Origin of Hole-Trapping States in Solution-Processed Copper(I) Thiocyanate and Defect-Healing by I$_2$ Doping

Pimpisut Worakajit, Pinit Kidkhunthod, Thanasee Thanasamsurapong, Saran Waiprasoet, Hideki Nakajima, Taweesak Sudyoadsuk, Vinich Promarak, Adisak Boonchun, and Pichaya Pattanasattayavong

Solution-processed copper(I) thiocyanate (CuSCN) typically exhibits low crystallinity with short-range order; the defects result in a high density of trap states that limit the device’s performance. Despite the extensive electronic applications of CuSCN, its defect properties are not understood in detail. Through X-ray absorption spectroscopy, pristine CuSCN prepared from the standard diethyl sulfide-based recipe is found to contain under-coordinated Cu atoms, pointing to the presence of SCN$^-$ vacancies. A defect passivation strategy is introduced by adding solid I$_2$ to the processing solution. At small concentrations, the iodine is found to exist as I$^-$ which can substitute for the missing SCN$^-$ ligand, effectively healing the defective sites and restoring the coordination around Cu. Computational study results also verify this point. Applying I$_2$-doped CuSCN as a p-channel in thin-film transistors shows that the hole mobility increases by more than five times at the optimal doping concentration of 0.5 mol.%. Importantly, the on/off current ratio and the subthreshold characteristics also improve as the I$_2$ doping method leads to the defect-healing effect while avoiding the creation of detrimental impurity states. An analysis of the capacitance-voltage characteristics corroborates that the trap state density is reduced upon I$_2$ addition.

1. Introduction

Copper(I) thiocyanate (CuSCN) has arisen as a novel 3D coordination polymer (CP) with promising characteristics such as attractive hole transport properties, high optical transparency, and solution processibility.

As a result, a variety of CuSCN-based optoelectronic devices have been demonstrated, particularly organic solar cells (OSCs),

perovskite solar cells (PSCs),

organic light-emitting diodes (OLEDs),

and thin-film transistors (TFTs). The breadth and consistency of device demonstrations establish CuSCN as a unique CP-based semiconductor for practical applications, and improvements in the properties of CuSCN can have a wide-ranging impact for its use.

CuSCN is typically solution-processed at relatively low temperatures, resulting in low crystallinity which likely contains a high degree of structural disorder. Understanding the defect properties in order to engineer them proves a highly successful strategy in the development of semiconductors and electronic devices.

Indeed, a high density of tail states and hole-trapping states is known to exist in CuSCN, but their origin has not been clearly elucidated. It has been shown that the p-type conductivity of CuSCN increases under Cu-deficient conditions and decreases under Cu-rich conditions. Accordingly, theoretical studies show that the two basic native defects, Cu$^+$ vacancies ($V_{Cu}$) and SCN$^-$ vacancies ($V_{SCN}$), should result in acceptor and donor states, respectively. As the acceptor states receive electrons from the valence band of CuSCN, they increase the hole concentration. In contrast, the creation of donor states compensates for the acceptors, acting as hole killers, hole traps, or hole scattering centers. The presence of compensating donor states would present a serious problem to the hole transport in p-type CuSCN, and their passivation is therefore of high importance. Detailed studies into the defect engineering of CuSCN greatly lack behind other semiconductors. It is the aim of this work to advance the fundamental understanding of defect states in CuSCN as well as present a defect-healing strategy by I$_2$ doping.

The solution processability of CuSCN allows doping procedures to be carried out simply by mixing dopants into the CuSCN solution. For example, molecular dopants with low-lying lowest unoccupied molecular orbital (LUMO) energy levels have been investigated. A fluorinated fullerene derivative C$_{60}$F$_{48}$ was shown to be effective at p-doping CuSCN, employed
as a p-channel layer in TFTs (optimal doping level = 0.5 mol.%) and a hole-transport layer (HTL) in OSCs (optimal doping level = 0.005–0.01 mol.%), respectively. Improved device performance is evident from higher field-effect hole mobility, bias-stress stability, solar cell fill factor (FF), and power conversion efficiency (PCE) which could be attributed to increased hole concentration and better interfacial uniformity. Similarly, CuSCN-CuI composites were investigated as HTL for polymer-based OLEDs (optimal CuI concentration = 3.3 mol.%), and the enhancement in device performance is evident from higher field-effect hole mobility, i.e., increasing the hole concentration and better energy matching between the HTL and the emissive layer.

