Han, Jiye; Nam, Jeong Seok; Seo, Seungju; Lee, Aram; Lee, Changhyun; Park, Sangeun; Kang, Yoonmook; Lee, Hae Seok; Kim, Donghwan; Zhang, Qiang; Sung, Hyokyung; Kauppinen, Esko; Jeong, Hyuck; Oh, Jin Woo; Maruyama, Shigeo; Jung, Im Doo; Jeon, Il

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Published in:
Advanced Energy and Sustainability Research

DOI:
10.1002/aesr.202100155

Published: 01/05/2022

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Utilization of Multifunctional Environment-Friendly Organic Dopants Inspired from Nature for Carbon Nanotube-Based Planar Heterojunction Silicon Solar Cells

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1. Introduction

Issues, such as environmental pollution, microplastics, and raw material shortage, have become the direst problem of modern society. Researchers around the world are making efforts to solve these complications by substituting conventional materials using natural or nature-inspired alternatives.[1–3] These materials are biodegradable, biocompatible, and most importantly, lower cost than synthetic materials.[4–7] Organic acids, which consist of hydrocarbons with carboxyl, sulfonic, or phosphoric groups, are biodegradable, easy to synthesize, and easily obtained from nature. Examples include acetic acid from vinegar, formic acid from ants, lactic acid from milk, and citric acid from fruits. Although such organic acids are known to be weak acids, their acidity is strong enough to dissolve tissues, corrode metals, and electronically dope electronic materials. Therefore, organic acids quality for replacing inorganic acids, many of which are toxic, environmentally...
harmful, or explosive.[8–10] However, there has not been a report on natural acids replacing inorganic dopants in electronic devices to the best of our knowledge. Despite many attempts, most of the demonstrations have been either ineffective or inadequate.[9,10]

The carbon electrodes, such as graphene and carbon nanotubes (CNTs), are environment-friendly materials in the perspective of raw material shortage and pollution-free synthesis. Therefore, technologies involving carbon electrodes are emerging as next-generation materials.[11,12] In particular, CNT transparent electrodes among the nanocarbon material have drawn great attention for their high conductivity, transparency, and especially excellent mechanical properties leading to high reproducibility.[13] Similar to the other carbon electrodes, CNTs have to be chemically doped for their conductivity to match up with the conventional transparent conductors. Conventionally, acids have been used to p-doped CNTs. Nicric acid and trifluoromethanesulfonic acid (TFMS) have been the common choice of p-dopant.[14–16] However, nicric acid produces toxic NOx and explodes when mixed with organic compounds. In addition, TFMS is a superacid with a pKₐ value of −14.7 and therefore extremely corrosive beyond measure.[17,18] Relatively safer polymer-based acid dopants, namely, Nafto,[19–21] poly(acrylic acid) (PAA),[22] and poly(styrene sulfonate) (PSS),[23] have been reported. However, the synthesis of these polymeric acids is a costly process and causes environmental pollution because the synthesis involves the use of toxic organic solvents.

In this work, we tested naturally available acids, specifically, acetic acid, formic acid, lactic acid, and citric acid as the p-dopant for the CNT transparent electrode. From the van der Pauw four-probe measurement, the Raman, photoelectron yield, and absorption spectroscopy, we revealed that acetic acid does not induce a sufficient p-doping effect due to relatively low acidity (pKₐ of acetic acid is 4.76). Furthermore, formic acid and citric acid do not have enough doping durability due to the volatility and solidification, respectively. Therefore, lactic acid was the best choice as it possessed an adequately strong p-doping effect of 22.1% in the sheet resistance drop and stable doping durability of more than 20 days. Incidentally, lactic acid induced an antireflection effect thanks to its tendency to densify CNT and form a thin and uniform coating via a large network of hydrogen bonding.[20,24] This was evidenced by atomic force microscopy (AFM), ellipsometry, finite-difference time-domain method (FDTD), and reflectance measurement. When CNT-based planar heterojunction silicon solar cells (SiSCs) were fabricated, the power conversion efficiency (PCE) improved from 8.2% to 10.3% upon doping the CNT electrode by lactic acid. The improvement of each photovoltaic parameter was assessed by using various techniques. In addition to the p-doping effect and the antireflection coating of lactic acid, the carboxylic and hydroxyl groups in lactic acid could passivate the Si surface defect, which was confirmed by the Fourier-transform infrared (FTIR) and quasi-steady-state photoconductance (QSSPC) lifetime measurement. Developing acidic dopants that are safer, low cost, and environmentally compatible has ever been necessary and the nature-inspired lactic acid, which is toxin-free, nonexplosive, and freely available in nature, is the solution we provide. The environment-friendly doping agents introduced in this work will contribute greatly to a renewable energy-based sustainable society.

