Thermochromic and electrical properties of silica/DEA-CuCl₄ sensory composite

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Abstract. A flat tape composed of several hundreds of silica filaments was used as a carrier for the thermochromic dye bis (diethylammonium) tetrachloridocuprate (II) (DEA-CuCl₄) and coated with a methyl silicate resin. The thermal transition of the created composite was around 42 °C and its surface color change was mainly influenced by the low thermal conductivity of silica fibers. In addition to thermochromic behavior, the composite also exhibited electrical properties. Measurements indicate that in the temperature range of 4 to 24 °C the dye behaves as a semiconductor, while at higher temperatures it exhibits behavior of conductor. This pilot study suggests the sensory potential of the DEA-CuCl₄ dye, which provides both a visual color and electrical responses to a thermal stimulus.

Keywords: Diethylammonium tetrachloridocuprate, Thermochromism, Semiconductor dye.

1 Introduction

1.1 Thermochromic sensors

Sensors and devices with integrated chromism find application as practical visual detectors indicating chemical or physical changes. New operating systems are a challenge for advanced research into multifunctional sensors, which require fast response, reversibility, and mechanical strength or flexibility in some applications. Thermochromism is the ability to change color (mainly reversibly) induced by a change in temperature. Thermochromic sensors can be used to monitor the temperature of electronic and optical devices, machine components, or motors to warn users if the ambient temperature exceeds certain values. [1-3] They can also be used in smart clothing to monitor body temperature or warn of the danger of overheating. [4,5]

Organic thermochromic systems exist in the form of multicomponent and often microencapsulated leucodyes [6] or the form of liquid crystals [7]. Since charge transfer occurs in thermochromic substances in a band close to the visible region, they are substances with a conjugated system of double bonds. The cause of the reversible thermochromism of inorganic materials can be either a first-order phase transition or a
transfer of charge due to a change in the bonding of the ligands and the central metal cation. [8]

1.2 Diethylammonium tetrachloridocuprate (II)

The crystalline pigment bis-(diethylammonium) tetrachloridocuprate (II) with the chemical formula $\text{[NH}_2\text{C}_2\text{H}_5\text{]}_2\text{CuCl}_4$ (abbreviated DEA-CuCl$_4$) is known to exhibit thermochromic behavior. Its color transition temperature is often reported to be between 38 and 57 °C depending on thermocycling, rate of temperature, dye crystal size, or interaction with the polymer matrix. [9] At a lower temperature, the dye is bright green, while at a higher temperature, the dye is yellow. The cause of these changes is the complicated crystal structure and structural changes of the crystal caused primarily by the thermal influence on hydrogen bonds. The copper-chlorine complex changes its geometry from planar to deformed tetrahedral and the appropriate rearrangement of the d-orbitals of the copper atom will occur. At high temperatures, the tetrahedral arrangement of the crystal is associated with weak hydrogen bonds between the chlorine ions and the copper ion (yellow phase). At low temperatures, organic groups participate in the formation of a two-dimensional network of strong hydrogen bonds that stabilize the planar arrangement (green phase). [10]

Unlike continuous thermochromism, which describes gradual color changes, DEA-CuCl$_4$ is characterized by discontinuous thermochromism, where a dramatic color change occurs at a certain temperature or a small temperature range.

The electrical properties of DEA-CuCl$_4$ have not yet been described. However, because of the similarity of the molecular structure with organic-inorganic hybrids of perovskites, which have been intensively researched in recent years as promising materials for solar cells, a similarity in electrical behavior can also be assumed. Halide perovskites exhibit a mixed conductivity with the contributions of both ions and electrons. The relatively high mobility of their halide ions is the cause of ionic conductivity and point defects such as impurities, vacancies or interstitials determine the transport of electrons. [11-13]

Like perovskites, the problem of DEA-CuCl$_4$ dye is its poor stability regarding humidity, heat, light, and oxygen. [14,15] DEA-CuCl$_4$ tends to react with a lot of chemicals and substrates, which subsequently leads to the loss of thermochromic properties. However, we found that the dye is well compatible with silica and silicon-based compounds, so we created a relatively stable composite in which we used silica fibers as a dye carrier and a transparent methyl silicate resin as a protective layer of the composite.