A closely related compound, copper(I) iodide (CuI), is also emerging as a promising solution-processable p-type inorganic semiconductor. CuI has been employed to dope CuSCN or form composites with CuSCN as well. CuI doping of electrolyte-gated CuSCN TFETs (doping level = 5 wt.%, equivalent to 3.3 mol.%) shows an increase in the field-effect hole mobility. The improvement is attributed to a p-doping effect that increases the hole concentration and the co-existence of the CuI phase which is reported to have higher mobility. CuSCN-CuI composites were investigated as HTL for polymer-based OLEDs (optimal CuI concentration = 25 wt.%, equivalent to 17.6 mol.%). The enhancement in device performance is ascribed to higher hole mobility due to the coincident CuI phase and better energy matching between the HTL and the emissive layer.

The abovementioned examples rely primarily on the p-doping effect, i.e., increasing the hole concentration and using the excess holes to overcome the trapping states (trap filling). While the current and hole mobility may apparently increase, other device characteristics could suffer in a trade-off. Particularly for the TFT application, the p-doping effect leads to adverse increases in the off-current and subthreshold swing due to higher hole concentration and higher tail state density from the dopants. Herein, we report a doping route based on solid I2 which is processable in the standard diethyl sulfide (DES)-based solution for CuSCN TFT device fabrication. Crucially, we show that an optimal amount of I2 leads to a defect-healing effect that remarkably improves the hole transport properties of CuSCN and device performance in all metrics. By conducting the synchrotron-based X-ray absorption spectroscopy, we reveal that the Cu centers in the pristine CuSCN sample are under-coordinated, suggesting the presence of VSCN. At low I2 doping amounts, the iodine is found to exist as I− that can fill in the voids of VSCN and complete the coordination around Cu. At the optimal doping concentration of 0.5 mol.%, the field-effect hole mobility increases by more than five times. Importantly, the on/off current ratio also increases to more than 104, which is distinct from previous doping attempts. The VSCN defect passivation by I− is also reflected in the decrease in the trap state density, evident from the reduction in the TFT subthreshold swing as well as from a detailed capacitance–voltage characterization. The optimally doped devices also exhibit a lower contact resistance and superior bias-stress stability. Additionally, a theoretical study based on density functional theory (DFT) confirms that the donor states generated by VSCN are reduced upon I− substitution. We note that the first version of this manuscript was posted to the arXiv preprint server.

2. Results and Discussion

2.1. Chemical and Microstructural Analyses of I2-doped CuSCN

I2 doping of CuSCN has been attempted previously; however, the reported method proceeded by treating CuSCN films with halogen gases, which carried risks and setup complications. The method reported herein is very simple; solutions of I2 beads and CuSCN powder, each dissolved separately using DES as a solvent at 10 mg mL−1, were mixed with different volume ratios to yield various concentrations of I2 doping (full experimental details and Table S1, Supporting Information). Hereafter, the samples are designated by their doping concentrations or as “pristine” for undoped CuSCN. The color of I2-doped CuSCN solutions changed from colorless to brown when I2 concentration was equal to or higher than 5 mol.% as shown in Figure S1. The color of drop-cast samples also changed from greyish-white to brown at the same concentration. However, spin-coated samples retained the fully transparent appearance of CuSCN thin films following the annealing step (data shown in Section 2.3).

Raman spectroscopy was used to investigate the influence of the I2 dopant on the chemical structure and bonding properties of CuSCN. Samples prepared by drop-casting were employed in this case (see Supporting Information). The Raman spectra of pristine and doped samples at 0.5, 5, and 40 mol.% recorded in the wavenumber range of 50 to 3500 cm−1 are shown in Figure S2 (Supporting Information). With the increasing I2 doping concentration, a significant change can be observed in the low wavenumber region. Specifically, Figure 1a shows a band at ≈170 cm−1 appearing for 5 and 40 mol.% doping conditions. For solid I2, a Raman signal is found at 180 cm−1, and the shift to lower wavenumbers is attributed to molecular I2 acting as an electron acceptor (partially reduced) in our case can be coupled with Cu+ as a possible electron donor. The X-ray absorption data, discussed in the next section, corroborates this analysis. We note that the molecular I2 character was not observed in the 0.5 mol.% doping conditions (optimal doping level for TFETs as shown later).

