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Bio-Based Transparent Conductive Film Consisting of Polyethylene Furanoate and Silver Nanowires for Flexible Optoelectronic Devices

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Exploiting biomass has raised great interest as an alternative to the fossil resources for environmental protection. In this respect, polyethylene furanoate (PEF), one of the bio-based polyesters, thus reveals a great potential to replace the commonly used polyethylene terephthalate (PET) on account of its better mechanical, gas barrier, and thermal properties. Herein, a bio-based, flexible, conductive film is successfully developed by coupling a PEF plastic substrate with silver nanowires (Ag NWs). Besides the appealing advantage of renewable biomass, PEF also exhibits a good transparency around 90% in the visible wavelength range, and its constituent polar furan moiety is revealed to enable an intense interaction with Ag NWs to largely enhance the adhesion of Ag NWs grown above, as exemplified by the superior bending and peeling durability than the currently prevailing PET substrate. Finally, the efficiency of conductive PEF/Ag NWs film in fabricating efficient flexible organic thin-film transistor and organic photovoltaic (OPV) is demonstrated. The OPV device achieves a power conversion efficiency of 6.7%, which is superior to the device based on ITO/PEN device, manifesting the promising merit of the bio-based PEF for flexible electronic applications.

1. Introduction

The recent development of consumer electronics has been focused on the exploitation of flexible devices with transformative properties. At this transition from rigid devices to flexible apparatus, the exploration of flexible materials for using as semiconducting components and substrates is highly demanded. To this end, functional polymers with well flexibility have attracted wide research interests. Taking the development of flexible substrate as an example, versatile polymers, such as polyimide, polycarbonate, polyethylene naphthalate (PEN), and polyethylene terephthalate (PET), have been utilized to fabricate plastic substrates for manufacturing flexible optoelectronic devices.[1] Among which, PET, as the most commonly used plastic substrate thus far, has been proven to offer decent mechanical/chemical robustness, optical clarity and, moreover, low-cost production, which have been successfully used to realize high-performance flexible optoelectronic devices.[2]

Recently, in order to meet the goal of the sustainable development of society, bio-based plastics have raised extensive interest in replacing the conventional petrochemical-derived products since large demand of fossil-based products might beget several concerns, such as the depletion of fossil resources and the environmental impact caused by immense volumes of anthropogenic greenhouse gas emissions. In this regard, using renewable and abundance bio-based feedstocks as the raw material for the plastic substrates is certainly beneficial for reducing fossil-derived CO_2 emissions and security of raw material supply. Therefore, it is of great interest to develop efficient bio-based plastic materials to substitute the petroleum-sourced PET for device applications.

Besides using 100% bio-based feedstocks to synthesize PET,[3] an alternative approach is to change the petrochemical building blocks of PET to produce novel 100% bio-based polyester. For instance, a bio-based polymer, polyethylene furandicarboxylate (PEF, the chemical structure is shown in **Figure 1**), can be synthesized using monoethylene glycol (MEG) and 2,5-furandicarboxylic acid (2,5-FDCA) that serves

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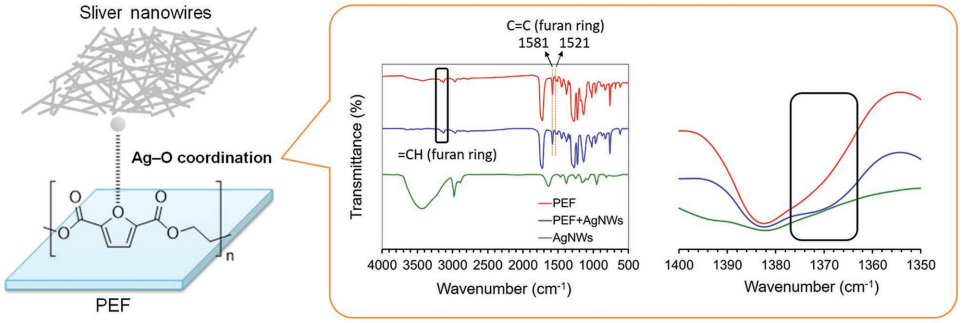

