Cryogenic FIB Lift-Out Reveals Atomic-Scale Photoactive Homojunctions in Cadmium Yellow Paint from Matisse's "Flower Piece"

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Microscopy and Microanalysis, **30** (Suppl 1), 2024, 118–120
https://doi.org/10.1093/mam/ozae044.057

Microscopy AND Microanalysis

Meeting-report

Cryogenic FIB Lift-Out Reveals Atomic-Scale Photoactive Homojunctions in Cadmium Yellow Paint from Matisse's "Flower Piece"

Michael Colletta[1], Barnaby D.A. Levin[2], Jennifer L. Mass[3], Adam C. Finnefrock[4], and David A. Muller[1,5,*]

[1]*School of Applied and Engineering Physics, Cornell University, Ithaca, NY, USA*
[2]*Direct Electron L.P., San Diego, CA, USA*
[3]*Bard Graduate Center, New York, NY, USA*
[4]*Scientific Analysis of Fine Art LLC, New York, NY, USA*
[5]*Kavli Institute for Nanoscale Science, Cornell University, Ithaca, NY, USA*

*Corresponding author: david.a.muller@cornell.edu

Cadmium-sulfide-based yellows, which can be found in works by Edvard Munch, Vincent Van Gogh, Henri Matisse, and their contemporaries, are known to suffer from severe degradation issues, including discoloration, flaking, and whitening [1–3]. The major preservation challenges with this color are linked to the cadmium sulfide pigment itself, which is a photocatalyst for visible light. These particles may react with their surroundings, including moisture, air, and paint binder through photodegradation. Crucially, the structure of these CdS particles may play an important role in the speed of degradation, as previous studies have shown that stacking faults in similar photocatalysts can greatly impact their photocatalytic efficiency [4]. In addition, previous work has also shown evidence of such disorder within similar paint samples [5]. This emphasizes the need for thorough, direct characterization of these paints in order to better understand what it is about cadmium yellow paints from the late 19th and early 20th centuries that cause such rapid degradation. Here in this work, we present high resolution cryogenic scanning transmission electron microscopy (cryo-STEM) structural analysis of cadmium yellow paint from the 1906 version of Henri Matisse's "Flower Piece" (Figure 1a), enabled through the use of advanced cryogenic focused ion beam (cryo-FIB) sample preparation methods.

One of the main challenges in studying these historic paint samples in STEM is achieving high quality, electron transparent lamella. Traditional sample preparation techniques such as the FIB-based "lift-out" method are particularly challenging due to the poor structural integrity of the sample, which consists of a soft linseed oil paint binder that holds the cadmium particles together. This soft material can create severe bending and voiding in the lamella throughout the thinning process, ultimately leading to a thick sample that limits the spatial resolution achievable in TEM. By utilizing the cryo-FIB, the paint lamella can be cooled to -175°C, hardening the binder and allowing for sufficient thinning down to <50 nm (Figure 1b).

While at micron to submicron-scale resolution of x-ray and Raman spectroscopies, the CdS paint might appear as a singular solid flake, high-resolution cryogenic STEM imaging reveals that it in fact consists of an agglomeration of nanoparticles, each ~5 nm in diameter (Figure 1c). With our thinner samples, we are able to directly resolve the structural disorder within single CdS nanoparticles (Figure 1d). CdS possesses two distinct stable crystalline phases in its bulk form: a polar, hexagonal wurtzite structure and a non-polar, cubic zinc-blende structure, otherwise known as greenockite and hawleyite respectively (Figure 1e). Within a single nanoparticle, we can resolve several phase boundaries, including twinned cubic and cubic-hexagonal boundaries. These nanoparticle homjunctions are important to resolve as they have been shown to improve charge separation within similar materials, which in turn leads to highly efficient photocatalytic activity [4].

We are able to readily visualize the domain boundaries between the cubic and hexagonal phases as well as any collection of random stacking sequences by mapping the local Cd-Cd bond angle (Figure 2a,b). Using integrated differential phase contrast (iDPC) STEM imaging, we can detect the orientation of the much lighter sulfur atoms within these nanoparticles (Figure 2b-c). With this information, we can more accurately identify 'ABA', 'ABC', and polytype stacking sequences in the CdS nanoparticles. With the advancement of cryo-FIB sample preparation, we can now access the angstrom scale structures within cadmium yellow paint via sufficiently thinned samples. This work aims to use this information to enable a better understanding of the mechanisms for degradation in these historical paints as well as the relationship between the photocatalytic activity of these particles and the local atomic structure [6].