To investigate the crystalline phases, we carried out X-ray diffraction (XRD) of the drop-cast samples. First, the results of the pristine sample and reference CuSCN (powder, 99%, Sigma-Aldrich, also used for CuSCN solution preparation) were compared against data of the reported structures. As shown in Figure S3 (Supporting Information), the reference CuSCN powder was predominantly of the 3R β-CuSCN polytype (ICSD 24372) with a small presence of α-CuSCN (ICSD 124). The pristine drop-cast sample exhibited lower crystallinity, and only the 3R β-CuSCN phase can be identified with diffractions at 2θ = 16.2°, 27.3°, 32.7°, 34.7°, 47.2°, and 50.0° associated with (0 0 6), (1 0 2), (0 0 12), (1 0 8), (2 1 0), and (2 1 6) planes (Figure Ib, inset). The preferred orientation along the crystalline c-axis of the pristine CuSCN sample is noted from the highest intensity of the (0 0 6) diffraction. Upon the addition of I2, the XRD pattern changed as displayed in Figure 1b. The six peaks of 3R
β-CuSCN were still present, suggesting that the dominant crystalline phase remained the same. At 0.5 mol.% I$_2$ concentration, the c-axis orientation became even more pronounced, with very strong intensities from the (0 0 6) and (0 0 12) planes. With a further increase in I$_2$, the degree of the preferred orientation decreased but persisted. At 5 and 40 mol.% concentrations, new diffractions were observed to arise, evident from a small peak at $2\theta = 9.9^\circ$ and also two additional peaks at $2\theta = 8.1^\circ$ and $12.2^\circ$ for the latter (40 mol.%). The new diffractions are likely related to the inclusion of molecular I$_2$ in the CuSCN structure that appears at high doping concentrations as discussed in the next section. In addition, DFT results presented in Section 2.6 also further suggest that additional diffractions in the low $2\theta$ region are likely due to impurity defects.

### 2.2. Local Atomic Structures and Defect Healing by I$_2$ Doping

The effects of I$_2$ addition on the local atomic structures of CuSCN were investigated in detail by X-ray absorption spectroscopy (XAS). The samples were similar to those used for Raman and XRD experiments. The XAS measurements of the Cu K-edge and I L3-edge were conducted at the beamline BL5.2 SUT-NANOTEC-SLRI, Synchrotron Light Research Institute (SLRI), Thailand. The XAS spectra were recorded in both the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectral ranges. The standard samples for reference were CuSCN powder (99%, Sigma-Aldrich), CuI powder (99.5%, Sigma-Aldrich), and I$_2$ beads (99.9%, Wako).

The XANES results of the Cu K-edge are shown in Figure S4a (Supporting Information). Specifically, only those of pristine, 0.5 mol.% I$_2$-doped (optimal condition for TFTs), and CuSCN standard samples are displayed in Figure 2a for clarity. For all samples, the rising edge showed a feature at 8984 eV associated with the 1s→4p electronic transition of Cu$^+$. No pre-edge features at energies < 8980 eV related to 1s→3d transition of Cu$^{2+}$ were detected.$^{[45,46]}$ This indicates that Cu centers were in the d$^{10}$ Cu$^+$ state (no 3d holes) and I$_2$ doping did not alter the oxidation state of Cu. The overall spectra of all samples were generally consistent with a 4-coordinate Cu$^+$ (ref. $^{[45,46]}$) and similar to previously reported data of CuSCN.$^{[47,48]}$ Interestingly, we observe that the pristine CuSCN sample exhibited a noticeably lower white line intensity (strong absorption peak after the edge, at 8997 eV in this case) than the CuSCN standard, indicating a slightly lower coordination number of the Cu atoms in the pristine sample.$^{[49–51]}$ As discussed below in the EXAFS analysis, the incomplete coordination around Cu$^+$ centers is restored at the optimal I$_2$ doping concentration of 0.5 mol.%.

