in the future.[3] The most widely used method for generating AgNWs was template-directed synthesis.[6] However, this method was characterized with problems such as irregular morphology, low aspect ratio, and low yield. Until 2002, Xia's group first proposed a polyol process to produce AgNWs as a simple and large scale way,[7] which used poly(vinylpyrrolidone) (PVP) as capping agent and ethylene glycol (EG) as reductant to reduce the silver nitrate. In order to obtain the transparent electrodes from AgNWs, many attempts such as preparation, coating methods, and annealing process of AgNWs have been reported.[8-21] Some applications of the transparent conductive electrodes obtained from AgNWs have been reported such as solar cells,[22-27] touch screen,[28] heater,[29-33] and light-emitting diodes.[21,34-36] In addition, the transparent electrodes derived from AgNWs also have potential to be applied as transparent electrochromic devices (ECD) and memory devices.[37-39]

For the practical applications, the poor adhesion property of AgNWs and lower T_g of flexible substrates are crucial issue confronted with AgNWs/polymer hybrid electrodes. Therefore, some approaches were used to improve this problem, such as using polyethylene oxide as polymer binder,[40] conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS), heat-resistant copolymer, colorless polyimide as protectors.[30,33,41,42] However, the complex synthesis procedure, organic-soluble behavior, and deep coloration of these polymers resulted in insufficient to endure high temperature or post film-processing for practical application.

In this study, the thermally stable, high Tg, and colorless polyimide (PI) with high transmittance in visible light region

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therefore was chosen as binder to prevent AgNWs from peeling off. To the best of our knowledge, this is the first time to prepare AgNWs/PI hybrid electrodes with not only low electrical resistance, excellent optical transparency, and flexibility, but also high thermal stability that could withstand the high temperature during annealing process or working as heaters. Furthermore, the multifunctional applications of AgNWs/PI electrodes have also developed by the combination of electrochromic polymer. Because of adoption of the polyimides substrates and electrochromic materials, smart windows with defog or desnow functions would have great potential to become practical applications in the future.

2. Experimental

2.1 Materials

Silver nitrate (99.85%, ACROS), polyvinylpyr-rolidone (PVP) (MW=58,000, ACROS), ethylene glycol (EG) (SHOWA), copper(II) chloride (98%, SHOWA), lithium tetrafluoroborate (98%, ACROS), heptyl viologen (TCI), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), *N,N*-dimethylacetamide (DMAc) (TEDIA), acetic acid glacial (SCHARLAU), pyridine (TEDIA), acetic anhydride (>99%, Sigma-Aldrich), poly-L-lysine solution (0.1wt%, Ted Pella) were purchased and used without purification. Commercially available monomers, 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) (Chriskev), 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhy-dride (6FDA) (Chriskev), and 4,4'-(hexafluoroiso-propylidene)dianiline (98%, ACROS), were purified by sublimation. Trans-1,4-cyclohexanediamine (99%, ACROS) was purchased and purified by recrystallization from n-hexane to get white crystal. 2,2'-Bis(trifluoromethyl)-benzidine (TFMB), 1,2,4,5-cyclohexane tetracarboxylic dianhydride, and PMMA (Mw: 120,000) were supplied by Industrial Technology Research Institute of Taiwan, and TFMB was purified by recrystallization from ethanol and water to get white crystal, while 1,2,4,5-cyclohexane tetracarboxylic dianhydride was dried in vacuum oven at 120 ^{o}C for 6 hours. Electrochromic polyamide triphenylamine-containing polyamide (TPA-PA) was synthesized according to previously reported procedures.[43]

2.2 Synthesis of Colorless Polyimides

The colorless polyimide 6FCHPI and copolymer used in this study were synthesized according to conventional two-step method by chemical and thermal imidization, respectively, as shown in scheme 1 and Fig. 1.[44,45] The PI binder 6FCHPI was synthesized as following: 0.2442 g (1 mmol) of 1,2,4,5-cyclohexane tetracarboxylic dianhydride was added in one portion (30 wt% solid content) into the solution of 0.3343 g (1 mmol) of diamine 4,4'-(hexafluoroiso-propylidene)dianiline in 1.4 mL of DMAc at room temperature under nitrogen flow. The mixture was kept stirring at room temperature for about 3 days. Then, pyridine 0.4 mL and acetic anhydride 0.95 mL were added into the reactor, and the imidization reaction proceeded at room temperature for 12 h. The resulting polymer solution was poured into 200 mL of methanol giving a white precipitate and collected by filtration.

