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Nanoscience of an Ancient Pigment

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Supporting Information

ABSTRACT: We describe monolayer nanosheets of calcium copper tetrasilicate, $CaCuSi_4O_{10}$, which have strong near-IR luminescence and are amenable to solution processing methods. The facile exfoliation of bulk $CaCuSi_4O_{10}$ into nanosheets is especially surprising in view of the long history of this material as the colored component of Egyptian blue, a well-known pigment from ancient times.

"Egyptian blue" is an inorganic material with tremendous cultural significance. This term refers to a complex, sintered mixture of primarily $CaCuSi_4O_{10}$ and SiO_2 (both glass and quartz) that has the distinction of being the first synthetically produced pigment in human history; historical and archeological evidence indicates that it already was being manufactured during the third millennium BC.[1,2] Egyptian blue was used extensively for decorative purposes in ancient Egypt, Mesopotamia, Greece, and the geographical expanse of the Roman Empire. Many specimens have survived until the present under unfavorable environmental conditions, and from an archeological perspective, Egyptian blue is viewed as a relatively durable pigment.[2,3]

Modern scientific efforts to prepare and characterize Egyptian blue began during the 19th century, in large part prompted by the spectacular discoveries made during excavations at Pompeii.[4] The source of the brilliant blue color is square-planar Cu^{2+} linked by $[SiO_4]$ tetrahedra (Figure 1a),[5] but relatively little is known about the chemical reactivity of $CaCuSi_4O_{10}$, aside from observations of decomposition above 1000−1080 °C and claims that the pigment is acid-resistant.[2,4,6−8] Therefore, we were surprised to discover that the $CaCuSi_4O_{10}$ in Egyptian blue delaminates under remarkably simple reaction conditions: hot water. Stirring Egyptian blue in 80 °C water for several days provides a colloidal dispersion that includes both nanosheets (<10 nm thick) and nanoplatelets (>10 nm thick) of $CaCuSi_4O_{10}$. After purification and isolation, this product is pale blue-gray in dry powder form (Figure S1 in the Supporting Information), which is consistent with prior observations of color tone versus grain size, an effect that originates in the dichroic properties of $CaCuSi_4O_{10}$.[2,9]

Transmission electron microscopy (TEM) reveals that the lateral dimensions of the nanosheets are several hundred nanometers to several micrometers in length (Figure 1b). The carbon support of the TEM grid is clearly visible through the thin $CaCuSi_4O_{10}$. Upon sonication in toluene, any multilayer nanosheets in the dispersion further exfoliate into sheets with a thickness of only ~1.2 nm, as measured by atomic force microscopy (AFM) (Figure 1c). This thickness is consistent with an individual $CaCuSi_4O_{10}$ monolayer (~0.9 nm, Figure 1a) plus a contribution from surface hydration on both the nanosheet and silicon surfaces.

The results of diffraction analyses are uniquely consistent with exfoliation via basal cleavage along the (001) plane. The X-ray diffraction (XRD) pattern of the nanosheets matches the ditetragonal-dipyramidal structure of $CaCuSi_4O_{10}$, although the relative peak intensities also indicate a preferred orientation along the $\{00l\}$ series and show that $\{hk0\}$ peaks are diminished (Figure 2). The selected-area electron diffraction (SAED) pattern (Figure 1b inset) exhibits square symmetry with interplanar angles of 90°. The pattern can be indexed exactly to the (200) and (020) reflections, which provides a zone axis of [001]. In addition, the two-dimensional nanosheets can be reassembled by annealing at 900 °C; the resulting product's three-dimensional, bulklike character is manifested by the increased intensities of the $\{hk0\}$ reflections along with the reappearance of the rich color characteristic of Egyptian blue (Figure S1).

One of the most interesting features of Egyptian blue is its strong near-IR emission properties (luminescence quantum yield of 10.5% at 910 nm).[10] Both photoluminescence spectroscopy and near-IR digital imaging show that this near-IR emission is preserved in exfoliated samples of $CaCuSi_4O_{10}$ (Figure 3). In addition, excitation spectra show that the nanosheets have a feature at 540 nm (corresponding to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square-planar field) that is less intense than the corresponding peak for three-dimensional samples because of reduced vibronic coupling in the two-dimensional form of $CaCuSi_4O_{10}$.

Colloidal dispersions of $CaCuSi_4O_{10}$ nanosheets can be processed in a variety of ways, including ink-jet printing. Using a materials printer and an ink of $CaCuSi_4O_{10}$ nanosheets dispersed in *N*-methylpyrrolidone, we printed a pattern of twelve 5 mm^2 squares on glass (Figure 1d). The luminescence of this pattern is clearly visible during near-IR imaging.