Figure 1. Schematic illustration and FT-IR spectra of the PEF substrate, PEF/Ag NWs conductive film, and Ag NWs.

as a green replacement for terephthalic acid.[4] Moreover, both MEG and FDCA moieties can be produced by the most abundantly available biomass components.[5] Utilizing such biomass components, which can be transformed from the renewable bio-based feedstocks such as lignocellulosic and agricultural biomass, are of notable significance for alleviating the dependence on fossil energy resources. It is worthwhile to note that PEF has been shown to possess 11- and 2-fold permeability reduction of oxygen and moisture, respectively, as compared to PET.[6] Also, it possesses improved mechanical properties and a higher glass transition temperature along with a lower melting point compared to PET. Provided these advantages, PEF reveals competent potential for the applications in flexible electronics since it can enhance the durability of the derived device against thermal annealing, oxygen, and moisture.

Another important aspect that needs to be considered for the development of flexible electronics is the exploitation of flexible conductive electrodes. It has been well documented that the transparent indium tin oxide (ITO) electrode, which is widely use in the rigid devices, can no longer be competent on the flexible substrates due to its fragility under mechanical stress.[2] Its brittle and unsatisfactory bendable nature necessitates the exploration of alternative conductive materials for electrodes.[7] Hence, various kinds of materials, such as conducting polymers,[8] graphene,[9] carbon nanotubes,[10] and metal nanowires,[1c,11] have been exploited as the flexible, transparent electrodes for fabricating low-cost and high-performance flexible devices. As considering the production cost, transparency, conductivity, and capability for mass production, Ag NWs have attracted the most attention for fabricating flexible optoelectronic devices nowadays.

In this Communication, we first describe a bio-based transparent, conductive film by coupling a renewable PEF plastic substrate and Ag NWs. Besides the advantage of renewable biomass, we also manifest the polar furan moiety of PEF enables a more intense interaction with Ag NWs than the benzene moiety of PET, which implants better adhesion of Ag NWs on a plastic substrate. Finally, we demonstrate the efficacy of PEF/Ag NWs conductive films in fabricating flexible thin-film transistor (OTFT) and organic photovoltaic (OPV). This is the first report of using renewable PEF as the substrate for efficient organic electronic devices, to the best of our knowledge.

2. Experimental Section

2.1. Fabrication and Characterization of PEF/Ag NW Film

All materials and chemicals were used as received unless stated otherwise. Silicon wafers treated with a self-assembled layer of *n*-octadecyltrichlorosilane (ODTS) were prepared by spin-coating a solution of ODTS in trichloroethylene, followed by a vapor treatment in ammonium hydroxide.[12] The PEF powders were prepared by Industrial Technology Research Institute, Taiwan, using the literature-reported methods.[4] The PEF-based substrate/film was prepared by casting the hexafluoroisopropanol solutions (10 mg mL^{-1} of PEF) onto the ODTS-treated silicon wafer, followed by annealing at 45 °C for 1 h.

Ag NWs as suspensions in isopropyl alcohol were purchased from Zhejiang Kechuang Advanced Materials Co., LTD (Zhejiang, P. R. China). The dispersion was further diluted down to various concentrations (2–4 mg mL^{-1}). The Ag NWs were spin-coated onto the PEF film, followed by proper thermal treatment to complete the fabrication of PEF/Ag NW conductive films. The UV–vis transmission spectrum was recorded using a Hitachi U-4100 UV–vis–NIR spectrophotometer in the wavelength range of 300–800 nm. Optical images were taken using an Olympus BX51 optical microscope system. The resistance of the films was measured by the two-point probe method using a digital sourcemeter (Keithley 2400). The IR spectra were performed using Perkin-Elmer Spectrum Two Fourier transform infrared (FT-IR) spectrometer.

