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TEM Characterization of Heterojunctions for Photocatalytic Application: ZrO_2-TiO_2 and CuO/ZrO_2-TiO_2

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Hydrogen (H_2) is an alternative fuel that can be produced from clean and renewable energy sources such as water, special semiconducting materials and sunlight. TiO_2 can be used as a photocatalyst to reduce water but it has a rather low efficiency thus coupling with other oxides becomes relevant especially to reduce charge recombination [e.g. 1]. Coupling TiO_2 and ZrO_2 improves considerably the photocatalytic activity to maximum levels of 5-7 mol % ZrO_2. Additionally coupling TiO_2 and CuO also enhances the hydrogen production efficiency for the water reduction reaction. The impact of CuO on the charge transfer process during the photocatalytic water reduction has been recently investigated for the ZrO_2-TiO_2 heterojunction. Different loadings (0.5 – 5 wt% CuO) of CuO have been under study with optimum results for the material containing 1 wt.% CuO [2, 3]. Electron microscopy is particularly well suited to determine the existence of the CuO phase in such low contents undetected by e.g., X ray diffraction. Thus this work deals with exit wave reconstruction of focal series taken in transmission electron microscopy under low dose conditions. The TEAM 0.5 microscope is used at 80 kV to acquire focal series with an electron dose of typically 5 $e^-/Å^2s$. The focal series are processed with the software MacTempas ® in order to determine the reconstructed electron exit waves and the corresponding phase and amplitude images.

Figure 1 shows a phase image of a hetereunion formed by ZrO_2 and TiO_2. The nanoparticle (ZrO_2) is shown after exposure with a dose rate of 5 $e^-/Å^2s$ and different exposure times. The time required to take a focal series of 40 images is around 2 min. The rather low dose in use reduces the beam –sample interaction and no difference in the atomic distribution can be registered after acquiring 240 (Fig. 1b) or 300 (Fig. 1c) images. The only effect resides in an increasing deposition of amorphous material around the nanoparticles (see arrows). Thus the genuine structure of the nanostructure is preserved after a normal single focal series. Figure 2 shows a typical phase image of the material containing the ZrO_2-TiO_2-CuO heterostructure. Fig. 1a shows a general view with sections belonging to ZrO_2, TiO_2 and CuO as partially labelled. Identification of phases is done by measuring lattice constants and referring to the corresponding crystalline structures. Fig. 2b gives a detailed region where the CuO coverage around a ZrO_2 nanoblock is shown. This image is further treated to determine the inverse Fourier image by masking some diffraction spots as shown in the insets. The CuO coverage can now be more clearly appreciated. The observed increased activity can then clearly related to the distribution of CuO [4].

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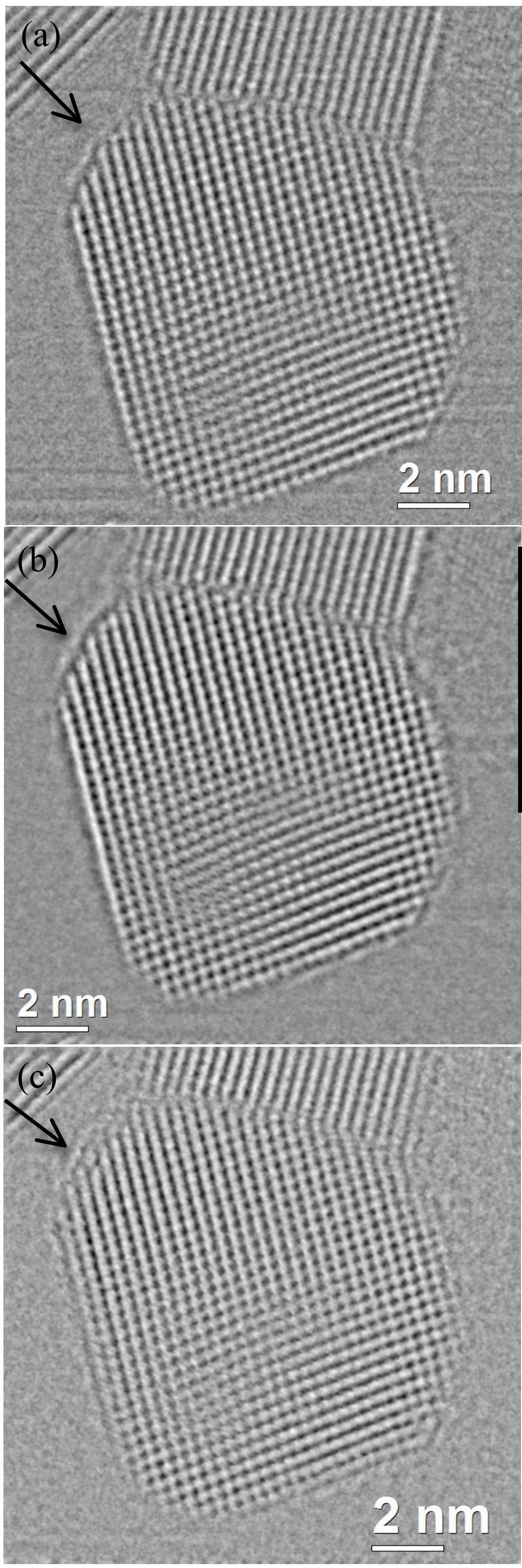

Figure 1. ZrO_2-TiO_2 heterostructure phase image after different exposure times (a) 2 min, (b) 8 min (c) 12 min.