A further interesting question is whether water-mediated $CaCuSi_4O_{10}$ delamination affects archeological samples. It seems likely that under aqueous conditions, $CaCuSi_4O_{10}$ delamination should occur on exposed Egyptian blue surfaces where the SiO_2 matrix and pigment binders have already deteriorated through known alteration processes (e.g., SiO_2 dissolution).[3b] Even though delamination is slow at temperatures <40 °C, the reaction time scale for ancient samples is very long. Both our own examination of archeological Egyptian blue (by scanning electron microscopy) and examples in the literature[7,8] show the presence of nanoplatelets in various

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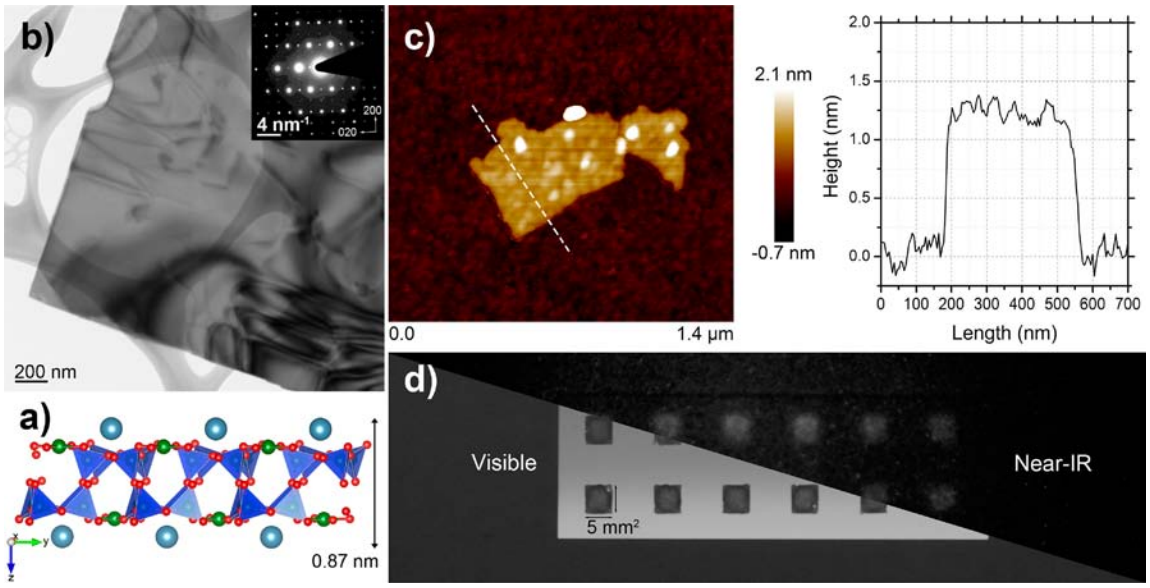

Figure 1. (a) Side view of the structure of a single layer of $CaCuSi_4O_{10}$ (green spheres = Cu, red spheres = O, blue spheres = Ca). (b) TEM image of a $CaCuSi_4O_{10}$ nanosheet. The inset shows the SAED pattern. (c) Topographic AFM image of a $CaCuSi_4O_{10}$ nanosheet (left) and height profile along the dotted line (right). (d) Visible and near-IR images of a pattern of squares printed using a $CaCuSi_4O_{10}$ nanosheet ink.

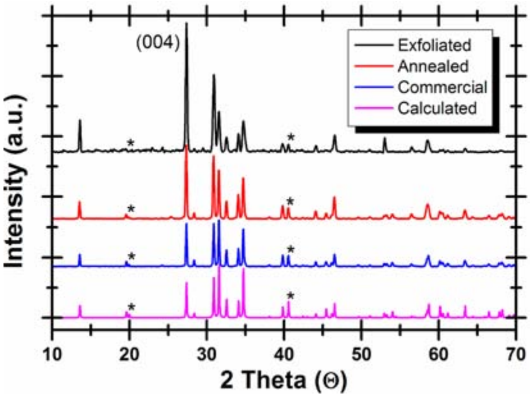

Figure 2. Powder XRD data for exfoliated $CaCuSi_4O_{10}$ nanosheets, recrystallized (annealed) $CaCuSi_4O_{10}$ nanosheets, and commercial Egyptian blue along with a calculated pattern for $CaCuSi_4O_{10}$. Asterisks mark the diminishing (110) and (220) peaks.