2. Results and Discussion

We selected four naturally occurring acids that are transparent and low cost; they were acetic acid from vinegar, formic acid from ants, lactic acid from milk, and citric acid from fruits. These acids were tested in terms of p-doping strength, doping stability, and antireflection effect upon application to CNT electrodes. Subsequently, this extended to the device applicability of the natural acid-doped CNT electrodes. CNT electrode has been reported to replace electrode and p-type silicon wafer in heterojunction SiSCs, realizing low cost, facile, and eco-friendly solar energy harvester. Therefore, the best performing natural acid was applied and examined using CNT-laminated heterojunction SiSCs (Figure 1a).

Regarding the choice of CNTs, aerosol-synthesized single-walled CNT films were used as the electrode.[25,26] The CNTs possessed uniform diameters of 1.3–2.0 nm and the tube length of 1–5 μm.[27] The film thickness was estimated to be approximately 40 nm according to Qian et al.[20] The degrees of the p-doping capability of the four natural acids were measured by the four-probe van der Pauw method, Raman and visible to near-infrared (vis–NIR) spectroscopy, photoelectron yield spectroscopy (PYS), and X-ray photoelectron spectroscopy (XPS). First, sheet resistance changes of the CNT films upon acid treatment were probed by the four-probe measurement. In the case of citric acid, it initially exhibited a significant drop in sheet resistance thanks to the lowest pKₐ value of 3.13 among the proposed four acids. However, the effect was only instant and it quickly disappeared as the solvent evaporated from the CNT electrode (Figure S1, Supporting Information). This is because citric acid is solid at room temperature and it crystalized as the evaporation took place. When citric acid was dissolved in water instead of ethanol, the solution jellified. It is important that the acidic dopants are in the liquid state or viscous enough to interact with CNTs at a molecular level. For the other natural acid dopants, they were tested in different concentrations using water as the solvent. It was interesting that the acids showed strong doping effects when they were either highly concentrated or lowly concentrated, but the doping effect was mediocre when the concentration was in between (Figure S2, Supporting

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Information). Acetic acid showed the weakest doping effect in both high and low concentrations attributed to the relatively low acidity ($pK_a = 4.76$) (Figure 1b). This left us with lactic acid and formic acid as the $p$-dopant candidates. Lactic acid and formic acid manifested sufficiently strong doping effects in both high and low concentrations. Lactic acid induced a sheet resistance change of 22.1% and 15.4% in high and low concentrations, respectively. Formic acid induced a similar but slightly stronger doping effect of 24.6% and 15.7% in high and low concentrations, respectively. The lactic acid showed a marginally weaker doping effect. According to FTIR, the $C=O$ stretch peak shifts to a higher frequency when electron density on $C=O$ of COOH group is lowered.$^{[28]}$ Therefore, the doping strength difference is reflected by the peak shift and it can be inferred that lactic acid showed a marginally weaker doping effect owing to the attached hydroxyl group withdrawing electrons from the carboxylate group, destabilizing the conjugate base (Figure S3, Supporting Information). Nevertheless, from the doping durability point of view, the lactic acid-doped CNT films showed much greater stability than the formic acid-doped CNT films (Figure 1c). The $p$-doping of lactic acid on CNTs was stable for more than 20 days. We ascribe this to the heavier molecular weight of the lactic acid than formic acid as well as the two hydroxyl groups on lactic acid increasing the boiling point.

