

## Low Dose Electron Microscopy of ZnS–Bipy based Hybrid Organic–Inorganic Materials for Energy Applications.

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A strong interest in organic–inorganic hybrid materials has developed lately because of the variety of options they can offer in the modulation of electronic properties. ZnS is an interesting material for photocatalysis with a good resistance to photocorrosion and adequate conduction band position. There are a few examples in the literature regarding ZnS structural surface modification by using organic aliphatic bidentate amines [1]. Additionally a recently published investigation shows the complete synthesis procedure using solvothermal methods and characterization of ZnS and ZnS–Bipy (4,4-bipyridine) hybrid based organic–inorganic materials [2]. These materials are tested as catalysts in the photocatalytic reduction of 4-nitrophenol to 4-aminophenol, under UV light irradiation and show a high performance in photocatalytic activity. As for this work, the corresponding characterization by using electron microscopy is reported. Transmission electron microscopy has been performed in the TEAM 05 microscope (NCEM-LBNL) in conditions of low dose rate in TEM mode together with a routine in MacTempas® in order to apply the exit wave reconstruction procedure with 40 experimental images. Organic substances are normally rather beam sensitive and in particular 4,4-bipyridine tends to evaporate as the sample is observed in high dose rate.

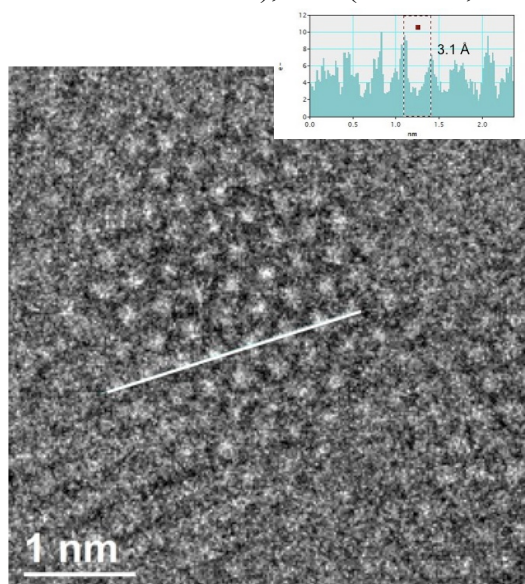
Figure 1 shows a typical experimental image of the ZnS-Bipy (4,4-bipyridine) hybrid based organic–inorganic materials taken at approximately  $30 \text{ e}^-/\text{\AA}^2\text{s}$ . It is rather noisy but some features can still be distinguished as shown by the inserted intensity profile. On the other hand, Fig. 2 shows the corresponding phase image after processing 40 experimental images taken at different defoci. This phase image shows both the inorganic and the organic materials forming a layered composite and with atomic resolution (see phase line profiles). The different domains are all in nanometric size and show a fine distribution of the organic and inorganic components as well as section where the two main phases can be readily identified. Figure 3a shows the phase image that corresponds exactly to the area in Fig. 1. The regular hexagonal atom arrangement corresponds to ZnS. There is also a section with a rather irregular hexagonal pattern most likely representing a thin layer of bipyridine. Figure 3b shows a model interpretation of the atomic distribution of ZnS along a [110] zone axis in the phase image. This has been done by assuming a cubic structure of the ZnS as suggested by X-ray diffraction [2]. Nevertheless the interatomic distances measured in the projection (Fig. 3b) point out to rhombohedral distortions of the lattice. Such deviations from the atomic positions are in average larger than those normally found for nanoparticles or other nanophases where crystalline planes elastically deform as a consequence of the size. Modelling and image simulation of the organic-inorganic arrangement complement this work.

