

Deliquescent Chromism of Nickel(II) Iodide Thin Films

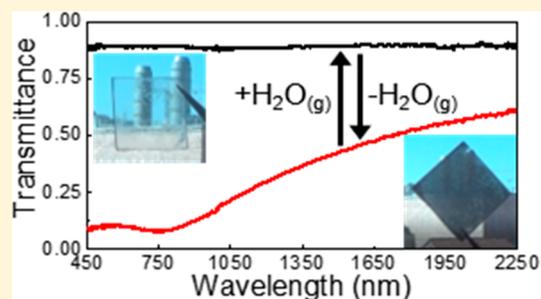
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Supporting Information

ABSTRACT: Color-changing materials have a variety of applications, ranging from smart windows to sensors. Here, we report deliquescent chromism of thin, color neutral films of nickel(II) iodide (NiI_2) that are less than $10\ \mu\text{m}$ thick. This behavior does not occur in the bulk material. Dark brown thin films of crystalline NiI_2 turn clear when exposed to humidity and can be switched back to the dark state when mildly heated ($>35\ ^\circ\text{C}$). This optical transition between dark and clear states of an NiI_2 thin film is reversible with thermal cycling.



INTRODUCTION

Color-changing materials are used in a variety of applications, ranging from sensors¹ to dynamic window coatings^{2,3} and even switchable photovoltaic windows.^{4–6} These materials change color in response to shifts in temperature, applied voltage, or chemical environment. Nickel compounds, especially organometallic Ni(II) halides, have been widely studied in this context because of their propensity to change color when halide ligands are exchanged with other ligands.^{7–16} Several patents have mentioned ligand exchange of nickel complexes as a useful strategy to create glass that exhibits color neutral switching between transparent and dark states with uniform light absorption across the visible spectrum.^{9,17,18} Color neutral transitions are especially desirable to minimize distortions in the appearance of objects viewed through tinted window glass.^{9,18–20} Color neutrality has also been achieved by layering different thermochromic materials,^{9,18} or by using materials that undergo insulator–metal transitions to switch between transparent and mirror states.^{20,21} Here, we report a color neutral deliquescent chromism in thin films of nickel(II) iodide (NiI_2) that does not occur for bulk NiI_2 powders. When exposed to humidity, the thin films rapidly take up water and transition to an amorphous, optically transparent state that can be reversibly switched back to the dark crystalline state with mild heating. A transitory, intermediate solid NiI_2 -hydrate phase is also observed, which is most likely the pentahydrate or hexahydrate phases known to occur in the bulk.

EXPERIMENTAL SECTION

Materials. Nickel(II) iodide (NiI_2 , 99.5%, VWR), anhydrous dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, DMF, 99.8%, Sigma), anhydrous dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$, 99.9%, Sigma), and (3-aminopropyl)-triethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, >98%, Sigma) were purchased and used as received.

Preparation of Silane Coated Glass Substrate. Glass slides were sonicated in ethanol for 30 min. The slides were then immersed into a solution of (3-aminopropyl)triethoxysilane (APTES) in ethanol with a volumetric ratio of ethanol:APTES of 9. A drop of water was added to the ethanol/APTES solution to catalyze APTES grafting to the glass substrate. After 5 min, glass substrates were rinsed with isopropanol (IPA) and then heated at $100\ ^\circ\text{C}$ in ambient air for 10 min.²²

Preparation of Nickel(II) Iodide Thin Films. Nickel(II) iodide thin films were deposited on APTES-treated glass substrates by spin coating a solution of 1 mmol (313 mg) NiI_2 in 200 μL of DMSO and 800 μL of DMF. This solution is prepared by heating for 2 h at $125\ ^\circ\text{C}$. If this solution cools to room temperature, it changes color from brown to green and forms a viscous gel; therefore, the solution temperature is maintained at $125\ ^\circ\text{C}$ by stirring on a hot plate throughout the deposition. 50 μL of solution was pipetted directly from the heated solution on the hot plate and deposited onto the substrate by dynamically spin coating at 5000 rpm for 30 s in a nitrogen-filled glovebox. After deposition, the film was heated at $150\ ^\circ\text{C}$ for 48 h to remove DMSO from the film and eliminate any possibility of ligand–metal chromism. The thickness of films spin-coated at 5000 rpm was around 600 nm. Films that were 900 nm or 15 μm thick were deposited by spin coating at lower speeds of 1000 and 100 rpm, respectively. Films with 140 μm thickness were deposited by drop casting 150 μL of solution onto glass substrates heated to $150\ ^\circ\text{C}$.