To confirm the difference in the doping strength between lactic acid and formic acid, we carried out Raman spectroscopy, vis–NIR absorption spectroscopy, XPS, and PYS. The Raman G-bands of the lactic acid-doped CNT films and formic acid-doped CNT films shifted to a higher Raman shift at a similar degree.$^{[29,30]}$ While it was clear that stronger shifts were observed of highly concentrated acids in both lactic acid and formic acid, the difference in the doping strength between the two acids was not clear (Figure 2a,b). In the case of the 2D bands, the shift and the peak suppression indicate the degree of the $p$-doping effect.$^{[22,31]}$ Based on this, both the lactic and formic acids showed a similar degree of doping effect when low concentrations (40 wt%) were used, but formic acid induced a stronger $p$-doping effect than lactic acid when high concentrations (90 wt%) was used (Figure 2c,d). This means that unless we use extremely high concentrations, the strength of the doping effect is expected to be similar for lactic acid and formic acid. PYS was conducted to probe the changes in the Fermi level of the CNT films upon doping (Figure S4, Supporting Information). The acetic acid (5.06 eV) and citric acid (5.05 eV) showed similar energy to the pristine CNT (5.04 eV). The unchanged Fermi level of the citric acid-doped CNT film is due to the rapid evaporation of citric acid as the sample had to be loaded into a vacuum before the PYS measurement. The other two natural acids, formic acid
and lactic acid, significantly lowered the Fermi level of CNTs to 5.10 and 5.15 eV, respectively. The degree of the Fermi level drop upon doping by the natural acids follows the strength order of their $pK_a$. vis–NIR absorption measurement was carried out to confirm the difference in the doping strength between formic acid and lactic acid (Figure S5, Supporting Information). Pristine CNT films show obvious van Hove transition peaks ($S_{11}$, $S_{22}$, and $M_{11}$) coming from both semiconducting and metallic single-walled CNTs. It has been reported that successful p-doping of CNTs suppresses the van Hove transitions due to the Fermi level decreasing below the valence bands of the CNTs.[17,32–34] Figure S5, Supporting Information, shows that the peaks intensity of the semiconducting $S_{22}$ and $S_{11}$ decreased conspicuously in both acids’ cases. The suppression in the van Hove transitions of the lactic acid-doped CNTs was slightly greater than that of the formic acid-doped CNTs. Overall, despite the four-probe measurement data showing that the formic acid is a stronger dopant, all three of Raman spectroscopy, PYS, and vis–NIR pointed toward lactic acid being a stronger dopant than formic acid. This was finally confirmed by XPS measurement. The carbon peak and oxygen of XPS shifting to a lower binding energy indicate the Fermi level is getting closer to the valence band (Figure S6a, Supporting Information).[35,36] In addition, we can also deduce that the doping effect of lactic acid is slightly weaker than that of nitric acid from the intensity difference of the $C=O$ convolution peak.

Antireflection is an equally important factor for the performance of CNT-based SiSCs. Many SiSCs harness the optical advantage from the antireflection coating.[37–39] In this regard, the morphology of the CNT electrodes after application of acidic p-dopants is important because the roughness data provide hints on the uniformity of the antireflection effect.[40] We used AFM to probe the surface roughness of the natural acid-applied CNT films (Figure 3). The AFM images in Figure 3a,b show that the CNT films become more densified and smoother when lactic acid is applied. This phenomenon gets stronger with the higher concentration of lactic acid. However, the same effect is not observable for the formic acid-applied CNT films (Figure 3c,d). We hypothesize that the additional hydroxyl group on lactic acid forms hydrogen bonding, which leads to crystallization and a gluey layer. To verify this, citric acid, which also has many hydroxyl groups, was applied to the CNT films and the AFM measurement was conducted. The citric acid-applied CNT films showed similar crystallization leading to CNT densification. This indicated that the lactic acid-applied CNT films can induce an antireflection effect. To maximize this effect, the thickness (or concentration) of lactic acid had to be optimized. We used an ellipsometer to find the accurate refractive index of the lactic acid-applied CNT film (Figure S7, Supporting Information). Based on this, a computational calculation was run by modeling lactic acid coating on a Si wafer to find the optimal thickness of lactic acid. The FDTD simulation results show that the thickness between $\approx$50 and $\approx$100 nm is optimal for the best antireflection effect (Figure S8, Supporting Information). The antireflection effect of the natural acid-doped CNT-laminated SiSCs was confirmed empirically by the reflectance measurement (Figure S9, Supporting Information). The lactic acid-doped CNT films showed a decrease in reflectance while the formic acid-applied CNT films rather increased the reflectance. It is worth noting that highly concentrated lactic acid-doped CNT films showed a

![Figure 2. Raman G band spectra of CNT films doped with a) lactic acid, b) formic acid, and c) citric acid in high and low concentrations. Raman 2D band spectra of CNT films doped with d) lactic acid, e) formic acid, and f) citric acid in high and low concentrations.](image-url)
greater antireflection effect than the lowly concentrated lactic acid-doped CNT films (Figure S9a, Supporting Information). Using the same concentration, lactic acid was spin-coated and the cross-sectional SEM image confirmed that ≈57 nm-thick lactic acid was coated (Figure S10, Supporting Information).