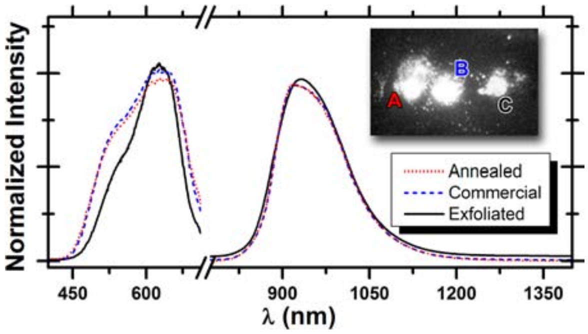

Figure 3. Excitation and emission spectra of powder samples of commercial Egyptian blue (Kremer Pigment), exfoliated $CaCuSi_4O_{10}$ nanosheets, and recrystallized (annealed) nanosheets. The inset shows a luminescence image of the three powder samples.

degrees of detachment from $CaCuSi_4O_{10}$ surfaces. However, similar features can be produced by the mechanical cleavage of $CaCuSi_4O_{10}$, so we cannot distinguish between the products of these different delamination mechanisms.

Although the first 5000 years of Egyptian blue's history were dominated by pigment applications, the exfoliation of $CaCuSi_4O_{10}$ provides a route to a new class of two-dimensional nanomaterials that are particularly interesting with respect to state-of-the-art pursuits like near-IR-based biomedical imaging,[11] IR light-emitting devices (especially telecommunication platforms), and security ink formulations. In this way we can reimagine the applications of an ancient material through modern technochemical means.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and optical images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Warner, T. E. *Synthesis, Properties and Mineralogy of Important Inorganic Materials*; Wiley: Hoboken, NJ, 2011. (b) Berke, H. *Chem. Soc. Rev.* **2007**, *36*, 15−30. (c) Pradell, T.; Salvado, N.; Hatton, G. D.; Tite, M. S. *J. Am. Ceram. Soc.* **2006**, *89*, 1426−1431. (d) Jaksch, H.;

Seipel, W.; Weiner, K. L.; El Goresy, A. *Naturwissenschaften* **1983**, *70*, 525−535.

(2) Riederer, J. Egyptian Blue. In *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol. 3; Fitzhugh, E. W., Ed.; National Gallery of Art: Washington, DC, 1997.

(3) (a) *Tracking Colour: The Polychromy of Greek and Roman Sculpture in the Ny Carlsberg Glyptotek*; Østergaard, J. S., Ed.; Ny Carlsberg Glyptotek: Copenhagen, 2012. (b) Kakoulli, I. *Greek Painting Techniques and Materials from the Fourth to the First Century BC*; Archetype Books: London, 2009. (c) *Art and Eternity: The Nefertari Wall Paintings Conservation Project, 1986−1992*; Corzo, M. A., Afshar, M., Eds.; The Getty Conservation Institute: Los Angeles, 1993.

(4) Davy, H. *Philos. Trans. R. Soc. London* **1815**, *105*, 97−124.

(5) (a) Hughes, E. M.; Pack, M. J.; Dann, S. E.; Weller, M. T. *An. Quim. Int. Ed.* **1997**, *93*, 233−236. (b) Mirti, P.; Appolonia, L.; Casoli, A.; Ferrari, R. P.; Laurenti, E.; Amisano Canesi, A.; Chiari, G. *Spectrochim. Acta* **1995**, *51A*, 437−446. (c) Pabst, A. *Acta Crystallogr.* **1959**, *12*, 733−739.

(6) (a) Mazzocchin, G. A.; Rudello, D.; Bragato, C.; Agnoli, F. *J. Cult. Heritage* **2004**, *5*, 129−133. (b) FitzHugh, E. W.; Zycherman, L. A. *Stud. Conserv.* **1992**, *37*, 145−154.

(7) Canti, M. G.; Heathcote, J. L. *J. Archaeol. Sci.* **2002**, *29*, 831−836.

(8) Bayer, G.; Wiedemann, H. G. *CLB, Chem. Labor Betr.* **1976**, *27*, 432−437.

(9) (a) Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *The Pigment Compendium: A Dictionary of Historical Pigments*; Butterworth-Heinemann: Oxford, U.K., 2005. (b) Tite, M. S.; Bimson, M., Cowell, M. R. Technological Examination of Egyptian Blue. In *Archaeological Chemistry III*: Lambert, J. B., Ed.; Advances in Chemistry Series, Vol. *205*; American Chemical Society: Washington, DC, 1984. (c) Chase, W. T. Egyptian Blue as a Pigment and Ceramic Material. In *Science and Archaeology*; Brill, R. H., Ed.; MIT Press: Cambridge, MA, 1971.

(10) (a) Accorsi, G.; Verri, G.; Bolognesi, M.; Armaroli, N.; Clementi, C.; Miliani, C.; Romani, A. *Chem. Commun.* **2009**, *23*, 3392−3394. (b) Verri, G. *Anal. Bioanal. Chem.* **2009**, *394*, 1011−1021. (c) Pozza, G.; Ajò, D.; Chiari, G.; De Zuane, F.; Favaro, M. *J. Cult. Heritage* **2000**, *1*, 393−398.

(11) Pansare, V. J.; Hejazi, S.; Faenza, W. J.; Prud'homme, R. K. *Chem. Mater.* **2012**, *24*, 812−827.