The PI substrate was synthesized as following: 0.1827 g (1.6 mmol) of trans-1,4-cyclohexanediamine was dissolved in DMAc at 70 ^{o}C under nitrogen flow, and cooled down to room temperature. Then, 0.2112 g (3.52 mmol) of acetic acid added slowly to form the salt. Subsequently, 0.5884 g (2 mmol) of BPDA was added into the solution. After mechanical stirring for 3 hours at room temperature, another diamine 0.1281 g (0.4 mmol) of TFMB was added to react for another 3 hours. The obtained PAA solution was coating on glass substrate to form PI thin film. Finally dry *in vacuo* at room temperature overnight, then raised temperature slowly to 300 ^{o}C for 1.5 hours to complete thermal imidization.

2.3 Synthesis of Silver Nanowires

AgNWs was prepared by the modified polyol process; ethylene glycol 50 mL was added into 250 mL three necks flask, and stirred at 155 ^{o}C for one hour under nitrogen flow. At the same time, the silver nitrate of 0.094 M and PVP of 0.147 M were prepared in 15 mL of ethylene glycol respectively. After preheating for an hour, 400 µL of 4 mM copper (II) chloride in EG was added into the reactor and stirred for 15 minutes, PVP solution then was added at a time and $AgNO_3$ drop by drop. Finally, the resulting AgNWs was obtained for another one hour reaction, the washed by ethanol with centrifugation filtration many times to remove the residual PVP and silver nanoparticles.

2.4 Fabrication of AgNWs/PI Electrodes

The schematic diagram of fabrication procedure for AgNWs/PI electrodes is depicted in Fig. 2a. By using solvent exchanging method, the AgNWs were firstly transferred from ethanol to the DMAc, and the weight fraction of AgNWs in the DMAc solution could be measured by thermogravimetry analysis. Then, the PI solutions with various concentration of AgNWs (80-320 mg m^{-2}) were coated on the substrates which were immersed in poly-L-lysine water solution for a while.[46] After drying in vacuo to form the random network of AgNWs, the thermal annealing at 180 ^{o}C for an hour was adapted to decrease the electrical resistance of the AgNWs/PI hybrid electrodes. The thickness of dried film is about 10µm observed by OM microscopy shown in Fig. S2.

2.5 Fabrication of Electrochromic Device by AgNWs/PI Hybrid Electrodes.

The fabrication of the electrochromic device (ECD) shown in Fig. 6a, and the electrochromic polymer films were prepared by spinning solution of the TPA-PA (50 mg mL^{-1} in DMAc) onto an ITO-coated glass substrate (25 × 25 × 0.7 mm, 5–10 Ω sq^{-1}). The spin-coated polymer was drying on hotplate and removed the edge of polymer to obtain sample with final active area about 20 × 20 mm^{2}. A gel electrolyte based on PMMA (1.25 g) and $LiBF_4$ (0.15 g) was plasticized with propylene carbonate (2.75 g) to form a highly transparent and conductive gel. In addition, heptyl viologen ($HV(BF_4)_2$) (0.03 g) was added as counter electrode species or ion storage layer. The gel electrolyte was spreading on the polymer-coated side of the electrodes, and then the AgNWs/PI electrode was sandwiched.