2.2. Fabrication and Characterization of Flexible Organic Field-Effect Transistors

Poly(selenophene-alt-3,6-dithophene-2-yl-2,5-bis-(2-octyldodecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione) (PSe-DPP) was synthesized according to the methods reported in the literature.[13] The poly(methyl methacrylate) (PMMA) solution was spin-coated onto the prepared PEF/Ag NWs film to serve as the dielectric layer, followed by proper thermal annealing at 120 °C for 1 h. Afterward, the PSe-DPP active layer was deposited onto the PMMA layer via spin-coating, followed by thermal annealing at 120 °C for 1 h. Finally, the source and the drain electrodes were thermally deposited with Au to complete the FET fabrication, for which the

channel length (L) and width (W) were 1000 and 50 µm, respectively. The electrical performance of the device was recorded using a Keithley 2634B semiconductor parameter analyzer.

2.3. Fabrication and Characterization of Flexible Organic Solar Cells

For solar cells, we employed a polymer semiconductor, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b; 4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th), as an active layer mixed with [6,6]-Phenyl-C71-butyric acid methyl ester ($P_{71}BM$) and modified an interlayer, poly [(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) to improve the performance. The photovoltaic devices were fabricated with the structure of PEF/Ag NWs/ZnO/PFN/PTB7-Th:$PC_{71}BM$/MoO_3/Ag. Zinc acetylacetonate hydrate precursor solution (20 mg mL^{-1} in ethanol) was spin-coated onto the PEF/Ag NWs substrate and followed by thermal annealing at 130 °C for 5 min to form a dense ZnO layer. Subsequently, a solution of 0.125 mg mL^{-1} PFN (consisting of 0.125 mg PFN and 0.125 µL acetic acid in 1 mL methanol) was deposited onto the prepared ZnO film. The active PTB7-Th:$PC_{71}BM$ bulk-heterojunction layer was spin-coated onto the PFN layer at the optimized rotation rate to get desired thickness. Finally, MoO_3 and Ag electrodes were thermally evaporated through shadow mask to complete the device fabrication.

For the current density–voltage (J–V) measurement, the devices were characterized under illumination of a Newport LCS-100 solar simulator with 1000 W m^{-2} intensity calibrated with a silicon reference diode. The J–V characteristics were recorded using a Keithley 2400 source meter. All devices were measure under ambient atmosphere without encapsulation. Reference ITO-based device was fabricated and characterized using the similar procedures and conditions.

3. Results and Discussion

As mentioned, PEF can be synthesized from biomass components and has shown an appealing feature as a promising green replacement for PET. We herein explored its effectiveness as a plastic substrate coupling with Ag NWs, the most prevailing transparent, conductive materials used for devices to date. Different to PET, the PEF comprises a polar furan moiety and it thus can be inferred that a more intense interaction exist at the PEF/Ag NWs interface than the PET/Ag NWs interface.

To scrutinize this plausible interaction, FT-IR spectra of pristine PET, PEF, and Ag NWs and the bilayered samples (PEF/Ag NWs and PET/Ag NWs) are shown in Figure 1 and S1 (Supporting Information), respectively. The characteristics of both PET and PEF compounds are in a good agreement with the results reported in the literature.[14] Noteworthily, a broad band located at ≈1382 cm^{-1} (Figure 1) referred to the furan ring of PEF[15] was divide into two peaks in the PEF/Ag NWs sample. While the new peak appeared at ≈1371 cm^{-1} is not contributed from the characteristics of pristine Ag NWs, it indicates certain interactions existed between PEF and Ag NWs owing to the constituent polar furan ring. Such plausible interaction could be attributed to the heteroatom-metal coordination-type bonding between the lone pair electrons of the furan moiety and Ag NWs.[16]

As validating the enhanced interaction of Ag NWs on the PEF plastic substrate, we next prepared flexible, conductive electrode using different precursor concentration of Ag NWs (2–4 mg mL^{-1}), and the authentic picture and corresponding photomicrographs were shown in Figure S2, Supporting Information. As expected, the resistance (140, 90, and 45 Ω for the 2, 3, and 4 mg mL^{-1} Ag NWs-based film, respectively) of the prepared samples was decreased as increasing the precursor concentration of Ag NWs (under same spin-coating rate).