Figure S4b (Supporting Information) shows the Fourier-transformed EXAFS data in the R-space of the Cu K-edge X-ray absorption spectra which give crucial information regarding the local coordination environment around Cu. The CuSCN standard exhibited a major peak at 1.84 Å, which can be ascribed to the scattering path of the dominant Cu$^+$–S bonding.$^{[52]}$ The broadening of this peak may obscure the signal from the Cu–N scattering path, typically observed ≈1.5 Å. For the pristine sample, the amplitude of the main peak was significantly reduced when compared to that of the CuSCN standard. This can be attributed to a diminishing degree of bonding in the first coordination sphere around Cu$^+$, pointing to some deficiency of SCN$^-$ ligands surrounding Cu sites. This strongly suggests the presence of SCN$^-$ vacancies ($V_{SCN}$) in the pristine sample. As highlighted in Figure 2b, the addition of 0.5 mol.% I$_2$ to the processing solution led to the recovery of the local environment profile to be similar to that of the CuSCN standard. This result
corroborates that an optimal amount of I$_2$ can heal the defect sites around Cu. However, an excessive amount disrupts the bonding around Cu, particularly evident from the 40 mol.% doping concentration (Figure S4b, Supporting Information).

In addition to the Cu K-edge data, the analysis of I L3-edge XAS measurements allowed us to elucidate the oxidation state and local environment of the added iodine. The XANES spectra of CuSCN samples with various I$_2$ concentrations are shown in Figure S5a (Supporting Information). The absorption edges of CuI and I$_2$ standards were located at 4561.0 and 4562.4 eV, which can be assigned to iodine in the oxidation state -1 and 0, respectively. The L3-edges of the I$_2$-doped samples were located between the two standards, and by using a linear correlation analysis the oxidation state of iodine can be found as shown in Figure 2c.\cite{54} $-0.67$ for the 0.5 mol.% sample and around $-0.15$ for the 5 and 40 mol.% samples. This result confirms that, at 0.5 mol.% I$_2$, iodine exists as I$^-$ ligands which can replace the missing SCN$^-$ ligands, hence passivating V$_{SCN}$ as mentioned above. The slightly higher oxidation state than $-1$ is ascribed to unequal charge distribution between I$^-$ and the other SCN$^-$ ligands that surround the Cu$^+$ center. In contrast, when the doping amount was too high, iodine likely exists as I$_2$. The slightly reduced oxidation state agrees with the Raman spectroscopy results that showed molecular I$_2$ acting as an electron acceptor in the highly doped samples.

In addition, Figure S5b (Supporting Information) shows the I L3-edge EXAFS spectra in the R-space of I$_2$-doped samples. The CuI and I$_2$ standards showed a major peak at 2.2 and 2.6 Å, which can be ascribed to Cu–I and I–I scattering paths, respectively.\cite{55,56} Compared to the CuI standard, the sample with 0.5 mol.% I$_2$ exhibited a similar peak for the first Cu–I scattering but with an absence of the second peak at 3.8 Å. The latter indicates that the outer coordination sphere of iodine in this sample was different from that in CuI; this further substantiates that I$^-$ was filling in for V$_{SCN}$ in the structure of CuSCN. This result is consistent with the XRD data which did not show the presence of the CuI phase. The EXAFS spectra at higher doping concentrations of 5 and 40 mol.% showed different profiles to both CuI and I$_2$ standards. From Raman and XANES analyses, molecular I$_2$ likely existed in these samples; the EXAFS data then supplements that they did not exist as solid I$_2$ clusters but were included in the main CuSCN structure which led to a different local environment when compared to that of the I$_2$ standard.

By combining the Raman spectroscopy, XRD, and XAS findings, we deduce that adding a small amount of I$_2$ (e.g., 0.5 mol.%) to the CuSCN processing solution leads to the defect-healing effect through I$^-$ filling in the vacancies of SCN$^-$, passivating the structural defects and improving the crystallinity. We speculate that the initial presence of SCN$^-$ vacancies is due to the removal of DES molecules during the film-forming and annealing steps. As shown in our previous publication,\cite{57} DES molecules coordinate strongly with Cu centers in CuSCN. During the solution-processing, DES molecules possibly compete with SCN$^-$ ligands to coordinate to Cu and remain in the wet film state. Upon annealing, the volatile DES molecules are removed, leaving behind SCN$^-$ vacancies in the CuSCN lattice. To this end, adding iodine can fill these voids. I$^-$ is well-known to act as a ligand that coordinates with Cu$^+$ centers in coordination polymers or complexes.\cite{58,59} The ionic radius of I$^-$ (220 pm)\cite{60} is comparable to that of SCN$^-$ (215–220 pm).\cite{61} Furthermore, both I$^-$ and SCN$^-$ can similarly stabilize Cu in the +1 oxidation state, emphasizing their chemical compatibility. However, when the doping concentration is too high (e.g., $\geq$ 5 mol.%), iodine exists as molecular I$_2$ units. Although they still coordinate to Cu$^+$ centers, their...
large size leads to more disorder around Cu$^+$ and decreases the overall crystallinity.