Having demonstrated that lactic acid is the best nature-inspired dopant, we fabricated SiSCs using the lactic acid-doped CNT electrodes in two different concentrations (Figure 4a and Table 1). Table 1 shows that lactic acid doping improved the PCE of CNT-based SiSCs from 8.2% to 10.3%. All three major

![AFM images of a) pristine CNT and the CNT films doped by b) lactic acid in low and high concentrations (40 and 90 wt%, respectively), d.f) formic acid in low and high concentrations (40 and 90 wt%, respectively), and e.g) citric acid in low and high concentrations (40 and 90 wt%, respectively).](image)

**Figure 3.** AFM images of a) pristine CNT and the CNT films doped by b) lactic acid in low and high concentrations (40 and 90 wt%, respectively), d.f) formic acid in low and high concentrations (40 and 90 wt%, respectively), and e.g) citric acid in low and high concentrations (40 and 90 wt%, respectively).

![J–V curves of a SWNT-SiSC (black) and a lactic acid-doped SWNT-SiSC by low and high concentration (red and blue). b) Nyquist plots of SiSCs with pristine CNT (black) and lactic acid-doped CNT at a low concentration (red). c) FTIR spectra of lactic acid on two different substrates, a Si wafer (red) and a KBr pellet (blue), measured in ATR mode. d) QSSPC lifetime of bare Si wafer and four natural acid-passivated Si wafers.](image)

**Figure 4.** a) J–V curves of a SWNT-SiSC (black) and a lactic acid-doped SWNT-SiSC by low and high concentration (red and blue). b) Nyquist plots of SiSCs with pristine CNT (black) and lactic acid-doped CNT at a low concentration (red). c) FTIR spectra of lactic acid on two different substrates, a Si wafer (red) and a KBr pellet (blue), measured in ATR mode. d) QSSPC lifetime of bare Si wafer and four natural acid-passivated Si wafers.
parameters of short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), and fill factor (FF) increased. The increase in $J_{SC}$ is attributed to the antireflection effect. The FF increase came from the p-doping effect, which decreased the series resistance ($R_S$). Low charge transfer resistance of the lactic acid-doped CNT-based SiSC from the impedance measurement corroborates this (Figure 4b). The $V_{OC}$ increment can be explained by the low-lying Fermi level of the lactic acid-doped CNT electrode as verified by the technology computer-aided design (TCAD) simulation (Figure S11 and S12; Table S1, Supporting Information). Furthermore, lactic acid demonstrated a passivation effect on the n-type Si wafer surface. The lone electron pair on the carbonyl group of the carboxyl group in lactic acid formed a Lewis coordination to the Si defects. This contributed to the high $V_{OC}$, which is confirmed by the attenuated total reflection (ATR) mode of FTIR measurement (Figure 4c and S13, Supporting Information). The shift of the C=O peak from the carboxyl group to a lower wavelength when lactic acid is in contact with the Si wafer evidences the passivation. The C=O peak from the carboxyl group and the hydroxyl group also shifted yet the degree of the shift is not strong as that of the C=O peak. All of the other natural acids except acetic acid, which showed negligible doping effect, exhibited downshift for both the C=O peaks and the C=O peaks (Figure S13, Supporting Information). The QSSPC lifetime provided direct evidence for the passivation of Si wafers by the natural acids. Figure 4d shows that the lactic acid-applied Si wafer has the longest minority carrier lifetime compared with other natural acids as well as the bare Si wafer (Figure S14, Supporting Information). This is because of not only the passivation effect of lactic acid on the Si surface but also its viscous nature compared to other acids coming from its tendency to form a large network of hydrogen bonding. From the device stability test, it was found that while the doping effect is stable up to 35 days, the passivation effect is not. The decrease in $V_{OC}$ and increase in shunt resistance prove the point and it is important to find ways to improve the passivation durability in follow-up research (Figure S15 and Table S2, Supporting Information).

### 3. Conclusion

We fabricated silicon-based light-harvesting devices using eco-friendly CNT film as the top electrode and the p-type hole-collector. While the CNT-laminated planar heterojunction SiSCs typically require p-dopants to enhance the conductivity and energy alignment of CNT as well as an antireflection coating, such conventional materials are toxic, corrosive, and inevitably produce pollutants during the synthesis. We tested nature-inspired organic dopants and demonstrated that lactic acid not only induces a strong and stable p-doping effect but also an anti-reflection effect originating from the large network of hydrogen bonding. By applying lactic acid, the PCE of 8.2% improved to 10.3% proving the multifunctional effectiveness of lactic acid. This work contributes greatly to the path toward the renewable energy-based sustainable society.