Figure 2a compared the transmittance spectra of the PEF substrate and its derived Ag NWs films. As shown, the bare PEF film possessed high transmittance over 90 % across the wavelengths of 390–750 nm, comparable to the property of the PET film. Notably, the transmittance can still be maintained over 75 % in the wavelength above 450 nm for the 4 mg mL^{-1} Ag NWs-based film (with a low resistance of 45 Ω), revealing the potential to serve as a flexible, transparent electrode.

To understand the mechanical property of the PEF/Ag NWs film, the bending test was first carried out with a bending radius of ≈5 mm and compared with the reference PET/Ag NWs film. No significant resistance change is observed during the bending process (Figure S3, Supporting Information). The variation of resistance as a function of bending cycles was depicted in Figure 2b, where the resistance of the PEF/Ag NW film was only slightly increased (<4%) after bending 500 cycles, in a striking contrast to the case of PET/Ag NWs film. This result clearly manifests the well flexibility of the PEF/Ag NWs film. Tape-peeling test was next performed by a 3 M scotch tape with finger pressure to assess the improved adhesion at the PEF/Ag NWs interface. As shown in Figure 2c, the resistance of the PET/Ag NWs film was significantly increased after a few peeling cycle, revealing the poor adhesion of Ag NWs to the PET plastic substrate as is evident from the apparent boundary shown in Figure S4a, Supporting Information.[17] By contrast, the PEF/Ag NWs sample only showed slightly increase in average resistance up to 10 peeling cycles. The similar optical images of the PEF/Ag NWs film before (Figure S2e, Supporting Information) and after (Figure S4b, Supporting Information) 10 peeling cycles confirm the enhanced adhesion of Ag NWs grown on PEF plastic substrate.

We next evaluate the practicability of the PEF/Ag NWs film by fabricating flexible OTFT and OPV. Illustrated in **Figure 3**a,b were the transfer and the output characteristics of a top-contact bottom-gate OTFT using the PEF/Ag NWs film as the gate electrode. In principle, in saturation region ($V_{DS} \geq V_G$), the drain current is linearly proportional to the square of the gate voltage. Charge mobility (μ_{sat}) thus can be obtained by using the following equation[18]

$$I_{DS} = \frac{W}{2L} \mu_{sat} C_i (V_G - V_T)^2 \quad (1)$$

where I_{DS} is the drain current, W/L is the ration of channel width to channel length, C_i is the capacitance per unit area of the dielectric layer (PMMA herein), V_G is the gate voltage, and V_T is the threshold voltage. As shown, the fabricated OTFT showed a stable characteristic and delivered a decent hole μ_{sat} of ≈0.04 cm^2 V^{-1} s^{-1} with a high on/off ratio of 3.2×10^4 and a low V_T of ≈–4 V. Such result is comparable to the performance