Optical Switching. UV-vis-NIR transmittance spectra were obtained using an ASD LabSpec 4 Standard-Res UV-vis-NIR spectrophotometer with a Linkam LTS420 heating stage equipped with the LNP95 cooling system and Linksys 32 software (Linkam Scientific) to control the film temperature. Stepped temperature profiles were generated using a heating rate of $10\ ^\circ\text{C}/\text{min}$ between steps, and holding the temperature at each step for 10 min before

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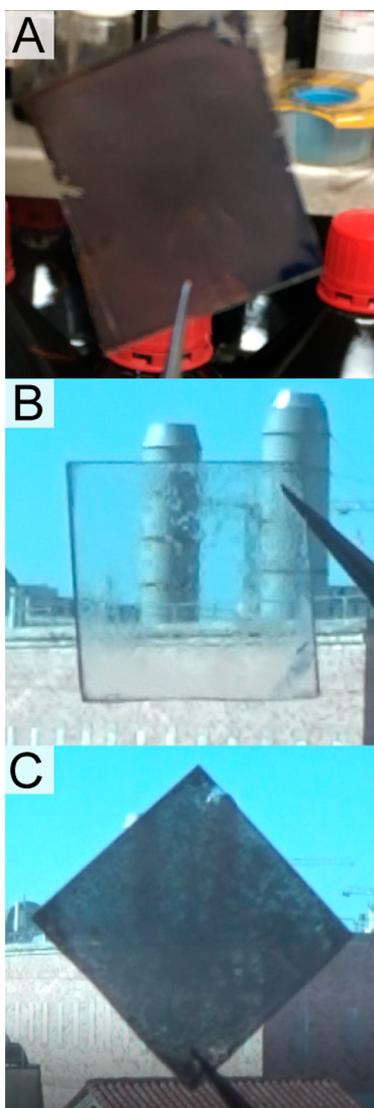


Figure 1. Thin film of NiI_2 (thickness 625 ± 125 nm) on glass cycled between its (A,C) dark and (B) clear states. The film is shown (A) immediately after spin coating and annealing, (B) after 5 min of exposure to air ($\sim 50\%$ RH, 20°C), and (C) after it had been heated at 100°C for 10 s. (See the Supporting Information for accompanying videos.)

acquiring spectra. Experiments with continuous ramping of the temperature were performed with rates of 0.25, 1, or $10^\circ\text{C}/\text{min}$.

The experiments examining the optical switching of the NiI_2 films by thermal cycling all began with a film in the dark state and exposure to air at 50% RH (relative humidity). Before cycling, initially dark NiI_2 films were taken out of the glovebox, transferred to the heating stage and heated at 100°C for 1 h to drive off any water vapor the film may have taken up during the transfer. The reversibility of the color change was tested by exposing the initially dark NiI_2 film to 50% RH air at 20°C for 15 min to obtain the clear state. This film was then heated to 80°C for 15 min, causing the film to become dark again. This cycle was repeated 10 times.

Materials Characterization. Powder X-ray diffraction (XRD) was performed with a Rigaku R-Axis Spider X-ray diffractometer using an image plate detector and $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ nm). XRD samples were transferred to a Hampton Research Mounted CryoLoop mount by scraping material from a film. XRD data were acquired for 10 min with 5 deg/s sample rotation under 40 kV and 40 mA radiation.

Fourier transform infrared (FTIR) spectra were measured using a Bruker Vertex 70 FTIR spectrophotometer. Nickel iodide films were