### 4. Experimental Section

**Synthesis of SWNT Film:** The SWNT films were synthesized by an aerosol (floating catalyst) CVD method based on ferrocene vapor decomposition in a CO atmosphere. The catalyst precursor was vaporized by passing room temperature CO through a cartridge filled with ferrocene powder. The flow containing ferrocene vapor was then introduced into the high-temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with additional CO. To obtain the stable growth of SWNTs, a controlled amount of CO$_2$ was mixed with the CO carbon source. SWNTs were directly collected downstream of the reactor by filtering the flow through a nitrocellulose or silver membrane filter (Millipore Corp., USA; HAWP, 0.45 µm pore diameter).

**Fabrication of SWNT-Si Solar Cells:** The SWNT-Si solar cell was fabricated by dry-transferring the SWNT film onto a 3 mm × 3 mm n-type Si contact window and surrounding electrodes. The n-type Si (Kojundo Chemical Laboratory) has the resistivity of 1–100 Ω cm and the thickness of ~321 µm. The n-type Si substrate was treated by RCA1 (H$_2$O: NH$_4$OH: H$_2$O$_2$ = 5:1:1) at 70 °C for 30 min to remove the dusts and organics on the surface. The SiO$_2$ layers on both sides of the n-type Si substrate were removed by 5 M NaOH at around 95 °C for 20 min. The etched substrate was then taken out from NaOH solution and quickly cleaned by RCA2 (H$_2$O:HCl:H$_2$O$_2$ = 5:1:1) for 3 s followed by distilled water rinsing. After blown dry by N$_2$ gas, the back electrode of Ti (10 nm)/Pt (55 nm) was sputtered onto the back side of the substrate. Dielectric layer of SiO$_2$ (100 nm) and front electrode of Ti (10 nm)/Pt (55 nm) were sputtered onto the front side of the substrate with 3 mm × 3 mm physical mask arrays. The SWNT film was transferred using the dry-transfer method onto the top surface of the as-prepared substrate after the removal of the physical masks. Ethanol was dropped onto the transferred film to improve the contact.

**Preparation of Dopant:** Four natural acids (Sigma-Aldrich) was diluted by water for different nominal concentrations. The obtained acid solution was then spin-coated on the SWNT-Si solar cells at 5000 rpm for 60 s. The samples were subsequently dried in the ambient.

**Characterization:** The optical reflectance and transmittance spectra were obtained by Shimadzu UV-3150. By using source meter (Keithley 2400), the sheet resistance of SWNT films (van der Pauw method) and J–V curves of the SWNT-Si solar cells were measured. The 100 mW cm$^{-2}$ AM1.5G light source was provided by the solar simulator PEC-L01 (Pecell Technologies). AFM was measured by SPI3800N, SII (Seiko Instruments Inc.). ATR–IR was measured using the Shimadzu IRAfinity-1S. The SEM analysis was conducted using Eli-SE (Eliips) Tech.). Lifetime and implied $V_{OC}$ were measured using QSSPC (WCT 120, Sinton Instrument, USA). TCAD simulation was done using software, Atlas, Silvaco. (version 4.5.2.R). Optical interference pattern of multiple reflection in lactic acid-coated Si wafer was simulated by 2D Maxwell’s Solver of Lumeral FDTD.

### Supporting Information

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

J.H. and J.-S.N. contributed equally to this work. This work was supported by the National Research Foundation of Korea and was funded by the Ministry of Science and ICT (MSIT), Korea (grant nos. NRF-2021R1C1C1009200 and NRF-2020R1A6A3A10375717). A part of this work was financially supported by the JSPS KAKENHI grant numbers JP18H05329, JP20H00220, and by JST CREST grant number JPMJCR2085, Japan. S.S. was financially supported by JSPS Fellowship 18J22263. This work was partially supported by the Academy of Finland (CNTstress, 316572). This work was supported by Kyungshin Holdings, SeGwang Resource Co. Ltd., and YUKNAMWITHYOU Co. Ltd.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

carbon nanotubes, eco-friendly doping, natural acids, organic acids, silicon solar cells

Received: September 19, 2021
Revised: December 5, 2021
Published online: January 5, 2022