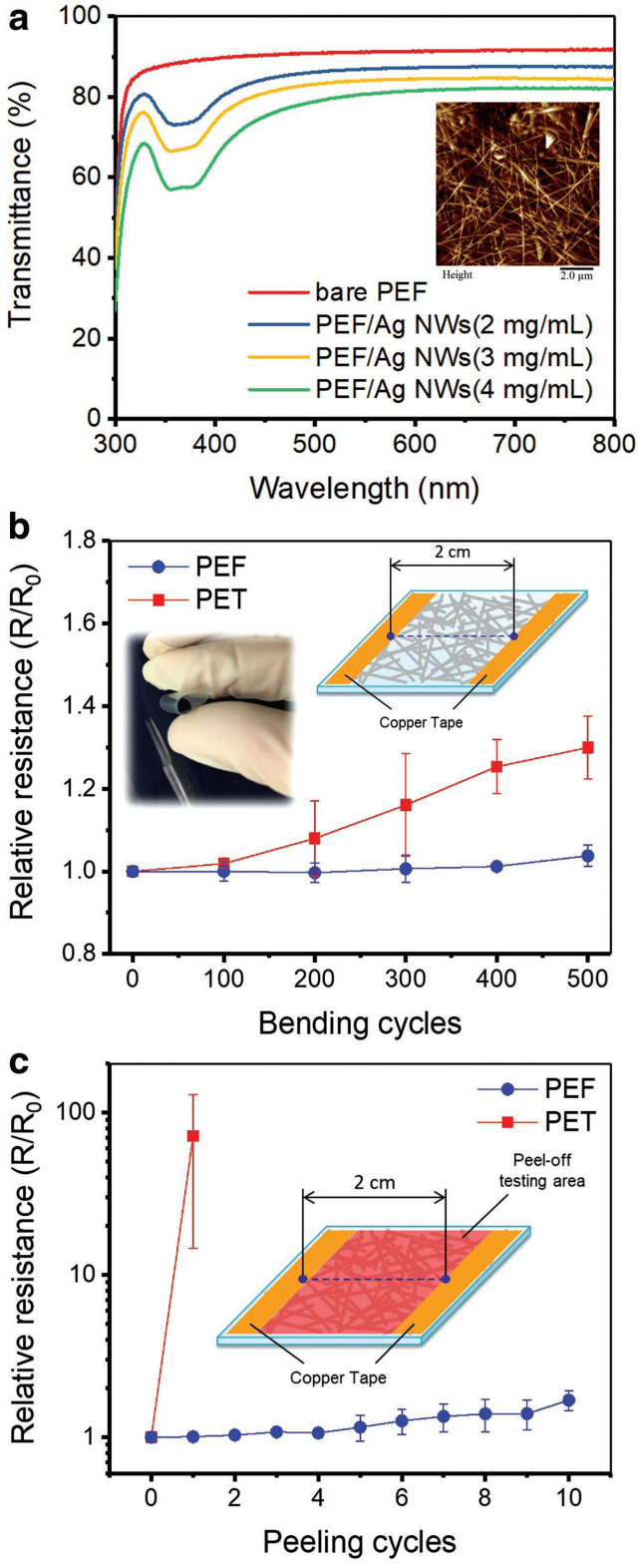

Figure 2. a) The transmittance spectra of the PEF substrate and the studied Ag NW s/PEF conductive films with different thickness of Ag NWs. Comparison of the electrical resistance of both PET/Ag NWs and PEF/Ag NWs conductive films as a function of b) bending cycles and c) tape-peeling cycles.