The aim of this pilot study is to investigate the sensory capabilities of the complex dye DEA-CuCl$_4$ incorporated into a composite of silica fibers and methyl silicate resin.
2 Materials and methods

2.1 Composite preparation

Smooth silica filament in the shape of a flat tape (width 5 mm, thickness 0.15 mm, basis weight 235 g/m², linear mass density 1200 tex), composed of approx. 300 glass filaments (filament diameter 16 µm) from BTTO, s.r.o. (CZ) was used as a dye carrier. The crystalline pigment DEA-CuCl₄ was prepared in the laboratory by the method of slow evaporation at room temperature based on [10] from aqueous solutions with a stoichiometric ratio of 2:1 of diethyl ammonium hydrochloride (C₄H₁₂ClN) and copper (II) chloride dihydrate (CuCl₂ · 2H₂O), both from Sigma – Aldrich (US). The mixed solutions were poured into a wide flat glass dish where slow evaporation and crystallization occurred at room temperature. The crystalline dye was then mechanically crushed using a glass apothecary mortar and pestle to form a fine powder with a particle size of 200 nm to 2 µm (Fig.1). This fine green powder was then rubbed into the glass yarn on both sides. A xylene solution of methyl silicate transparent resin (Lukosil M130, Lukopren, CZ) was used to fix the dye on the glass tape and to strengthen the composite after its thorough drying at temperatures of 22 - 40 °C (Fig.2).

![Fig. 1. Crushed particles of DEA-CuCl₄ with a size of 200 - 2000 nm.](image)

2.2 Measurement and characterization methods

To measure and characterize the silica/DEA-CuCl₄ composite, optical methods (Levenhuk DTX 30 digital microscope (Levenhuk, US), Levenhuk optical microscope (Levenhuk, US), UHR FE-SEM ZEISS Ultra Plus electron microscope (Carl Zeiss AG, DE), UV-VIS 2000 spectrophotometer (Mapada Instruments Co., CN)), electrical resistance measurement (Metex M-3270 multimeter, Metex Corporation, KR), and temperature changes measurement (non-contact IR industrial thermometer Fluke 568 (Fluke Corporation, US)) were used.
3 Results and discussion

3.1 Morphology

![Fig. 2. Silica/DEA-CuCl$_4$/methyl silicate resin composite (40x).](image)

The dye coated silica tape was weighed before the protective methyl silicate resin was applied and the basis weight of this intermediate was 270 g/m$^2$. From the difference between this value and the weight of pure silica tape, it follows that approximately 35 g of DEA-CuCl$_4$ crystalline dye per 1 m$^2$ was applied to the silica carrier, which is approximately 1.75 µg of dye applied per 1 cm of the composite length. This amount can also be expressed as 15% of the weight of the silica carrier.

Table 1 shows a comparison of the dimensions, area weight, and surface properties of the pure silica fibers carrier and the silica/DEA-CuCl$_4$ with methyl silicate resin composite.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Pure silica tape</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.15 mm</td>
<td>0.30 mm</td>
</tr>
<tr>
<td>Basis weight</td>
<td>235 g/m$^2$</td>
<td>375 g/m$^2$</td>
</tr>
<tr>
<td>Water contact angle</td>
<td>80.4° ± 5.7° (a)</td>
<td>94.8° ± 3.7°</td>
</tr>
<tr>
<td>Iodomethane contact angle</td>
<td>immediately absorbed</td>
<td>67.7° ± 5.4°</td>
</tr>
<tr>
<td>Surface free energy (b)</td>
<td>47.4 mJ/m$^2$</td>
<td>27.6 mJ/m$^2$</td>
</tr>
</tbody>
</table>

(a) absorbed after 10–15 seconds  
(b) calculated according to Owens – Wendt model

The crystalline dye DEA-CuCl$_4$ is well soluble in water. The protective methyl silicate resin prevents the dye from being rubbed or washed off from the silica carrier.
and additionally gives the composite a hydrophobic surface. The contact angle of the composite surface with the water drop was over 90° (based on 20 measurements). At the same time, the surface free energy decreased by almost half, which, together with the value of the contact angle of the water drop, indicates good resistance and hydrophobicity of the composite surface.

3.2 Thermochromic properties

Spectrophotometric measurement of the dry crystalline dye DEA-CuCl₄ was performed at temperatures of approximately 15 and 60 °C, i.e., at temperatures below and above the transition temperature point, which visually corresponds to the yellow and bright green color of the dye (Fig.3). Above the transition temperature, the green color of the dye suddenly changes to yellow: in the graph, this transition was manifested by a slight shift of both peaks of absorption maxima to the right (bathochromic shift) and a more significant increase in absorbance (hyperchromic shift).