2.3. Optical Properties and Electronic Energy Levels

We note that thin-film morphology was also characterized by atomic force microscopy (AFM) with the results shown in Figure S6 and Table S2 (Supporting Information). As discussed in Note S2 (Supporting Information), the change in the morphology was not drastic, except at high doping concentrations in which the grain size was reduced in the same trend as the reduced crystallinity mentioned in the XRD section. The optical properties of the films were studied by the UV–vis-near infrared (UV-Vis-NIR) spectroscopy. Following the thin-film fabrication by spin-coating and annealing at 100 °C, all films became transparent. The measured optical transmittance and reflectance of pristine and I$_2$-doped films (on fused silica substrates) are shown in Figure S7a,b (Supporting Information). In the 400–1400 nm wavelength region, all films demonstrated an average transparency higher than 95%. The converted absorption spectra are displayed in Figure 3a. All samples show similar absorption peaks at 236 and 303 nm, which are characteristics of CuSCN.$^{[30,57]}$ The increase in the transmittance and the corresponding decrease in the absorbance with the increasing doping concentration are attributed to the slight reduction in the film thickness (Figure S8, Supporting Information). The optical band gaps ($E_{\text{opt}}^g$) of the samples were determined from the Tauc plots as presented in Figure 3b and found to be in the range of 3.95–3.97 eV (Table S3, Supporting Information). This result suggests that I$_2$ doping does not affect the optical properties of CuSCN films in general.

To study the electronic energy levels of the samples, photoelectron spectroscopy (PES) was performed using synchrotron radiation at the Beamline BL3.2Ua, Synchrotron Light Research Institute (SLRI), Thailand.$^{[62]}$ Figure S9 (Supporting Information) shows the PES spectra of pristine and I$_2$-doped CuSCN films (0.5, 5, and 40 mol.%) prepared on indium tin oxide (ITO) substrates, and the resulting energy levels analyzed from the data are reported in Table S4 (Supporting Information). The spectra exhibit similar characteristics to the previous report of CuSCN.$^{[17,30]}$ The PES data combined with the $E_{\text{opt}}^g$ from the optical measurements allow the construction of the energy diagrams as illustrated in Figure 3c. We can observe that with respect to the reference Fermi level ($E_F$), the band edge positions did not vary significantly, nor did they exhibit clear trends. No additional states from doping were observed because our process of adding I$_2$ does not lead to a strong p-doping effect but rather a defect-healing effect. Some variations in the work functions (i.e., Fermi level or $E_F$ with respect to the vacuum level or $E_{\text{vac}}$) are likely to result from the changes in the crystallinity and orientation of the microstructure.$^{[63–65]}$
2.4. Thin-film Transistors and Analysis of Hole Transport Properties

TFTs based on the pristine and I₂-doped CuSCN layers were fabricated to elucidate the effects of doping on the hole transport properties. Details of the fabrication and characterizations can be found in Note S1 (Supporting Information). The representative transfer and output characteristics of all samples are included in Figures S10 and S11 (Supporting Information). For clarity of comparison, only the forward-sweep transfer curves of pristine, 0.5, 5, and 40 mol.% I₂-doped conditions operated in the saturation regime are shown in Figure 4a. The results reveal that the p-type characteristics of CuSCN transistors were greatly improved by I₂ doping at 0.5 mol% condition. The on drain current (I_D,on) was increased by one order of magnitude with a small increase in the off drain current (I_D,off). The same data in Figure 4a is plotted as I_D versus the gate voltage (V_G) in Figure 4b, clearly showing the positive shift of the threshold voltage (V_th) and the increase in the saturation hole mobility (μ_sat) which are reflected in the x-intercept and slope, respectively. Full TFT device parameters are reported in Table S5 (Supporting Information). For each condition, at least 10 devices were measured, and the average and uncertainty (from the arithmetic mean and standard deviation) were computed.

