

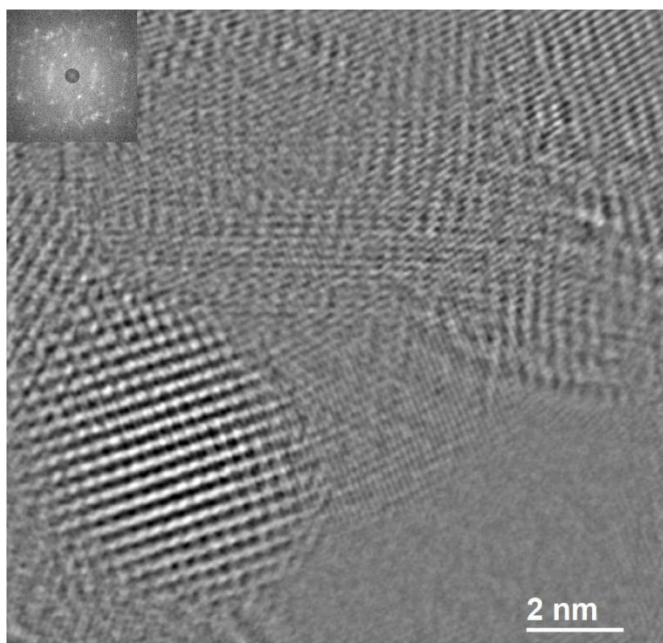
## Electron Microscopy of Co-catalyst CuO on Bi<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> Structures.

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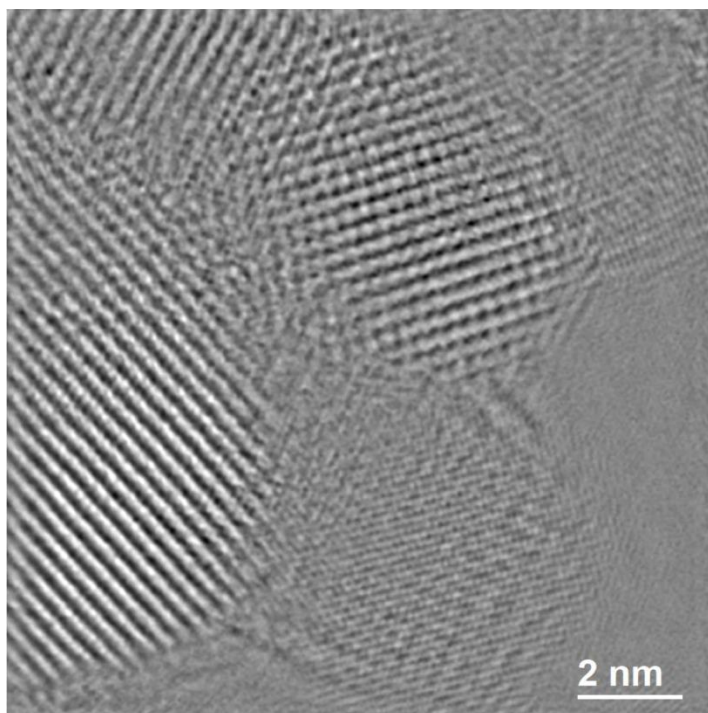
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Organic chemicals are essential for a many pharmaceuticals, pesticides and food additives. Conventional methods typically require extreme operating conditions e.g., high temperature and pressure. In this way the photocatalytic reduction is considered as an attractive alternative to reduce 4-nitrophenol. TiO<sub>2</sub> has been applied for the photocatalytic reduction of 4-nitrophenol, but it shows a high electron-hole pair (e<sup>-</sup>-h<sup>+</sup>) recombination. Alternatively, the formation of heterojunctions to other semiconductors has been explored and shown that the formation of the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure improves the photocatalytic hydrogen production due to the increase of the charge carrier separation. In this work, electron microscopy is used to characterize an heterostructure formed by Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> with several CuO as Co-catalyst. The synthesis of the material is described elsewhere [1]. Here special attention is given to determine the intimate contact between the co-catalyst on the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure. Electron microscopy is performed at MF-LBNL in the aberration corrected TEAM 05 microscope at 80 kV and in conditions of low dose. Exit wave reconstruction techniques are applied with focal series of 50 images and with an electron dose of approximately 10 e/Ås.

The identification of heterostructures and the diverse phases in the sample is summarized in the following images. Figure 1 shows a phase image from the EWR procedure. This is a section of the sample having CuO as co-catalyst and the heterostructure Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>. The nanocrystals forming the heterostructure have sizes of approximately 2-5 nm depending on the specific material. In the case of Bi<sub>2</sub>O<sub>3</sub> a higher atomic contrast and intensity can be used for identification. In all cases the lattice spacing can be used as reference for identification. In this figure CuO can be seen in small crystallites of around 2 nm. In all cases the nanocrystallites are joined firmly and a rather good contact between them can be easily observed. The corresponding diffraction pattern is shown in the upper left corner of this figure and shows the mixture of nanocrystal. This is has also been used for phase identification a location of the different phases in the material. Figure 2 shows further evidence of the good contact between phases. This type of images allows determination, in some cases, of phase identification as well as the contact boundary between them. Clearly this is related to the minimization of the total surface energy in the system. CuO can also be identified in the heterostructures rendering a further use of this technique.



**Figure 1.** Phase image after a EWR procedure with 50 images in a focal series. Nanocrystallites of the CuO, TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> phases can be found with a stable contact boundaries. The corresponding diffraction pattern is included.



**Figure 2.** Phase image after a EWR procedure with 50 images in a focal series. Nanocrystallites of the CuO, TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> phases can be found with a stable contact boundaries. Sizes are approximately 2-5 nm.

#### References

1. D. Guerrero Araque et al., *Top. Catal.* 64 112-120 (2021). <https://doi.org/10.1007/s11244-020-01335-7>.
2. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.