Electron Microscopy of TiO$_2$-CoTiO$_3$ based Materials for Photocatalysis

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Renewable energy is a major interest and concern in current life and for the future of a sustainable society. It is likely that in a decade or two, there will not be sufficient fossil fuels to supply the demands of society. Therefore, renewable sources become a key. A major goal is to exploit sunlight in combination with hydrogen. TiO$_2$ has demonstrated to be a good candidate for water splitting. However, its major disadvantage is the fact that it is only active under UV light, which is limited to 4-5% in the sunlight spectrum. Therefore, it is necessary to identify other materials capable of true environmental activity and able to take advantage of a larger portion of the sunlight spectrum. This is the case of Co-doped TiO$_2$ that has demonstrated tremendous applications and true activity under sunlight [1-2]. Here, the materials in this investigation (newly discovered) can make a difference. CoTiO$_3$-TiO$_2$ materials are not only sunlight active, but also effective to work in Near Infrared (NIR) excitation (1064 nm, equivalent to 1.17 eV or less) taking advantage of most of the sunlight spectrum, from NIR to UV and beyond. The synthesis of these materials is made by chemical methods described elsewhere [2]. Two types of samples are here presented, the as synthesized condition and that after a heat treatment at 500ºC. Electron microscopy has been performed in a low dose condition in order to image the genuine structure of the samples by using focal series and exit wave reconstruction in transmission electron microscopy. The microscope in use has been the TEAM 1 at 300 kV at the MF-LBNL [3]. The focal series consisted of 50 images at different focal settings and the software package MackTempas X has been used to recover phase and amplitude images with atomic resolution via exit wave reconstruction (EWR). The electron dose rate has been of approximately 10 e/Å$_2$s.

Figure 1 shows an image of the sample without any treatment after synthesis. The phase image shows a result of EWR. The untreated sample mostly consists of nanocrystals of TiO$_2$ (anatase) and CoO. Fig. 1 shows the heterojunctions between these bicrystal frameworks. The average crystal size is around 2 nm, in agreement with XRD [1]. The nanocrystals are apparently randomly oriented and clearly joining to other of different nature without any special type of arrangement, most likely only the reduction of total surface energy leads such a process. The synthesis technique clearly helps producing a nanostructured type of mixed compound sample. The corresponding diffraction pattern is given in the upper corner and confirms the two-phase distribution in the nanoscale for this sample. Alternatively, Figure 2 shows the heat treated sample. After heat treatment the most apparent effect is the grain growth. Although there are still areas with nanocrystals, the tendency to develop grains in the microscale is rather clear. The mixture of phase is preserved together with most likely atomic substitution of Co atoms into Ti sites. Additionally the stable phase for TiO$_2$ becomes rutile. Figure 2 shows a phase image after EWR treatment of 50 images with atomic contrast and a sufficiently high spatial resolution. This area shows basically only microcrystals although the sample still contains relatively small volumes with nanocrystals as can be seen in some section of Fig. 2 with some overlap. The phases are different in the micrograins, large rutile areas with smaller CoTiO$_3$ grains. This is most likely related to the volume fractions in the materials. Nevertheless the different intensities in the atomic columns in this image also indicate a substitution of metallic atoms. Co has a larger atomic mass than Ti and thus the column intensity variations can be due to substitution of Co for Ti in such areas giving rise to a different phase e.g. CoTiO$_3$. 
Figure 1. Phase image of untreated TiO2-CoO sample after synthesis. EWR has been applied to 50 images in a focal series.
Figure 2. Phase image of heat treated TiO2-CoTiO3 sample. EWR has been applied to 50 images in a focal series.

References
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