2.6 Characterization of AgNWs/PI Electrodes

Thermo-gravimetric analysis (TGA) of TA instrument Q50 used to measure thermal stability of the polymers and hybrids. Field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F), JEOL JEM-1230 transmission electron microscope (TEM), and optical microscopy (HRM-300) were used to examine the surface morphology and microstructure of the AgNWs and hybrid films. UV-vis spectra of the polymers and hybrid films were recorded by Hitachi U-4100 UV-vis-NIR spectrophotometer in the wavelength range of 300–800 nm. The resistance and sheet resistance of the transparent electrodes were measured by the handheld LCR meter (Agilent U1732C) and four point probes (Keithlink Technology), respectively.

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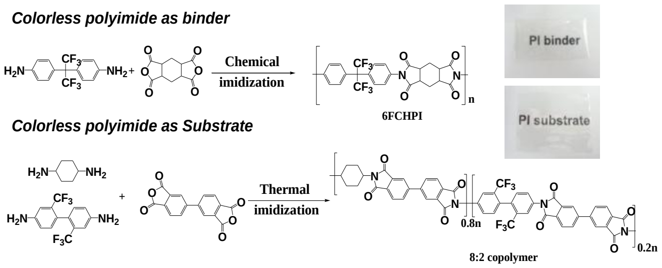
The electrical thermometer (TES 1310 TKPE-K) was used to measure the temperature of the defrost device.



Scheme 1 The synthetic scheme of the colorless polyimides 6FCHPI and 8:2 copolymer.

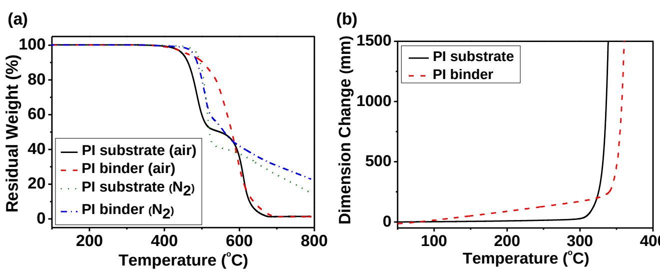


Fig. 1 (a) Thermogravi-metric analysis of the polyimides at a scan rate of 20 °C /min. (b) Thermomechanical analysis curves of the polyimides.

3. Results and discussion

3.1 Basic Characterization

The substrate materials used in this study are depicted in Fig. 1a, tables S1 and S2. All polymerization reactions proceeded homogeneously and gave high molecular weights that could afford tough, flexible, and transparent films *via* solution coating. Furthermore, PI binder exhibited good solubility in common organic solvent such as DMAc and NMP, which provide an easy blending method with AgNWs. On the other hand, the PI substrate showed excellent chemical resistance to these common organic solvent.

The optical properties are tabulated in Table S3. The transmittance at 450 nm of these two PIs was higher than 80 % with cutoff wavelength lower than 400 nm. By the proper structural design, the charge transfer effect could be depressed to result in the colorless polyimide. The introduction of high electronegative bulky fluorine atoms or adopting of aliphatic monomers could decrease charge transfer effect. Therefore, transparent, colorless, and soluble polyimide could be prepared from aliphatic dianhydride and fluorine-containing diamine by chemical imidization, while PI substrate with high chemical resistance was obtained by thermal imidizaiton from fluorine-containing and aliphatic diamine monomers with aromatic dianhydride BPDA. These prepared polyimides have excellent thermal stability, and the diagrams of thermogravimetric and thermomechanical analyses of the PIs are depicted in Fig. 1b and 1c, respectively, and the results are summarized in Table S4. The T_g of these two PI were higher than 325 °C, and 5 wt% decomposition temperatures were also higher than 450 °C even in air, indicating that the PIs are highly thermally stable. Moreover, the coefficient of thermal expansion of the PI substrate was only 8 ppm/ °C, which could maintain the dimension and endure large temperature variation of environment.