The evolution of μ_sat, V_th, and the subthreshold swing (S_th) with I₂ concentration are visualized in Figure 4c. We can clearly see that at the optimal concentration of 0.5 mol.%, the device characteristics were drastically improved from the undoped condition: the average μ_sat increasing from 1.3 × 10⁻² to 7.1 × 10⁻² cm² V⁻¹ s⁻¹; the average V_th shifting from −4.6 to −0.4 V; and the average S_th decreasing from 2.7 to 2.0 V dec⁻¹.

Doping concentration of higher than 0.5 mol.% led to a reversal of the effects: a decrease in μ_sat, a negative shift in V_th, and an increase in S_th. We note that the doped devices still showed superior performance to the pristine devices up to ≈10 mol.%. Although the thickness slightly decreased upon doping in this range (from 35 nm for pristine to 32/26 nm for 0.5/10 mol.% doping), the hole mobility was still larger by 3–9 times compared to the pristine sample with similar thicknesses (25 to 40 nm) as shown in our previous investigation, verifying that the higher mobility is a result of I₂ doping. The reduction in

![Figure 4. Transfer characteristics (forward sweep) in the saturation regime plotted as a) log(I_D) versus V_G and b) √I_D versus V_G. (a, inset) Schematic diagram of the top-gate bottom-contact thin-film transistors. Device dimensions: W = 1000 µm and L = 30 µm. c) Box plots of μ_sat, V_th, and S_th. The box and the horizontal line represent the 25th, 50th, and 75th percentiles. The black dots show the mean values, and the whiskers the standard deviation. d) Power law analysis of μ_sat. e) Results of trap state density analysis from the frequency dispersion of the metal-insulator-semiconductor capacitors (structure shown in the inset).](adv-funct-mater.2023.33.2209504.fig4)
performance beyond the optimal doping concentration likely reflects that around 0.5 mol.%, the dopant concentration already saturates the amount of the vacancy defect sites. Overdoping beyond this point would generate other impurity defects that become detrimental to carrier transport and transistor performance.

The improvement in the hole transport properties at 0.5 mol.% doping is further evident from the power law analysis (see Supporting Information) of the linear mobility \(\mu_{\text{ith}}\) as shown in Figure 4d. The reduction in the exponent \(\gamma\) from 0.71 to 0.13 indicates that the hole transport mechanism in CuSCN changes from the slower trap-limited conduction (TLC) to the more mobile percolation conduction (PC). A similar p-doping effect became detrimental to carrier transport and transistor performance.

The positive shift in \(V_{\text{th}}\) also signifies an increase in the hole density \(N_h\) in the channel as shown in Figure S12a (Supporting Information). In the I2-doped CuSCN channel, a smaller number of electric field-induced holes is required to turn the device on (or equivalently, at the same applied \(V_{\text{g}}\), a smaller number of electric field-induced holes is required to turn the device on (or equivalently, at the same applied \(V_{\text{g}}\), there is a higher hole density in the I2-doped CuSCN channel). The reason for this could be from: 1) a p-doping effect, i.e., an increase in the hole density in the semiconductor layer; or 2) a decrease in the hole-trapping states.

The improvement in the hole transport properties at 0.5 mol.% doping is further evident from the power law analysis (see Supporting Information) of the linear hole mobility \(\mu_h\) was manifested in the increase in \(D_{\text{on}}\). The p-doping effect in CuSCN can be clearly seen from the work by Wijeyasinghe et al., in which a strong electron acceptor \(C_{60}\) was used as a dopant. In their study, the positive shift in \(V_{\text{th}}\) was accompanied by a large increase in \(I_{\text{D,off}}\) which led to a reduction in the on/off ratio from \(2 \times 10^3\) (undoped CuSCN) to \(1 \times 10^3\) (0.5 mol.% \(C_{60}\)) despite the gain in \(I_{\text{D,on}}\). The p-doping was also manifested in the increase in \(S_h\); the added dopants gave rise to more impurity scattering. A similar p-doping behavior in CuSCN TFTs can also be observed from the report by Ji et al. In contrast, the p-doping effect was negligible in our results. \(I_{\text{D,off}}\) was only slightly increased from 1 to 3 nA upon doping whereas the on/off ratio increased from \(8 \times 10^3\) (undoped CuSCN) to \(2 \times 10^4\) (0.5 mol.% I2) due to the large increase in \(I_{\text{D,on}}\) (Table S5, Supporting Information). Furthermore, \(S_h\) was in fact reduced. This evidence strongly highlights that the addition of I2 leads to a reduction in the density of hole-trapping states. For an estimation, the interface trap density calculated from \(I_{\text{D,off}}\) decreased from \(6.1 \times 10^{13}\) to \(4.5 \times 10^{13}\) cm\(^{-2}\) eV\(^{-1}\) at 0.5 mol.% I2 concentration as displayed in Figure S12b (Supporting Information). We note also that the hysteresis was smallest at 0.5 mol.% I2, quantified as the difference in \(V_{\text{th}}\) between the forward and reverse sweeps (\(\Delta V_{\text{th}}\)) and plotted in Figure S12c (Supporting Information). The worsening performance metrics at higher doping concentrations can be attributed to over-doping as mentioned previously.