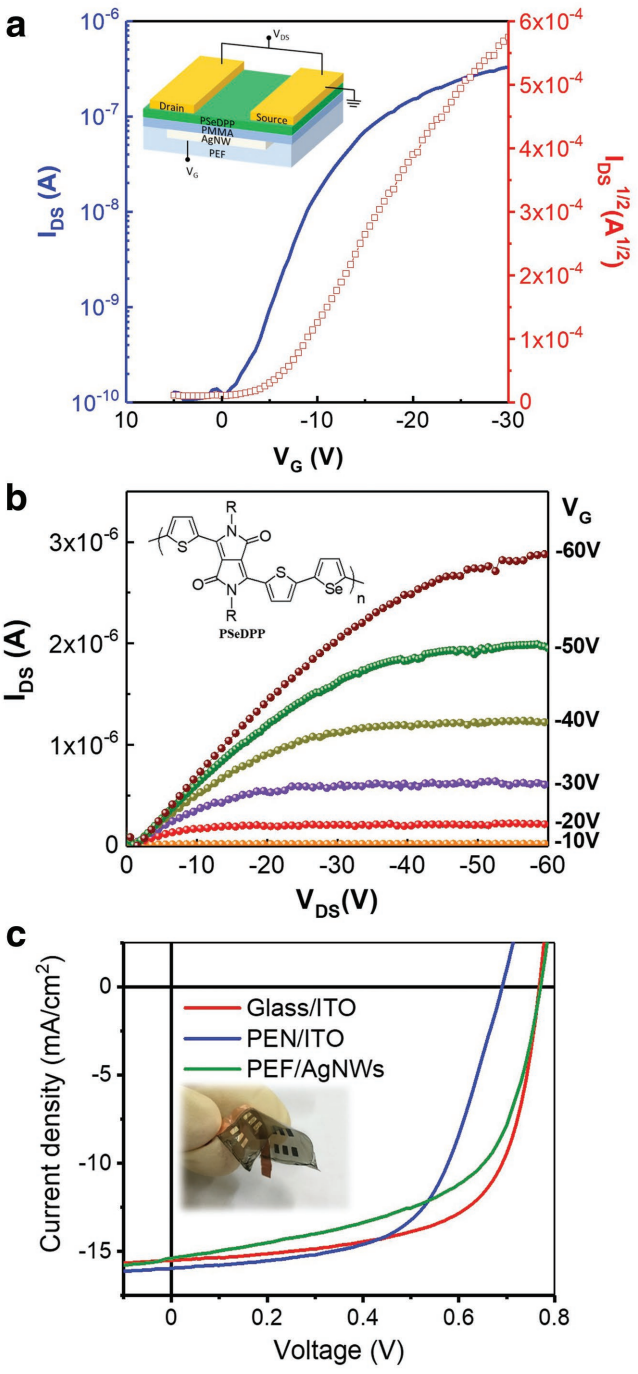

Figure 3. a) The transfer and b) output characteristics of a polymer FET using the PEF/Ag NWs conductive film as the bottom gate electrode and substrate (see insert). In (a), a constant V_d of –60 V is applied. c) The *J*–*V* curves of the inverted organic solar cells using different bottom electrodes, including glass/ITO, PEN/ITO, and PEF/Ag NWs substrates.

of OTFTs using same active material.[13a,19] This clearly demonstrated that the efficacy of PEF/Ag NWs to serve as an efficient gate electrode to fabricate flexible OTFTs.

Shown in Figure 3c were the *J*–*V* characteristics of the studied OPVs using different bottom electrodes, including

typical ITO (glass or PEN/ITO/ ZnO/PFN/PTB7-Th:$PC_{71}BM$/MoO_3/Ag) and flexible Ag NWs (PEF/Ag NWs/ZnO/PFN/PTB7-Th:$PC_{71}BM$/MoO_3/Ag). As shown, the device using PEF/Ag NWs film as the bottom electrode can show a best power conversion efficiency (PCE) of up to 6.7% with an open-circuit voltage (V_{oc}) of 0.77 V, a short-circuit current (J_{sc}) of 15.40 mA cm^{-2}, and a fill factor (FF) of 0.57, largely surpassing the performance (PCE: 6.62%; V_{oc}: 0.69 V; J_{sc}: 15.95 mA cm^{-2}; FF: 0.60) of the comment flexible OPV fabricated on a PEN/ITO substrate. This enhanced PCE of the flexible OPV validated the efficacy of PEF/Ag NWs to serve as an efficient transparent electrode to fabricate flexible OPVs. More detailed characterizations on device's durability and stability are under investigation. Notably, the shunt resistance (R_{sh}) of the PEF/Ag NW-based flexible device is still slightly lower than the value of the control rigid ITO device (PCE: 7.73%; V_{oc}: 0.77 V; J_{sc}: 15.40 mA cm^{-2}; FF: 0.65), which might be resulted from the high porosity existed in the Ag NWs.

4. Conclusions

In this work, we successfully developed a bio-based flexible, conductive film using a renewable PEF plastic substrate and Ag NWs. Besides the appealing advantage of renewable biomass, PEF also exhibited a high transparency around 90% in the visible wavelength range (390–750 nm) and its constituent polar furan moiety had an intense interaction with Ag NWs to largely enhance the adhesion of Ag NWs. Thus, the resistance of the PEF/Ag NW film was only slightly increased (<4%) after bending 500 cycles, in a striking contrast to the case of PET/Ag NWs film. The fabricated PEF/Ag NWs conductive film was employed to fabricate efficient flexible OTFT and OPV. The OPV device of PEF/Ag NWs/ZnO/PFN/PTB7-Th:$PC_{71}BM$/MoO_3/Ag achieved the power conversion efficiency of 6.7%, which was superior to the device based on ITO/PEN device, the promising merit of the bio-based PEF for flexible electronic applications. These results manifest the promising merit of the bio-based PEF to replace the petrochemical-derived PET for flexible electronic applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bio-based materials, conductive films, flexible electronic devices, polyethylene furanoate (PEF), silver nanowires (AgNWs)

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