Type of presentation: Poster

ID-7-P-1468 Aberration Corrected STEM to study an Ancient Hair Dyeing Formula

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Since the Greco-Roman period, organic hair dyes obtained from plants such as henna have been used, but other unusual formulas based on lead compounds, such as the recipes describing several methods to dye hair and wool black, were also common. It is remarkable that these Greco-Roman techniques have been used up to modern times: related recipes were described by Arabian authors during the medieval period, during the Renaissance as practical application of alchemical knowledge, and by modern chemists, from the Encyclopédie of Diderot and d’Alembert [1] through to the present day [2]. In these cases, the same specific formula is provided: a mixture of lead oxide, PbO, and slaked lime, Ca(OH)2, with a small amount of water to form a paste, is applied on the hair. Successive applications on gray or light hair give rise to the black color. It is known that the blackening of hair is due to the precipitation of galena (PbS) crystals during the chemical treatment: the lead is provided from the paste deposited on the hair shafts, and the sulfur involved in the reaction comes from the amino acids of hair keratins. Here, we show that a consequence of these practices consists of synthesizing galena (lead sulfide) nanocrystals to dye hair black [3]. This very simple chemical process seems promising for the production of other nano-size semiconductor sulphides, such as HgS. Mercury sulphide is a useful material with applications in many fields such as ultrasonic transducers, image sensors and photoelectric conversion devices. We have synthesized HgS nanoparticles in the hair, two forms of HgS have been grown during the treatment, i.e. cinnabar and metacinnabar (figures 1 and 2)[4].

STEM observations were performed on thin sections prepared by ultramicrotomy, deposited on a specific TEM grids and observed at 200 kV with a Jeol 2200FS TEM/STEM microscope equipped with a Cs probe corrector. HAADF-STEM images are particularly sensitive to the presence of heavy elements as lead or mercury, until the single atoms detection possible among the light elements (C,N,O,S) forming the hair.

References
[2] Gradual or progressive modern dyes, like Grecian Formula 16, contain lead acetate [Pb(CH3COO)2].
Fig. 1: Atomic resolution HRTEM image of HgS nanoparticles. Both hexagonal (cinnabar) and hexagonal (metacinnabar) crystalline phases are synthesized in the hair. The circled particle on the HRTEM image (a) reveals a cubic crystal structure with twins (I3 type).

Fig. 2: Atomic resolution HAADF-STEM image of HgS nanoparticles. The nanoparticle at the center of the HAADF image corresponds to cinnabar (see the Fourier Transform in insert with the six -1100 reflections of the HgS hexagonal structure).