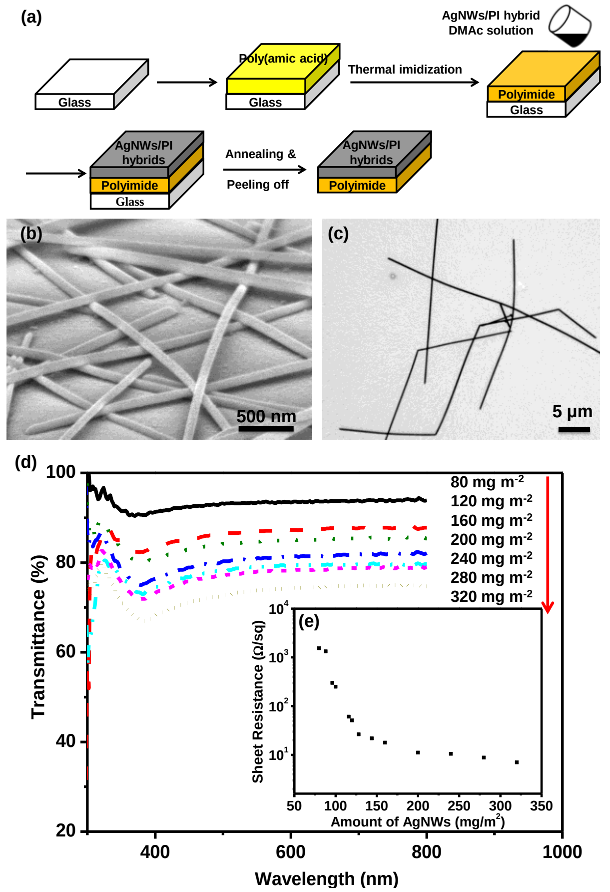


Fig. 2 (a) The scheme of procedure of transparent AgNWs/PI hybrids electrodes. Two kinds of PIs used as both binder and substrate. (b) SEM image of AgNWs tilted at 60 degree. (c) TEM image of AgNWs. (d) UV-Vis transmittance spectra of the resulted electrodes with various amount of AgNWs coated on glass, the transmittance based on the glass substrate as reference. (e) Amount of AgNWs plotted with sheet resistance values of AgNWs/PI hybrid coated on glass.

3.2 Properties of AgNWs/PI Hybrid based Transparent Electrode

The scheme of the procedure and the transparency of AgNWs and AgNWs/PI hybrids are shown in Fig. 2. The AgNWs were prepared by modified polyol process that used EG as reductant and solvent, PVP as capping agent, silver nitrate as provider of silver cations, and copper chloride as oxygen scavenger. The obtained AgNWs have average diameter around 100 nm and average length of 35 μm, and the morphology of AgNWs measured by SEM and TEM, respectively, was depicted Fig. 2b and 2c. The average aspect ratio of these AgNWs was around 350, which is high enough as transparent electrodes.

By this facile approach, the hybrid electrode films with high transmittance and low sheet resistance could be readily prepared. UV-Vis spectra of the obtained electrodes with different amount of AgNWs on glass are summarized in Fig. 2d. In the case of AgNWs only 80 mg m^{-2}, the transmittance at 550 nm was up to 93 %, but the sheet resistance was too high to be the electrode. Therefore, by increasing the amount of AgNWs to 200 mg m^{-2}, the transmittance

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of electrode was higher than 80% at 550 nm with sheet resistance only 11 Ω sq^{-1}, which were comparable to the commercial ITO

