

Visible-to-Infrared Converting $\text{CaCuSi}_4\text{O}_{10}$ Security Ink

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Abstract

A blue silicate, cuprorivaite ($\text{CaCuSi}_4\text{O}_{10}$), with strong conversion of visible input to infrared emission at around 910 nm, was previously demonstrated for use as a micron scale powder for latent fingerprint imaging. In this research, we prepare a cuprorivaite powder and subject it to mechanochemical treatments that organically modify and exfoliate the material to produce a pigment ideal for ink formulation. The prepared ink was then used to print a security feature.

Introduction

Visible-to-IR and IR-to-IR conversion materials have been gaining traction as potential security materials because of their ability to generate a covert signal from either a covert or overt feature that is difficult to replicate. NaYF_4 with various combinations of lanthanide doping have demonstrated impressive IR-IR upconversion. Several visible-to-IR materials exist, but often contain elements such as lead, tellurium, or selenium. Cuprorivaite has recently gained attention in security marking due to its visible-to-IR capabilities, non-toxic nature, and relatively easy production (1). A major hindrance towards the fabrication of a security ink utilizing cuprorivaite is often the large particle sizes yielded by its various synthesis methods (2)(3). Cuprorivaite is similar to phyllosilicates, where sheets of a copper silicate alternate with layers of alkali earth cations. However, the lack of hydrated galleries results in a rigid crystal that is not easily exfoliated. Current attempts at exfoliation require weeklong stirring in boiling water, or ultrasonication in organic solvents (4). In this research, we attempt to apply a similar strategy found in smectite clay organo-modification to intercalate and exfoliate cuprorivaite. If successful, the exfoliated material could be ideal for ink formulation due to nanoscale feature sizes alongside organically modified surfaces that can widen the number of solvents allowed for ink formulation.

This conversion of a bulk clay to a nanoscale organo-clay has been demonstrated in the literature for a variety of materials (5)(6). Typically, a shear force was applied to the particles in the presence of an ammonium salt that can replace the gallery ionic species. The shear force can be applied through methods such as twin-screw extrusion or ball milling, while the cation exchange was mediated by alkylammonium salts dissolved in aqueous solutions. Attrition milling provides an ideal scenario for particulate modification as particles are slowly reduced in size, and alkylammonium cations can exchange as particle surfaces are exposed. One caveat is that the organic species may be limited in its ability to intercalate if its molecular volume is too large relative to the gallery size. The exchanged alkylammonium species can allow further intercalation of larger organic species, such as alkylsilanes, that can result in exfoliation of the material. Once an exfoliated and surface-modified material is produced, ink formulation can commence.

Experimental

$\text{CaCuSi}_4\text{O}_{10}$ was prepared in a solid-state reaction involving stoichiometric amounts of calcium carbonate, copper monoxide, and SiO_2 . Powders were ground in a mortar and pestle with acetone to produce a homogenous premixture. The acetone was allowed to evaporate, and the dry powder mixture was fired at 1000°C for three hours.

The resultant cuprorivaite powder was added to an attrition mill with tetraoctyl ammonium bromide (TOAB) and zirconia grinding media in a 1:5:240 weight ratio. Water was added to cover the mixture (approximately 50 mL). The attritor was then operated at 1600 rpm for three hours.

Grinding media was separated from the mixture with a sieve, and the resulting solution was centrifuged at 3000 rpm for 10 minutes. The supernatant of this solution was discarded. Excess TOAB was removed by adding 20 mL of toluene to the resultant powder, followed by vortexing at 3000 rpm for five minutes. This solution was then centrifuged at 3000 rpm for 10 minutes and the supernatant discarded. This cleaning procedure was conducted a total of three times.

A 5 wt% solution of trichloro(octadecyl) silane (TCOS) in ethanol solution was prepared and the TOAB modified particles were immediately added. The solution quickly changed from dark blue to a grey color. A precipitate was formed and allowed to settle out of the solution, followed by decanting of the supernatant. Excess TCOS was cleaned by the same procedure described for TOAB cleaning.

The final collected material has a wax-like consistency and was subjected to Hansen solubility parameter (HSP) characterization as described here (7).

A final ink composition was chosen as 0.5 wt% modified cuprorivaite dissolved in toluene. 2 mL of this ink was prepared and printed with an Optomec M3D aerosol jet printer using a 300 μm nozzle and a 3 mm/s path speed.