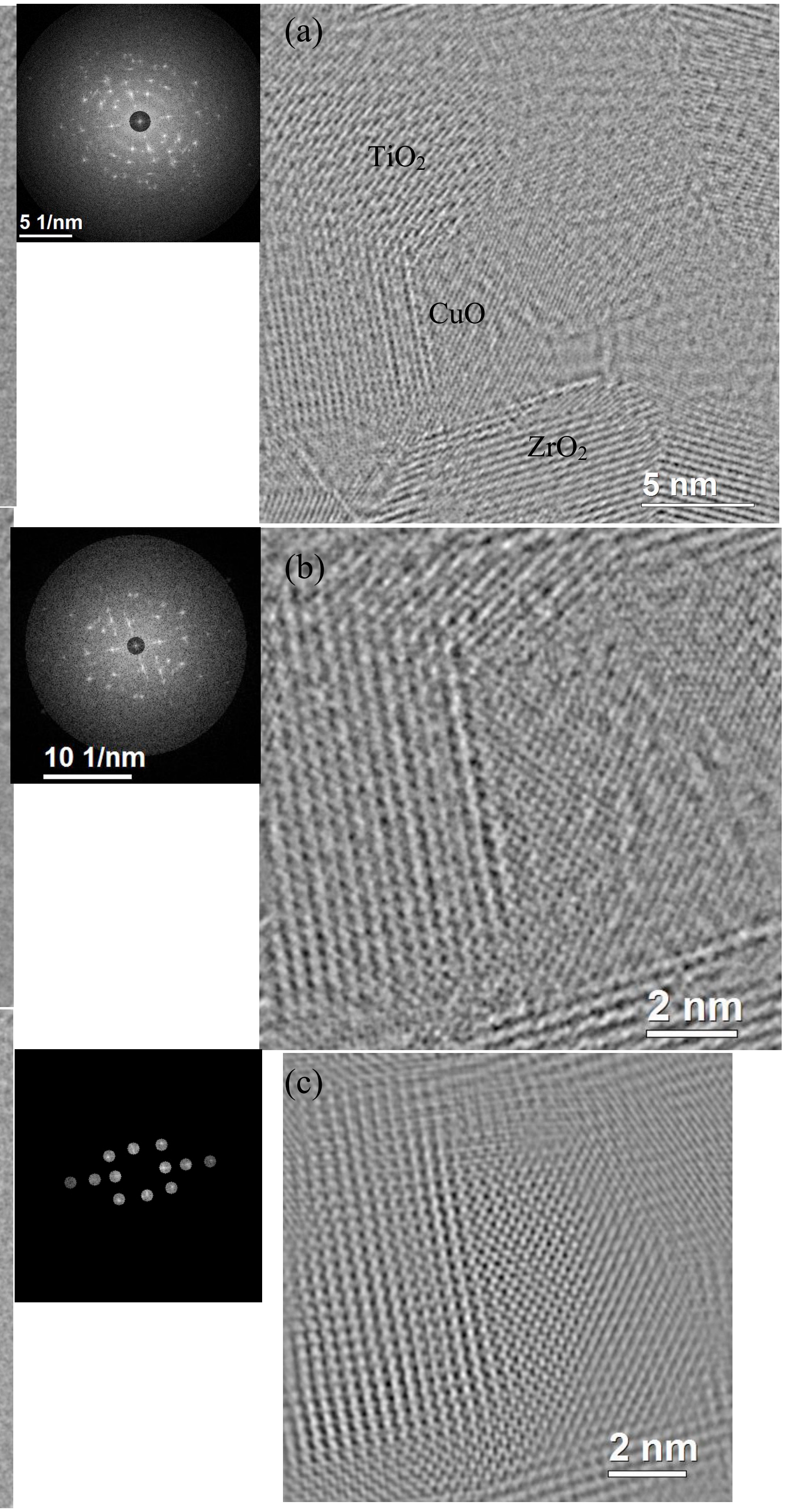

Figure 2. (a) Phase image with distribution of phases in ZrO_2-TiO_2-CuO. (b) Area with abundant CuO. (c) Inverse Fourier Transform image. Insets show diffraction patterns.

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