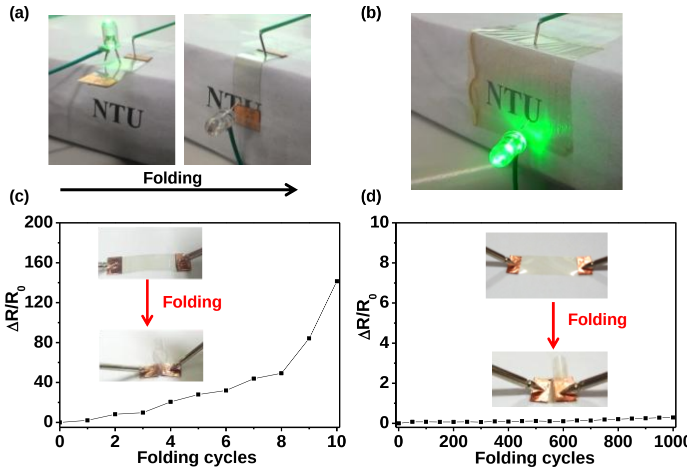

Fig. 3 (a) The ITO coated PEN lost the conductivity immediately after folding, thus the LED lamps no longer working. (b) The AgNWs/PI hybrid electrode connected with LED array, and the LED lamps kept working even under the continuous folding. (c) The change of resistance after folding for ITO coated PEN electrodes, Y-axis represented the change of resistance divided by original resistance. (d) The change of resistance after folding cycles of 1000 times for AgNWs/PI hybrids electrodes.

electrodes. Fig. 2e exhibits the amount of AgNWs plotted with sheet resistance of AgNWs/PI hybrids electrodes. It is very difficult to achieve high transmittance and low resistance simultaneously due to the dilemma relation between transmittance and conductivity. The figure of merit (FoM) is a quantity used to characterize the performance of transparent conductors,[47-49] and the FoM for transparent electrodes could express by

$$\frac{\sigma_{dc}}{\sigma_{op}(\lambda)} = \frac{Z_0}{2R_s}\ \frac{\sqrt{T}}{1-\sqrt{T}} \qquad (1)$$

where the σ_{dc} is the DC conductivity of the film, σ_{op} (λ) is the optical conductivity at wavelength of λ nm, Z_0 is the impedance of free space (377 Ω), R_s is the sheet resistance, and T is the transmittance at λ nm. For industrial application, the FoM values should be larger than 35.[50] The FoM value of AgNWs/PI hybrid electrodes in this study could be reached to 160, implying that the transparent electrodes fabricated by this facile approach reveal excellent combination of good optical and electrical properties.

Furthermore, AgNWs coated on PI substrates were also investigated, and the highly flexible PI electrode with low resistance of 25 Ω sq^{-1} and high transmittance about 86 % could be obtained successfully. For comparison, the folding test of commercial ITO coated polyethylene naphthalate (PEN) electrode shown in Fig. 3a was used as reference, ITO-PEN electrode connected with LED lamps lost conductivity very quickly while folding, and the lamps no longer worked. Nevertheless, the AgNWs/PI electrodes keep the lamps working well even on folding because the good ductility of nanowires networks could prevent breaking down under folding (Fig. 3b). In addition, resistance change with folding cycles for these two different electrodes were compared, and the resistance change of ITO-PEN increased to 140 times of the pristine value only for 10 cycles of folding as shown in Fig. 3c, while AgNWs/PI electrode exhibited excellent flexibility, revealing almost no change of resistance even after folding for 1000 cycles (Fig. 3d).

Although AgNWs electrodes equipped with good conductivity, flexibility, and high transmittance, the adhesion between AgNWs and substrate was too weak for long-term applications. By introducing colorless polyimide into nanowires, not only could bind AgNWs tightly to the substrates but also promote the dispersion of

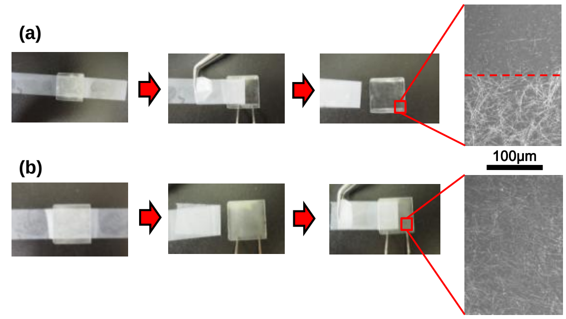

Fig. 4 Peeling off test of (a) AgNWs electrode without binder and (b) AgNWs/PI hybrid electrode by 3M scotch tapes. The SEM images used to observe the morphology of electrodes after peeling off test.

AgNWs. The peeing off test used to evaluate the behavior by using 3M scotch tape, the pristine AgNWs easily removed from substrates shown in Fig. 4a, while the AgNWs with the polyimide binder revealed extremely strong adhesion to the substrates (Fig. 4b). Moreover, thermal stability of the AgNWs/PI hybrid electrodes the temperature higher than 200 ^{o}C attributed to the limitation of AgNWs.