Results

$\text{CaCuSi}_4\text{O}_{10}$ was characterized by X-ray diffraction (XRD), diffuse reflectance Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and photoluminescence spectroscopy. During each processing step, XRD data was collected to determine if exfoliation had occurred, based on a change in lattice spacings of the material. SEM was used to determine particle morphology. FTIR was used to confirm the presence of organic materials after both milling in TOAB solution and silane treatment to determine the presence of intercalation and exfoliation by each organic respectively. photoluminescence spectroscopy was conducted to determine the effects of exfoliation on the emission spectrum and decay time.

XRD analysis of untreated $\text{CaCuSi}_4\text{O}_{10}$ confirmed the correct crystal structure (Figure 1a) with lattice parameters 0.7 nm and 1.5 nm, with narrow peaks implying micron-scale particle sizes. After milling in TOAB solution, the peak-widths slightly broaden with no

major change in peak shift, implying a reduction in particle size with no exfoliation (Figure 1b). After silane treatment, both peak broadening and peak shifting resulted, implying exfoliation of the material (Figure 1c).

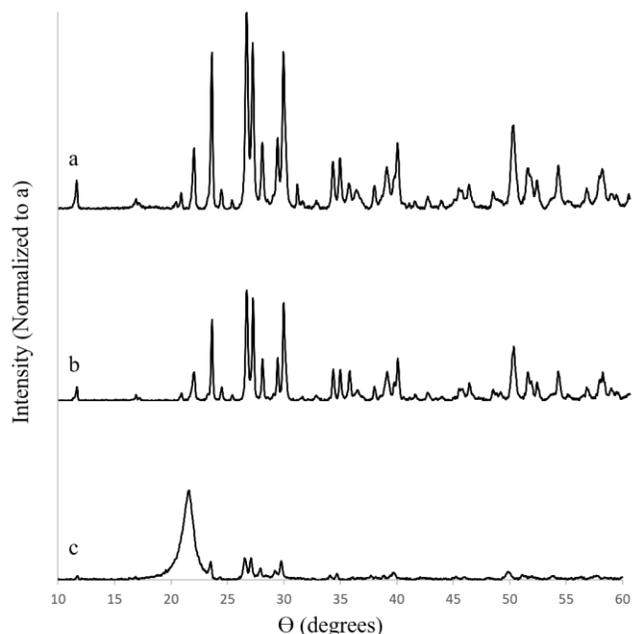


Figure 1. XRD of unmilled (a), milled in TOAB (b), and silane treated (c) $\text{CaCuSi}_4\text{O}_{10}$

SEM of untreated and subsequently exfoliated cuprorivaite can be seen in Figures 2 and 3. Particle size was reduced and exfoliation becomes apparent from the flake-like morphology of the imaged material in Figure 3.

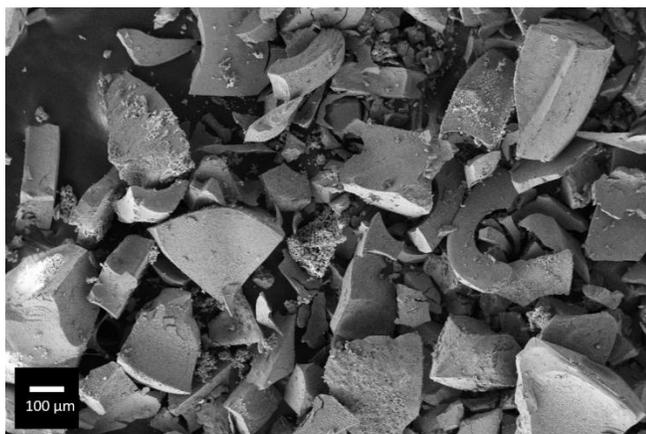


Figure 2. SEM image of untreated $\text{CaCuSi}_4\text{O}_{10}$

FTIR spectra of unmilled, milled in TOAB, and silane-treated cuprorivaite are displayed in Figures 4a-c. From unmilled to TOAB solution milled, bands appear between 2800-3000 cm^{-1} and at $\sim 1475 \text{ cm}^{-1}$ corresponding with C-H stretching and bending bands, respectively. After silane treatment, bands appear at 1675 cm^{-1} with a broad peak centered at 3350 cm^{-1} corresponding to OH bending and stretching.