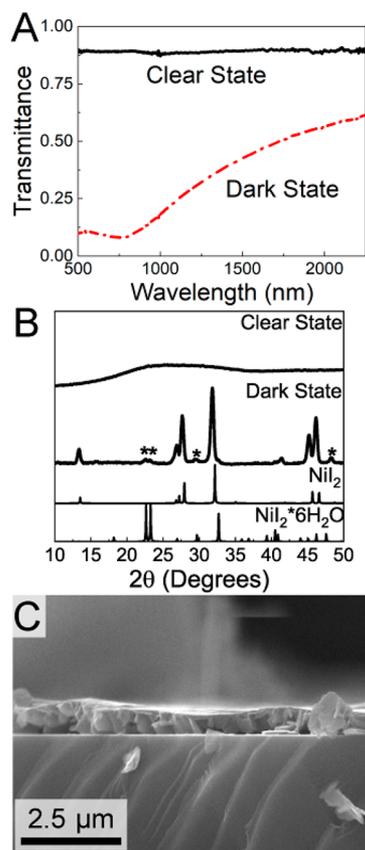


Figure 2. (A) UV-vis-NIR transmittance spectra and (B) XRD of an NiI_2 film on glass in its optically clear and dark states. The diffraction peaks in the dark film correspond to rhombohedral NiI_2 (PDF #00-020-0785) and trace hexagonal $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ (marked by *, PDF #00-016-0565). (C) SEM image of a cross sectioned NiI_2 film on glass in the dark state without exposure to air. The film is 625 ± 125 nm thick.

spin coated onto silicon substrates and placed in an airtight Buck Scientific Circular Aperture Cell Mount 6500 S liquid FTIR cell with a CaF_2 window. Dark and clear films were sealed into the cell mount in a nitrogen glovebox or in 50% RH air, respectively.

Scanning electron microscopy (SEM) was performed using a Quanta 650 SEM operated at 30 kV. To minimize exposure to air, the cross-sectioned films were loaded into the SEM using a Quorum Technologies Cryo-SEM Preparation System (model PP2000TR/FEI). All reported film thicknesses were determined from SEM images of cross-sectioned films.

Optical microscopy images were obtained with the optical microscope attachment on a Horiba LabRAM HR Evolution Raman microscope using a 10X zoom lens. Film temperatures were controlled with a Linkam LTS420 stage equipped with the LNP95 cooling system.

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA 2. For TGA, the nickel iodide films were spin-coated at 5000 rpm onto the flat surfaces of a $40 \mu\text{L}$ Mettler Toledo aluminum crucible standard lid.

The amount of water absorbed by the film when switching between dark and clear states was determined using a Mettler Toledo XSE205 DualRange balance. Films in the dark state were weighed immediately after preparation in a nitrogen-filled glovebox with less than 15 s of air exposure. The weight of the clear state films was then measured after the weight stabilized under exposure to ambient air at room temperature and 50% RH.

RESULTS AND DISCUSSION

Figure 1 shows a thin film of NiI_2 on glass reversibly switched between a color neutral dark state and an optically transparent