3.3 Properties of AgNWs/PI Heater (Defogging Device)

The defogging devices fabricated by the hybrid electrodes could remove water effectively within one minute while 6 V of potential was applied (Fig. 5a) due to the excellent performance on producing thermal energy according to the Joule's law described as the following:

$$Q = \frac{V^2}{R} \times t \qquad (2)$$

where Q is the heat produced, V is the applied potential, R is the resistance of electrode, and t is the working time. The higher applied potential on devices the higher temperature could be reached (Fig. 5b). As the applied potential was increased to 7 V, the temperature higher than 130 ^{o}C could be obtained. Therefore, the thermal stability of both substrates and binders should be good enough to withstand such higher temperature, and that will not an issue by using PI as substrates and binders. The defogging behavior of devices without any applied potential took about 10 minutes to recover the original visibility shown in Fig. 5c. When the potential of 6 V was applied (Fig. 5d), the condensed water on the device could be removed within only one minute by measuring the recovery of transmittance from UV-Vis spectra. The cycling heating performance measurement of AgNWs/PI defogging devices for evaluating long-term stability test was also conducted and shown in Fig. S1. As application of windshield in automobiles, the occurrence probability of accident maybe reduced by removing condensed water on the windshield more effectively. Moreover, this approach also can replace the traditional defogger on vehicle's back glass consisting of a series of parallel linear resistive conductors. Without the parallel linear on the back glass, it is more pleasing to the eyes.

3.4 Properties of Electrochromic Device Based on the AgNWs/PI Electrode

The AgNWs/PI hybrid electrodes also applied to the electrochromic devices (ECD). The scheme of procedure of electrochromic device using AgNWs/PI hybrid electrode is depicted

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in Fig. 6a, and the electrochemical behavior for ECD of TPA-PA[43] was investigated by cyclic voltammetry (CV). The polyamide film was casted on an indium-tin oxide (ITO)-coated glass substrate as working electrode. Another electrode used AgNWs/PI electrode as cathode. The oxidation and reduction cycles of the film samples were measured in

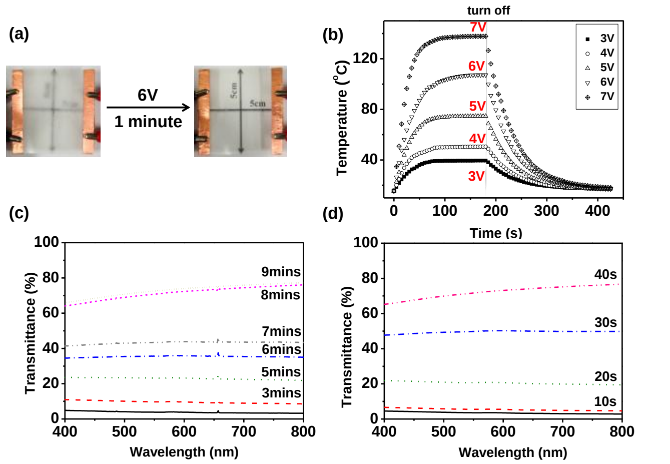

Fig. 5 (a) The defogging device fabricated by AgNWs/PI hybrids was put in refrigerator and then given an applied potential of 6 V, the water on the surface was removed after only one minute. (b) The temperature plotted with time at various applied potential. (c) UV-Vis spectra for the defogging device without any applied potential. (d) UV-Vis spectra for the defogging device with applied potential of 6 V.