The TOAB and TCOS modified cuprorivaite was characterized via photoluminescence spectroscopy. Under 621 nm excitation,

emission occurred from 780 to 1050 nm, with full width at half max of 120 nm centered on 915 nm, as seen in Figure 5. Lifetimes were measured to be 119 μs for the unexfoliated material and 42 μs for the TOAB- and TCOS-modified material. The reduction in lifetime of the exfoliated material is due presumably to the increased surface quenching effects resulting from the dramatic increase in the material's surface area.

Hansen solubility parameter (HSP) characterization showed dispersion of the material in chlorobenzene, p-xylene, toluene, and mesitylene, with settling in acetone, methanol, ethanol, dodecane, chloroform, methyl benzoate, 1-hexanol, and acetonitrile. These data points were analyzed in Hansen solubility parameters in Practice software to yield HSPs of δd : 18.4 δp : 2.5 δh : 1.7, with R: 2.3.

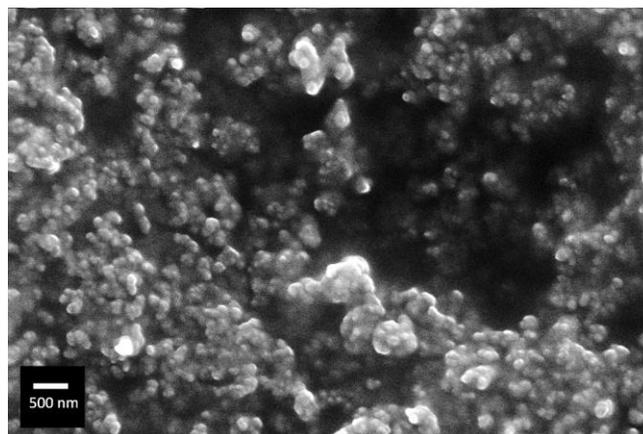


Figure 3. SEM of TOAB and TCOS treated $\text{CaCuSi}_4\text{O}_{10}$

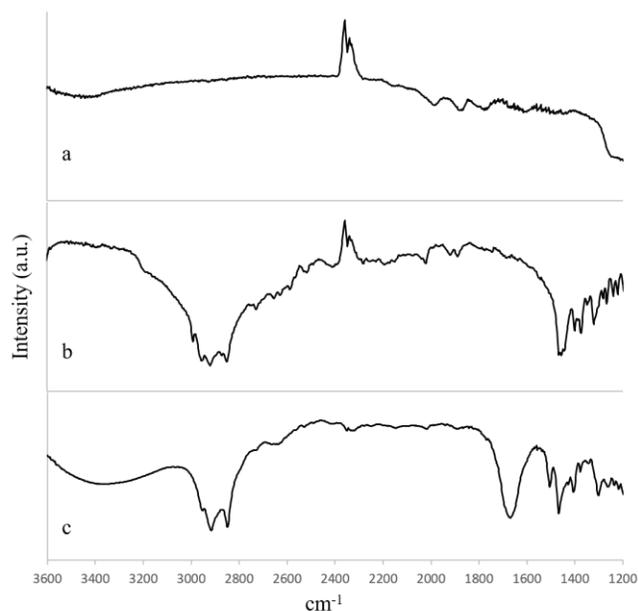


Figure 4. FTIR spectra of unmilled (a), milled in TOAB (b), and silane treated (c) $\text{CaCuSi}_4\text{O}_{10}$

Consequently, an ink formulation was prepared with 2 mL of toluene and 0.5 wt% nanoparticles. The ink was printed using an

Optomec M3D printer with a 300 μm tip, producing a security feature that was imaged in fluorescence mode under both visible and > 830 nm illumination on a Foster-Freeman video spectral comparator (VSC6000). See Figure 6.

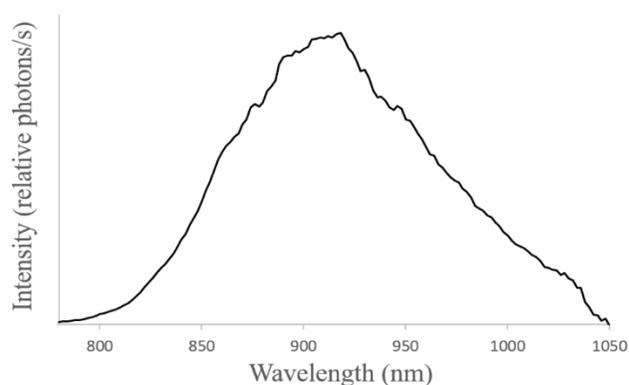


Figure 5. Luminescence spectrum of TOAB-TCOS modified cuprorivaite under 621nm excitation