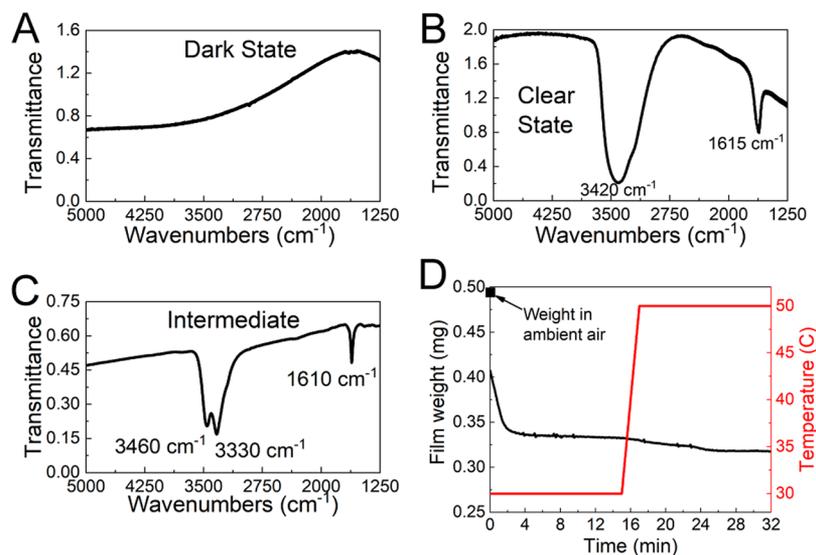


Figure 3. FTIR spectra for a thin film of NiI_2 in (A) the dark state, (B) the clear state, and (C) 30 s after removal from an inert atmosphere (i.e., an intermediate state). The FTIR on the clear state shows water is present in the clear film, with a characteristic stretching mode ν_1 peak at 3420 cm^{-1} and a characteristic bending mode peak ν_2 at 1615 cm^{-1} . FTIR on the intermediate state shows two condensed O–H stretching modes. Transmissions greater than one in FTIR spectra are due to reduced reflection of the silicon substrate once the thin film is deposited. (D) TGA of a clear hydrated NiI_2 thin film. Note that some weight loss has occurred during sample loading into the TGA and purging with dry nitrogen prior to beginning the measurement. The initial mass measured in ambient conditions with a benchtop balance is shown here as a solid black square at time 0. From this, we calculate a $\text{H}_2\text{O}/\text{NiI}_2$ molar ratio of 9.7 ± 0.6 .

state. The initially dark film shown in Figure 1A was stable in dry air until exposed to 50% RH air for 5 min, at which point it turned to the clear film shown in the photograph in Figure 1B. (Note that this transition was not observed when the humidity was less than 30% RH.) The film was then heated at $100\text{ }^\circ\text{C}$ for 5 s, and it reverted back to the dark state shown in Figure 1C. As shown in the UV-vis-NIR transmittance spectra in Figure 2A, the clear state of the NiI_2 film exhibits 90% optical transmittance between 350 and 2250 nm; whereas the dark state has less than 10% optical transmittance through the visible spectrum, with a gradually increasing transmittance through the near IR spectrum up to 2250 nm. Figure 2C shows an SEM image of a typical NiI_2 film without any exposure to air, with a thickness of about 625 nm.

Figure 2B shows XRD patterns from a film in its dark and clear states. Powder XRD shows the dark state is composed of crystalline, rhombohedral NiI_2 , with a trace amount of hexagonal $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$. The XRD pattern of the clear film is featureless, indicating that the layer lacks crystallinity. NiI_2 is hygroscopic, and in its bulk form, exposure to humidity changes the material from the black rhombohedral phase to crystalline penta- or hexahydrate, which has a green color.^{23–25} The trace amount of hexagonal $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ observed in the dark state film in Figure 2B is the result of brief air exposure during the sample preparation. XRD of the clear film does not show any evidence of hexagonal $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ or any other crystalline hydrate phase.

FTIR spectra were measured to determine if the clear film presented any evidence that the color change was due to ligand exchange or rearrangement. The FTIR spectrum of the dark film in Figure 3A is featureless. There is no residual DMF or DMSO in the film that could possibly give rise to a nickel-ligand rearrangement or a change in d-splitting of nickel due to change in coordination geometry.^{10,26–28} The FTIR spectrum of the clear film in Figure 3B exhibits two strong absorption bands at 3460 and 1610 cm^{-1} . Although these could come from nickel iodide hexahydrate;²⁴ these bands also correspond to the

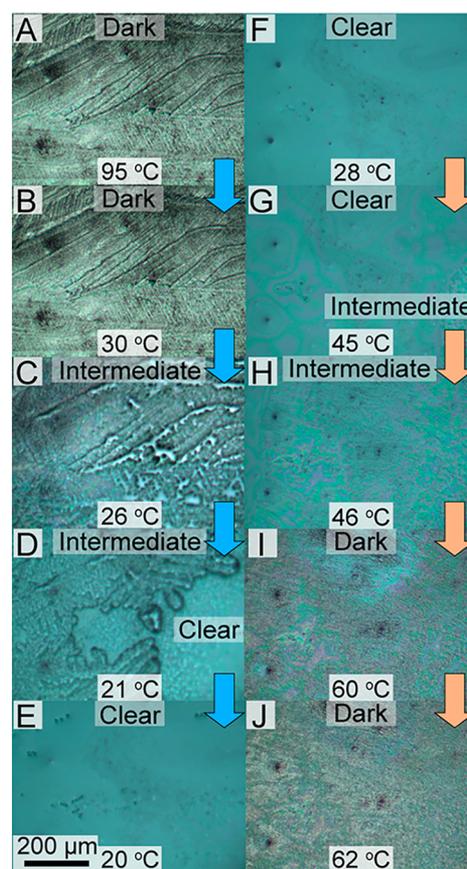


Figure 4. Optical microscope images of a nickel iodide film on glass as it is (A–E) cooled, as indicated by blue arrows and subsequently (F–J) heated, indicated by red arrows. Optical microscopy shows the coexistence of (D–G) a clear liquid and (C,D,G,H) clear solid phase during the clear-to-dark transition to (A,B,I,J) the dark solid phase, and that these transitions happen in a nucleation-and-growth mechanism. (See the Supporting Information for accompanying videos.)