the form of device with gel electrolytes, using PMMA as stiffener, propylene carbonate as solvent, $LiBF_4$ as electrolyte, and $HV(BF_4)_2$ as the counter electrode species or ion storage layer. The typical CV diagrams for ECD based on AgNWs/PI electrodes illustrated in Fig. 6b, and revealed reversible oxidation couple with the $E_{1/2}$ value of 1.09 V and good electrochemical stability from CV measurement. Spectroelectrochemical experiment was used to evaluate the optical properties of the electrochromic behavior. The device placed in the optical path of the sample light beam in a UV-vis-NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control. The typical spectroelectrochemical spectra of the device shown in Fig. 6c exhibited strong absorption at 345 nm, characteristic for TPA moiety in the neutral form (0.0 V), implying highly optical transparency and almost colorless in the visible region. Upon oxidation (applied voltage from 0.0 to 1.2 V), the intensity of the absorption peak at 345 nm gradually decreased while new peaks at 389 nm and 787 nm simultaneously increased in intensity due to the formation of a monocation radical of the TPA unit. In addition, other new peaks at 399 nm and 605 nm also enhanced due to the formation of monocation radical of the viologen moiety by gaining one electron. Combine these two electrochromic materials, the color switch from almost colorless neutral state (0.00 V) to the blue green (1.2 V) with very high contrast of optical transmittance at 787 nm.

5. Conclusions

In conclusion, the facile solution casting method without transfer of AgNWs has demonstrated as an effective approach to prepare transparent electrodes in this study. By introducing colorless PI into AgNWs as binder not only could prevent the peeling off from substrates due to the weak adhesion between AgNWs and substrates but also enhance the dispersion of nanowires. The resulting flexible AgNWs/PI hybrid electrodes exhibited highly transparent and electrical conductivity with FOM value up to 160. In addition, the excellent heat-resistant and thermal stability of these AgNWs/PI hybrids electrodes afford the potential to operate in high temperature working environment and also serve as the electrodes for wearable devices.

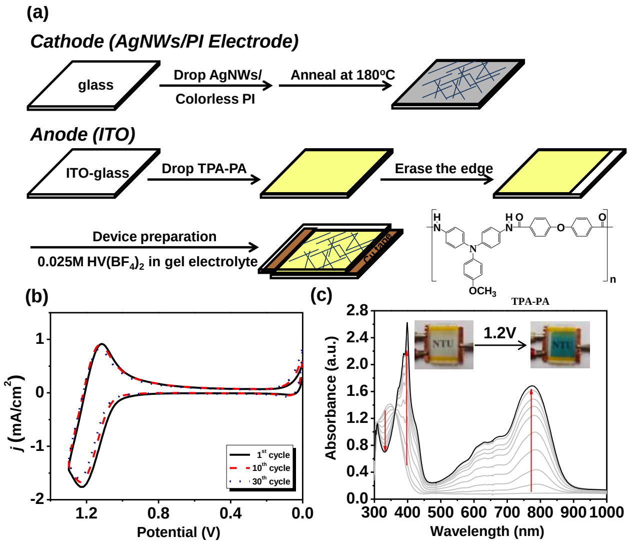

Fig. 6 (a) The scheme of procedure of electrochromic device based on AgNWs/PI hybrid electrode. (b) Cyclic voltammetric diagrams of the ECD based on AgNWs/PI electrode for 30 cycles. (c) The electrochromic behavior of ECD by using AgNWs/PI hybrids electrode and ITO coated glass as cathode and anode, respectively.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Basic properties of synthesized polyimides].

‡ Equal contribution to this work

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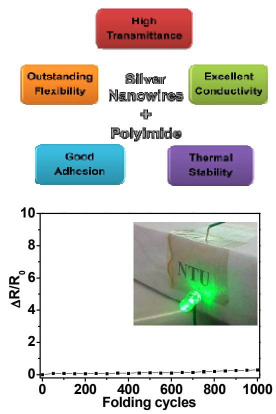
Highly Transparent and Flexible Polyimide/AgNWs Hybrid Electrodes with Excellent Thermal Stability for the Applications of Electrochromic and Defogging Devices

Heng-Yi Lu,‡ Chin-Yen Chou,‡ Jia-Hao Wu, Jiang-Jen Lin, and Guey-Sheng Liou*

By introducing colorless polyimide as binder, AgNWs transparent electrode exhibited excellent thermal stability, bendability, and adhesion property.



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