2.5. Trap States Passivation

To characterize the trap states in more detail, we studied the frequency dispersion of the capacitance-voltage (C–V) characteristics of metal-insulator-semiconductor (MIS) devices for the pristine and 0.5 mol.% I2-doped CuSCN. The MIS structure was fabricated using the same layer sequence as the TFT structure as illustrated in the inset of Figure 4e. The resulting C–V characteristics measured at various frequencies are shown in Figure S13a,b (Supporting Information). Both devices showed the typical hole-accumulation behavior when the voltage was swept to negative values. The onset voltages \(V_{\text{onset}}\) of the hole accumulation were shifted to more positive values with the decreasing frequency as shown in Table S6 and Figure S13c (Supporting Information).

At high frequencies, only trap states near the valence band edge are responsive; as the frequency decreases, more trap states at energies deeper in the tail start to respond, leading to higher capacitance and the shift in \(V_{\text{th}}\). The latter allows the analysis of the energetic distribution of the interface trap density \(D_{\text{it,off}}\) as shown in Figure 4e (see Supporting Information for detail). A rapid change in \(V_{\text{onset}}\) is associated with a large trap density; in contrast, a gradual change in \(V_{\text{onset}}\) is due to a small trap density. In the energy range of 0.0–0.1 eV with respect to the reference energy (corresponding to the highest frequency measured), the \(D_{\text{it,off}}\) profiles of both pristine and I2-doped CuSCN samples were similar. However, the broad feature in the 0.1–0.2 eV range seen in the pristine sample became significantly smaller upon the addition of 0.5 mol.% I2, showing the decrease in trap states upon doping.

The reduction in the trap state density, evident from both \(D_{\text{it,off}}\) (based on TFT subthreshold characteristics) and \(D_{\text{it,off}}\) (based on the frequency dispersion of MIS C–V characteristics), was concurrent with the defect-healing effect and improved crystallinity by I2 doping as discussed in the preceding sections. We surmise that the pristine CuSCN films prepared from the DES solution contain a large number of hole traps from \(V_{\text{SCN}}\) (high \(D_{\text{it,off}}\) and \(D_{\text{it,off}}\) with under-coordinated Cu\(^+\) centers). Indeed, excess SCN\(^-\) is known to increase the p-type conductivity of CuSCN accordingly, the deficiency in SCN\(^-\) (i.e., the formation of \(V_{\text{SCN}}\)) is then expected to reduce the hole concentration. This is also supported by a theoretical study of defects in CuSCN which reported that \(V_{\text{SCN}}\) forms donor states within the band gap of CuSCN as well as our own study reported in the next section. Electron-donating states are known to trap holes and result in the negative shift in \(V_{\text{th}}\) which is consistent with our results of the pristine CuSCN. At the optimal condition of I2 addition (0.5 mol.%), the incorporated iodine exists as I\(^-\) which fills in the void of \(V_{\text{SCN}}\) and effectively suppresses the hole-trapping states (low \(D_{\text{it,off}}\) and \(D_{\text{it,off}}\) with fully coordinated Cu\(^+\)). A recent study also reported on a similar passivation of iodine vacancies by Br\(^-\) and Cl\(^-\) in tin halide perovskite TFTs. Our ongoing investigation also shows that these two halide anions can also lead to the \(V_{\text{SCN}}\)-healing effect in CuSCN, and this will be reported in a separate publication.

In addition, we also compared the contact resistance and the negative bias stress (NBS) stability between the pristine and the optimally doped samples. The analyses (Note S3 with data presented in Figure S14, Supporting Information) show that the 0.5 mol.% doping also significantly improved both metrics, further highlighting the merit of our defect-healing method by I2 doping.