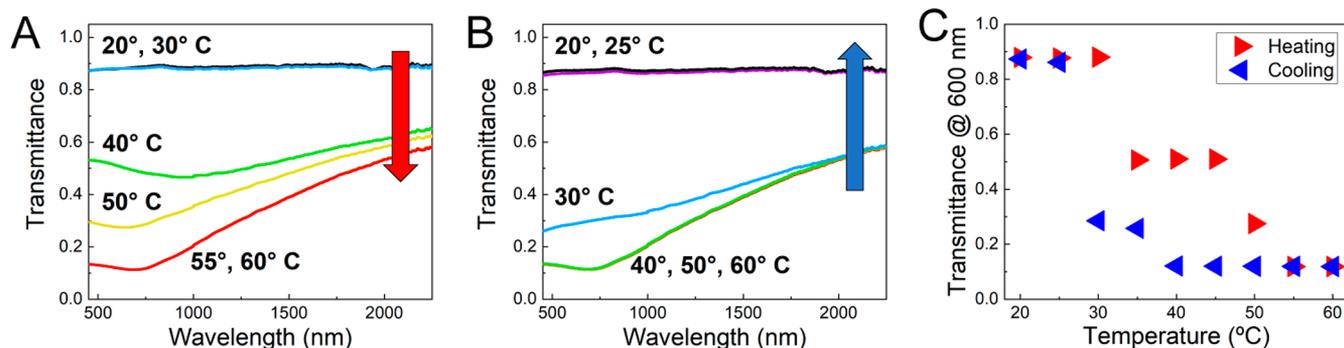


Figure 5. (A) In situ UV-vis-NIR transmittance spectra of clear state films heated to different temperatures via a 10 °C/min ramp and 10 min hold in ambient air (50% RH). Spectra show a broad clear-to-dark transition centered around ~40 °C. (B) Temperature-dependent spectra of the dark-to-clear transition cooled using the same procedure as (A), showing a sharper transition centered around ~30 °C. In plots (A) and (B), different colored lines correspond to different temperatures: 20 °C is represented by a black line, 25 °C by purple, 30 °C by blue, 40 °C by green, 50 °C by yellow, 55 °C by orange, and 60 °C by red. (C) Transmittance of the film at 600 nm plotted versus temperature. This transition exhibits a temperature hysteresis of ~10 °C at 50% RH.