### References:

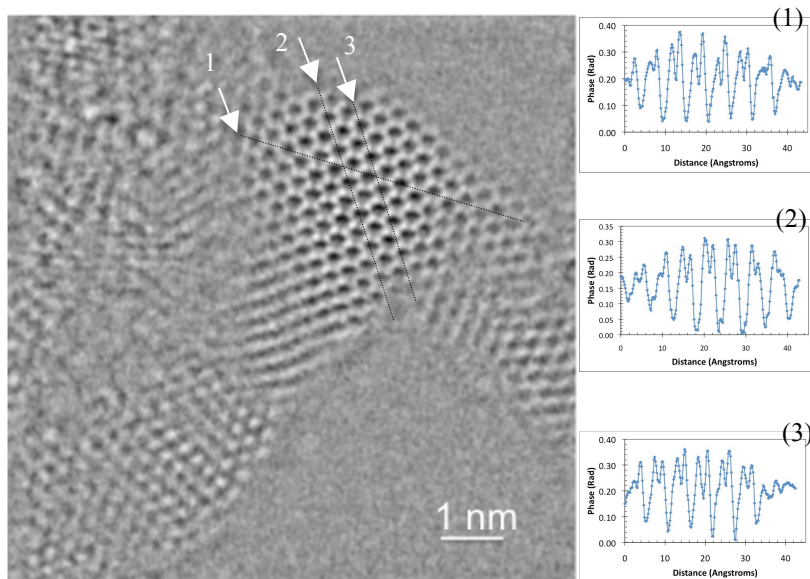
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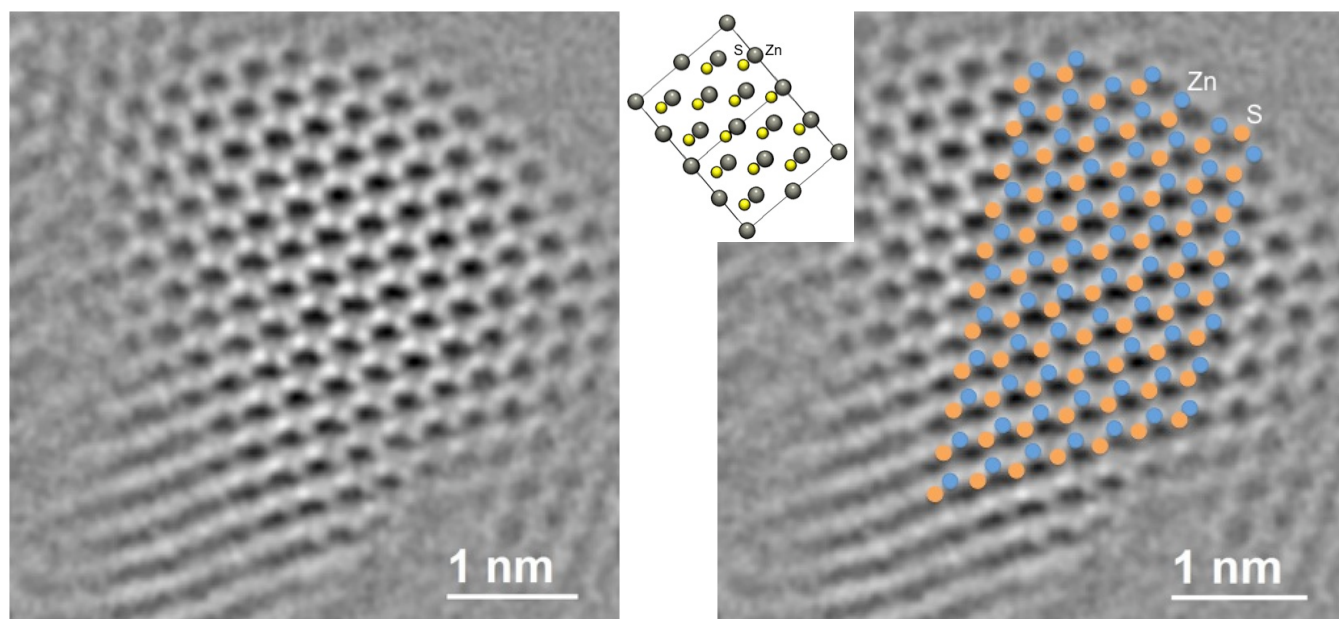
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**Figure 1.** Experimental TEM image of ZnS-Bipiridine hybrid material at a defocus of -20 nm. The intensity profile shows a periodicity of 3.1 Å.



**Figure 2.** Phase image after EWR procedure of ZnS-Bipiridine material. The intensity profiles show the phase recovery Vs position. Both organic and inorganic components are imaged.



**Figure 3.** (a) Phase image and (b) corresponding model interpretation showing both types of atoms in the ZnS component. Zn and S atom positions are indicated. The insert corresponds to the [110] projection of the unit cubic cell of ZnS.