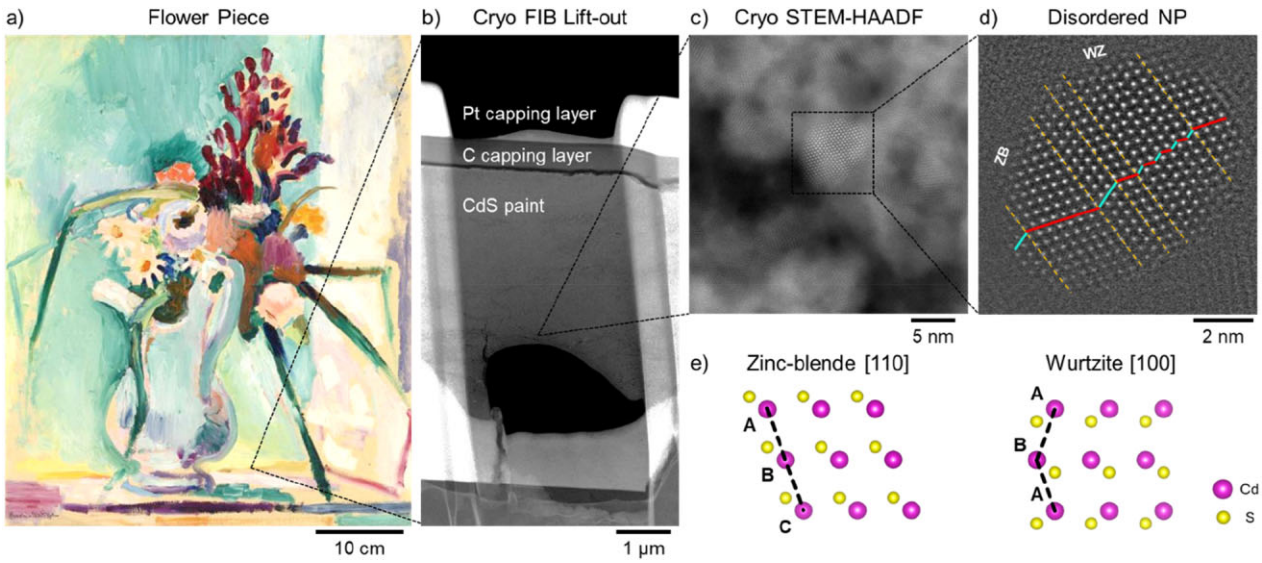

Fig. 1. a) Henri Matisse's 1906 "Flower Piece" oil on canvas. b) Electron transparent lamella thinned from micron sized flakes taken from region of painting indicated by dashed line in a). c) High resolution cryogenic STEM image shows cadmium paint consists of ~5 nm CdS nanoparticles. d-e) CdS nanoparticle (NP) shows a heterostructure, containing local regions of both hexagonal wurtzite (WZ) and cubic zinc-blende (ZB) type stacking sequences. Low frequency background signal in STEM image is subtracted for clarity.

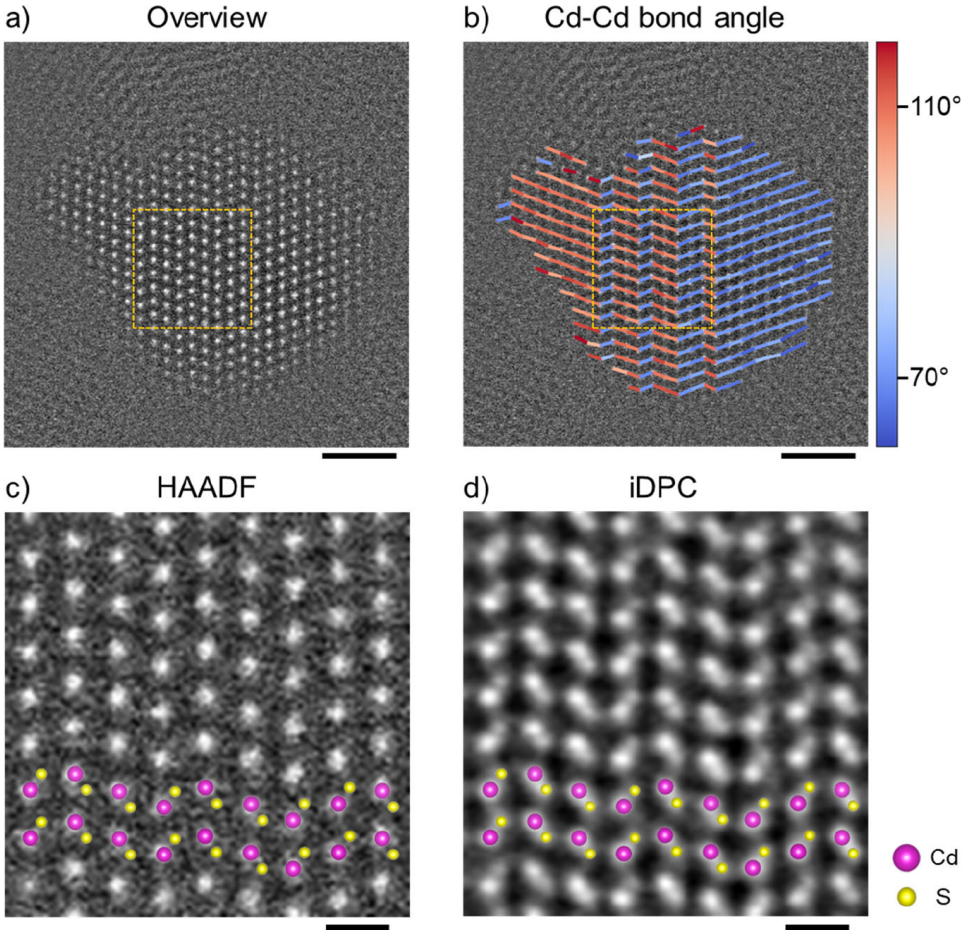

Fig. 2. a) Cryogenic STEM image of CdS nanoparticle. b) Cd-Cd bond angle map highlights areas with large disorder. a-b) Scale bars are 2 nm. c-d) Simultaneous HAADF and iDPC data collection reveals orientation of sulfur sites. Here we see an example of a random, polytype sequence which neither resembles 'ABA' hexagonal stacking nor 'ABC' cubic stacking, but is polar. c-d) Scale bars are 5 Å.

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6. This work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC program (DMR-1719875), including the use of a FEI Titan Themis 300 acquired through NSF-MRI-1429155.

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