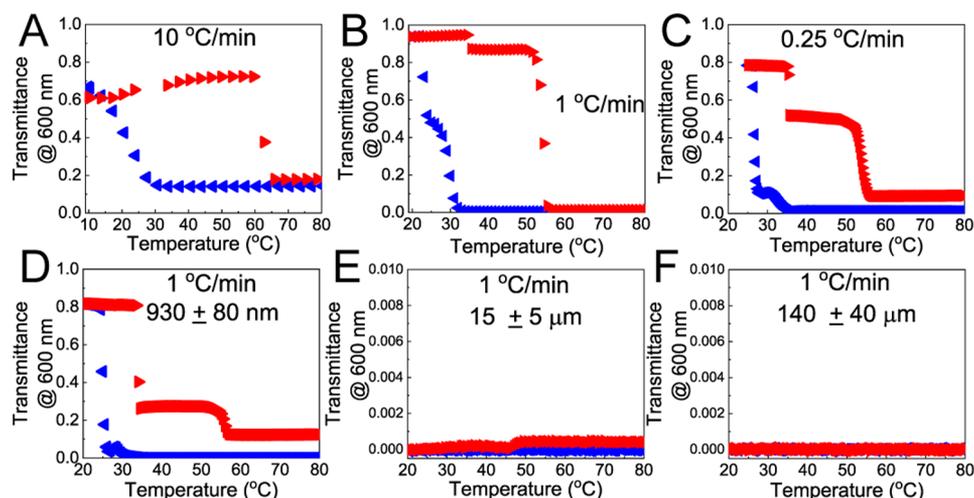


Figure 6. (A–C) Optical transmittance at 600 nm for NiI₂ films (625 ± 125 nm thick) heated (red) and then cooled (blue) in 50% RH air at various heating and cooling rates: (A) 10 °C/min, (B) 1 °C/min, and (C) 0.25 °C/min. Replicates are shown in Figures S1–S4. At high ramp rates as in (A), the transition hysteresis widens. (D–F) Optical transmittance at 600 nm as a function of temperature for (D) 930 ± 80 nm, (E) 15 ± 5 μm, and (F) 140 ± 40 μm thick films. Cross-sectional images of films are shown in Figure S5. Above 1 μm in film thickness, the optical transition disappears.

stretching and bending region of condensed water.^{29–32} Since there is no evidence of NiI₂·6H₂O by XRD (Figure 2B), these bands must be due to water. TGA (Figure 3D) also indicates a significant amount of water in the clear film, with a H₂O:NiI₂ molar ratio of at least 10, corresponding to a dissolved nickel iodide concentration of ~5.5 M.

The FTIR spectra also reveal that there is an “intermediate” state occurring as the film switches between dark and clear states. As shown in Figure 3C, this intermediate state of the film exhibits the water bending mode at 1610 cm⁻¹, similar to the spectra in Figure 3B for the clear film, but with an additional splitting of the stretching mode ν_1 into two peaks at 3460 and 3330 cm⁻¹. The additional ν_1 peak at 3330 cm⁻¹ corresponds to water with a lower degree of vibrational freedom and stronger hydrogen bonding.³³ These data indicate that this intermediate solid is a hydrate phase of nickel iodide with a lower hydration state than the clear liquid. Possibly, this intermediate is the pentahydrate or hexahydrate phase of nickel(II) iodide. The intermediate phase is also observed during switching in optical microscopy images and in the transmittance spectra, as discussed below.

Figure 4A,B shows optical microscopy images of a NiI₂ film as it is switched between dark and clear states. When the dark film

(Figure 4A) is cooled, a transparent solid is observed to form (Figure 4C,D) before the film finally turns clear (Figure 4E). This transparent solid material is the intermediate phase formed during switching. When the clear film is heated (Figure 4G), the clear solid material again appears (Figure 4G,H) before the entire film transitions to the solid dark state material (Figure 4I,J).

The intermediate is also observed as a step in the optical transmittance when the NiI₂ film is heated and cooled, as shown in Figure 5. Optical switching of the film occurs at 35 to 50 °C when heated and then at 30 to 35 °C when cooled. The observed hysteresis indicates that the transition temperatures are influenced by the kinetics of the transition. For example, the transition temperatures observed from the in situ transmittance spectra in Figure 5 are lower than those observed in the optical microscopy experiments in Figure 4 due to the difference in temperature ramp rate.

The rate dependence of the optical switching was further tested by following the transmittance of the film with various heating rates. Figure 6A–C shows the transmittance of NiI₂ films heated and cooled at three different rates: 10, 1, and 0.25 °C/min. The transmittance of the intermediate state and the amount of hysteresis depends on the heating rate.

When heated at 1 °C/min or slower, the films exhibit identical temperature-dependent changes in transmittance, similar to those shown in Figure 5. Additional data are provided in the Supporting Information.

Figure 6D–F shows transmittance of NiI₂ films with varying thickness all heated at the same rate of 1 °C/min. The 930 nm thick film exhibits a similar optical behavior and kinetic response as the thinner 625 nm films, but the transmittance of the intermediate state is significantly lower. Much thicker films, with thickness of 15 μm or more, did not exhibit the dark-to-clear optical transition. (See the Supporting Information for

SEM images of the cross-sectioned films.) While these films did not exhibit a change in optical transmittance, they still showed deliquescence, turning into a black sludge upon exposure to 50% RH air.