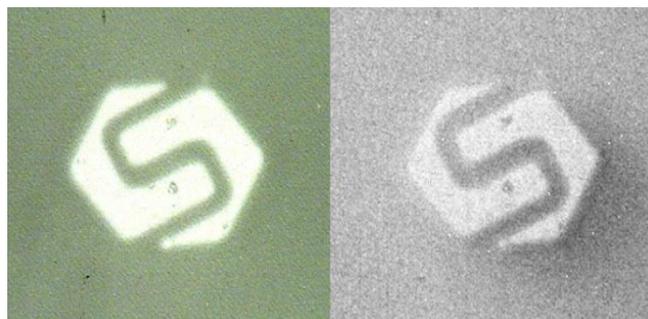


Figure 6. VSC6000 fluorescence imaging of printed cuprorivaite on a glass slide under 500-800 nm light (left) with an 830 nm longpass filter (right)

Discussion

Exfoliation of smectite clays relies on the galleries containing water-cation complexes. When placed in aqueous solutions, these complexes exchange cations and absorb water with the surrounding solvent. Cuprorivaite is a class of phyllosilicate that contains only alkaline earth cations in the gallery spaces, which appears to inhibit large molecule cation exchange. Attempts were made to use different alkylammonium salts such as butylammonium chloride and cetyltrimethylammonium bromide to intercalate the material without milling. Similarly, material was milled in water and then subjected to alkylsilane treatment. In these cases, no effective change in the galleries were noticed when these materials were analyzed using XRD and FTIR. However, SEM images indicated the particle size decreased from milling.

In the presented work, the specific combination of milling in a TOAB solution followed by silane treatment appears to exfoliate the material. Ion exchange between TOAB and Ca^{+2} may have slightly expanded the lattice while simultaneous milling exposed particle surfaces for enhanced ion exchange. Indirect confirmation of this process can be seen with the FTIR spectra of the material milled in a TOAB solution prior to silane treatment, where C-H groups alter the unmodified cuprorivaite spectrum. However, XRD analysis at this step shows virtually no change in lattice spacing, suggesting that

the alkyl groups may be present in the galleries, but the groups have not significantly expanded the lattice of the material.

After the material was treated with TCOS, significant changes in the FTIR spectra resulted. FTIR indicated the presence of C-H (bands near 1470 cm^{-1} and 2920 cm^{-1}) and -OH (bands at 1670 cm^{-1} and 3300 cm^{-1}) groups.

The exfoliated material has a few novel characteristics. When initially exposed to a solvent without heat, dissolution did not occur. However, the material softened and began to dissolve when heated with the aid of sonication. These requirements for dissolution imply good coverage of the capping agent, and strong interaction between the capping agents of two particulates that require work to separate individual layers of material. XRD of the isolated products did not correspond with bulk cuprorivaite diffraction data, but instead showed that most of the material had plane spacing centered at 0.21 nm, corresponding to the extended molecular length of a TCOS molecule.

Once an ink formulation was chosen, and the patterns were printed, an infrared emitting security feature was produced. Imaging of these features using the VSC6000 displayed a proof of concept for a security feature, where 500-800 nm illumination of the printed material produced a corresponding feature with infrared emission centered around 910 nm. These results indicate cuprorivaite has a broad capability of being incorporated into security inks. While TCOS was used as the final silane treatment, many other silanes could serve as potential means to exfoliate and modify the surface to have varying degrees of polarity for a desired ink composition or printer requirements.

Conclusion

$\text{CaCuSi}_4\text{O}_{10}$ was prepared from a solid state reaction followed by attrition milling in a TOAB solution to produce an organomodified material. The addition of TCOS exfoliates $\text{CaCuSi}_4\text{O}_{10}$ and modifies its surface chemistry to be non-polar, enabling its use as a security ink with a range of potential solvents. The exfoliated cuprorivaite was then incorporated into a non-polar ink formulation, and printed using an aerosol-jet printing system. The printed patterns imaged with a VSC6000 show potential as a visible-to-infrared security feature. Alternating the choice of silane or growing polymers with the use of functional silanes in situ expands the potential application of cuprorivaite in security printing.

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Author Biography

Jacob Petersen received his BS in Materials Science and Engineering from the University of California Merced (2012) and his MS in Materials Engineering and Science from the South Dakota School of Mines and Technology in 2014. He is currently pursuing a PhD in materials Engineering and Science from the South Dakota School of Mines and Technology, focusing on printed nanocomposites.

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