2.6. Density Functional Theory Study

To theoretically elucidate the SCN\(^-\) and deficiency-related effects, we carried out a computational study using DFT. The full method is described in Note S1 (Supporting Information),
and the full discussions are included in Note S4 (Supporting Information). In this section, we briefly summarize the key results for the conciseness of the article.

Four structures were modeled as shown in Figure 5a–d and Figure S15 (Supporting Information). Compared to the reference 3R–CuSCN structure (“perfect” structure), the removal of one SCN$^-$ unit [(V SCN)$^+$ structure, in which the + sign denotes the charge left behind due to the loss of SCN$^-$] leads to severe changes in the geometry of Cu atoms surrounding the vacancy site, supporting XANES and EXAFS results. This is accompanied by several donor defect states as seen from the density of states (DOS) plots shown in Figure 5e. These states are localized around the vacancy site, shown in Figure S16b (Supporting Information). Filling the vacancy with I$^-$ (ISCN structure, with I$^-$ substitution having the same charge as SCN$^-$) results in partial restoration of the geometry and elimination of most of the donor states, conclusively corroborating our discussions of the defect-healing effect presented in this article.

Remarkably, when the vacancy is replaced by one molecular I$_2$ unit [(I$_2$)SCN]$^+$ structure, in which a neutral I$_2$ substituting a SCN$^-$ unit also leaves a positive charge], the effect is even more acute: a shallow acceptor defect state is found while a strong p-doping effect is observed (Fermi level pulled into the valence band). We note also that the simulated XRD pattern of this model yields numerous small peaks, particularly in the low-angle region, while maintaining the overall pattern of the parent structure (see Note S4 and Figure S15e,f, Supporting Information). This substantiates our earlier discussions in Section 2.1 that the extra XRD peaks may come from impurity defects. Similar observations have been reported in metal-organic frameworks (MOFs) which are also coordination polymers.[75,76]

However, from the experimental results, the p-doping effect in our samples is negligible, and the XRD peaks do not yet perfectly match. We acknowledge that the structure modeled for [(I$_2$)SCN]$^+$ is possibly not accurate as we do not currently know the exact positions and distribution of I$_2$ within the CuSCN lattice. It is also possible that mixed defects (such as substitutional I$^-$ and I$_2$ coexisting) may be present. More detailed structural characterizations are required to pinpoint the exact positions of these defects, but we hope that the results shown herein will serve as a strong basis for further investigations.

3. Conclusions

We have shown experimentally and theoretically that SCN$^-$ vacancies are found in CuSCN processed from the widely used DES-based recipe and that they act as hole-trapping donor
states which are detrimental to the hole transport properties. At small concentrations of I₂ doping (optimal at 0.5 mol.%), the added iodine exists as I⁻ which can replace V⁻SCN and restore the coordination environment of Cu⁺, drastically enhancing the hole transport properties. Specifically, the hole mobility was increased from ≈0.01-0.02 to 0.07-0.08 cm² V⁻¹ s⁻¹ while the on/off current ratio was simultaneously increased from 8 × 10⁶ to 2 × 10⁷. The latter is distinct from previous doping attempts; the optimal I₂ doping can passivate hole traps while avoiding the p-doping effect and the undesired reduction in the on/off current ratio. Furthermore, the contact resistance is reduced, and the device stability under NBS is more robust. The current work advances the performance level of CuSCN-based TFTs further toward those of other transparent p-type inorganic semiconductors (Table S8, Supporting Information). As the I₂ doping introduced herein is extremely simple and based on a cost-effective, commercially available chemical, the process could be extended to a wide array of devices that already employ CuSCN as the HTL, such as PSCs, OSCs, and OLEDs.

In addition, this work highlights that there is still a large room for CuSCN property optimization. Although I⁻ is shown to passivate the hole-trapping states, the trap state density is still relatively high (on the order of 10¹⁰ cm⁻² V⁻¹ s⁻¹) compared to high-performance p-channel TFTs based on other semiconductor families, such as organics or oxides (with trap state density on the order of 10¹ⁱ–10¹² cm⁻² V⁻¹ s⁻¹).[77–79] We, therefore, expect that further defect engineering will be crucial to advance the performance of CuSCN-based devices beyond the current state of the art.

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.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Copper(I) thiocyanate, defect healing, doping, hole transports, thin-film transistors

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