![Spectrophotometric curves of the yellow and green form of the DEA-CuCl₄ crystal.](image)

Pure silica fibers have a low thermal conductivity (1.38 W/m·K), which means that it transfers heat at a low rate compared to other materials (such as metals). This low thermal conductivity can also be described as high thermal resistance, and this affected the discontinuous thermochromism of the DEA-CuCl₄ dye. Slow heat propagation in the composite was manifested by color inhomogeneities of the thermochromic transition: upon reaching the transition temperature, the color change first appeared at the edges of the composite and from there gradually and slowly spread to its center. A partial color transformation of the dye (from green to yellow) already occurred when the composite was heated to a temperature of around 42 °C. Due to the thermal capacity of the silica carrier and methyl silicate resin, the color change of the entire surface
of the composite was relatively slow and, above all, inhomogeneous. This can be a problem for sensors requiring a fast response, from another point of view, this slow full-surface color conversion can be used to indicate a temperature interval or time duration of a critical temperature.

### 3.3 Electrical properties

Electrical resistivity (or specific electrical resistance) is a material constant that indicates how strongly it resists electric current. The greater the resistivity, the smaller the conductivity of the substance and the greater the electrical resistance. The resistivity of materials depends on temperature. For metal conductors it increases with temperature, for semiconductors it decreases. The unit of electrical resistivity is the ohmmeter (Ω⋅m). Electrical resistivity \( \rho \) was calculated from the equation (1),

\[
\rho = \frac{R \cdot A}{L}
\]

where \( R \) is the resistance of the conductor, \( A \) is the cross-sectional area and \( L \) is the length of the conductor. The resistance \( R \) was measured as the surface resistance of the composite with a digital multimeter Metex M-3270 with a range of 400 Ω - 40 MΩ under the 9 V DC power supply, using electrodes with nickel-plated steel alligator clips, at the pressure 2.3 kPa, temperature \( T = 21 \) °C and the relative humidity \( \text{RH} = 54 \% \). The calculated resistivity from the thickness and width of silica/DEA-CuCl\(_4\) composite and distance between electrodes is around 500 Ω⋅m at room temperature. (For comparison: common metals have resistivity values of \( 10^{-7} \) to \( 10^{-8} \) Ω⋅m, silicon \( 10^{3} \) Ω⋅m, glass \( 10^{11} – 10^{15} \) Ω⋅m at 20 °C [16]).

![Temperature-dependent resistance curve of the silica/DEA-CuCl\(_4\) composite.](image)

The electrical changes were easily measurable and independent of the color phase transition of the dye, respectively the composite, even though these values ranged in
megaohm values. As can be seen in Fig.4, the surface resistance increased when heated above room temperature, as we would expect from a normal conductor. The behavior of the composite in the temperature range between 4 and 24 °C was unusual and interesting. The surface resistance demonstrably decreased with increasing temperature, which is behavior typical for semiconductors, repeatedly during 10 cycles when the composite was placed alternately for 20 seconds in a chamber with a temperature of 4 or 24 °C.

4 Conclusions

In this study, we tried to outline the sensory use possibilities of the crystalline thermochromic dye DEA-CuCl₄. We found that this dye, despite its considerable instability and reactivity, can be quite successfully incorporated in the form of a powder with a particle size of 200 nm to 2 μm into a filamentous silica carrier and covered with a protective layer of methyl silicate resin.

The color transformation of the composite was observed at a temperature of around 42 °C. The composite responded to changes in temperature with a color phase transition, which was slowed down due to the low thermal conductivity of the silica fibers and showed partially continuous thermochromism.

The previously unpublished electrical properties of the DEA-CuCl₄ dye showed some similarity to structurally related organic-inorganic hybrid halide perovskites, which are investigated as promising materials for solar cells. The electrical resistivity of the silica/DEA-CuCl₄ composite was calculated at around 500 Ω·m at room temperature. Measurements indicated that in the temperature range of 4 to 24 °C the dye DEA-CuCl₄ behaves as a semiconductor, while at higher temperatures it exhibits behavior of conductors.

This pilot study suggests the sensory potential of the DEA-CuCl₄ dye, which provides both a visual color and electrical responses to a thermal stimulus. However, the disadvantage of the dye remains its significant reactivity and instability regarding humidity, heat, light, and oxygen, which must be resolved if the dye is to be used as a sensor in practice.

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