We also tested the reversibility of the optical transition of the NiI₂ films. Figure 7 shows UV-vis-NIR transmittance spectra for an initially dark NiI₂ film exposed to air at 20 °C for 15 min, heated to 80 °C at 10 °C/min, and then held at 80 °C for 15 min. The transparency of the dark state of the film increases over the course of the first three to four cycles, with a slight decrease in transparency in subsequent cycles. This initial loss of dark state optical density most likely results from poor adhesion of the wet film to the substrate. To improve adhesion of the films to glass substrates, they were treated with APTES to improve the wettability of the polar solvents used in the spin coating procedure (DMF and DMSO); however, even with the polar APTES coating, the contact angle of water with the substrate remains as high as 58°, which is problematic for aqueous clear state films.³⁴ The hydrated, clear NiI₂ films often dewetted and moved off the substrate during the thermal cycling experiments. This also explains the observed increase in transmittance of the clear state with each cycle. As shown in Figure 7D, the optical transitions of the film stabilize after five cycles, and the change in transmission between clear and dark states never drops below 90% of its initial value.

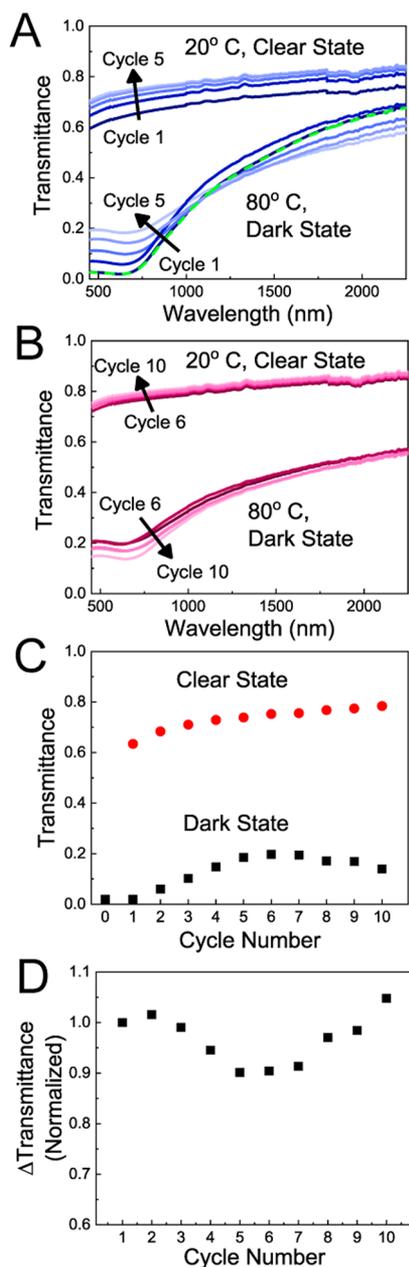


Figure 7. UV-vis-NIR transmittance spectra of a 550 nm thick film of NiI₂ undergoing thermal cycling from 20 to 80 °C in air at RH 50% over (A) cycles 1–5 and (B) cycles 6–10. Absorbance spectra are shown for both the clear state at 20 °C and the dark state at 80 °C. The green dashed line is the initial absorbance of the film. (C) Transmittance at 600 nm of the film in the dark and clear states. (D) Change in transmittance between light and dark states at 600 nm normalized to the first cycle.

CONCLUSION

Thin films of NiI₂ exhibit reversible, deliquescent chromism that does not occur in the bulk material. When exposed to humidity, the dark brown crystalline NiI₂ film absorbs water and becomes transparent. This deliquescence is reversible: the film turns back to the dark crystalline NiI₂ state when heated to drive off the moisture. The transition involves a solid intermediate species, most likely one of the known solid pentahydrate or hexahydrate phases of NiI₂. The transition is different than the known nickel halide chromism due to d–d transitions in nickel metal centers of organometallic complexes.^{10,26,35,36} The optically clear hydrated state of nickel(II) iodide has a H₂O:NiI₂ molar ratio of at least 10, which has not previously been reported. The kinetics of this optical transition depend on the humidity of the environment and the film thickness. With further research, this deliquescent chromism of NiI₂ thin films may find use in color-changing devices, such as smart windows, thermal sensors, or thermochromic inks.^{20,21}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b03979.

Replicates/UV-vis-NIR spectra of continuous ramp rate and thickness experiments, SEM figures of thick films, photographs detailing the deliquescence of bulk powder (PDF)

Initial dark-to-clear transition after removal of a NiI₂ film removed from a glovebox (MPG)

Full clear-to-dark-to-clear transition in 50% RH air (MPG)

Microscope images of the complete dark-to-clear-to-dark transition in 50% RH air (AVI)

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Notes

The authors declare no competing financial interest.

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