

Sunlight Active Perovskites ($\text{TiO}_2\text{-CoTiO}_3$) with Effective Dye Degradation and Water Splitting

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Here we present the characterization of titanias (Ti_xO_y) with up to 20at% Co additions that are sunlight active to degrade dyes and they are also effective for water splitting. The resultant perovskites we synthesize are by-crystal frameworks mainly composed by TiO_2 (rutile) substrates supporting an all inorganic perovskite (CoTiO_3). The particle size is near micrometric in range, which eliminates any potential for quantum confinement. Instead we propose that its high activity is the result of the habit plane arrangements at the interphase among the substrate and the perovskite. The perovskite is design to precipitate along the TiO_2 surface by a process known as “back diffusion” that is demonstrated in our previous work [1, 2]. The substrates are nearly-inactive in sunlight as the rutile band gap is approximately 3.01 eV. However, other active bandgaps for the perovskite is found in the visible spectrum (2.27 eV) as well as that for CoO (1.88 eV). The respective wavelengths to activate those bandgaps are: 546 nm and 659.5 nm, which are found in green and red light sources. In this work we used two light sources, one is near that range in the green (532 nm); yet, it is below the minimum energetic requirements. And the other wavelength used herein is in the near infrared or IR-A (1064 nm). While the first wavelength is unable to activate the perovskite or rutile and the second cannot activate any of the phases present in the material. Here is where the *philosophical* question emerge: what is the mechanism(s) that promotes such a level of activity in our material? To answer this question, we have developed a thorough characterization and had identified aberration corrected transmission electron microscopy (AC-TEM) as the only method capable of providing the right answer (Figure 1).

The results of characterization by means of X-ray diffraction (XRD), Raman spectroscopy and UV-vis are presented in Fig. 2a-c. Both, XRD and Raman spectroscopy are able to identify the presence of Rutile and CoTiO_3 in the investigated sample. At the same time UV-vis is capable of identifying three band gaps two of them are in agreement with those reported for the above mentioned phases, and the third one (1.88 eV) is rather characteristic of CoO. Here is important to say that in the event that our materials have CoO, the amount is in traces as the presence of this phase is not detectable by XRD or other methods. The degradation and water splitting results are in Figs. 2d-e. In those results is possible to observe how the perovskite are sunlight active and capable of degrading Acid Orange 7 as well as the presence of hydrogen, demonstrating the potential of this material for hydrogen evolution.

The ultimate characterization presented in this work is the ACTEM. Here we describe it as the “ultimate characterization” because is the only method that we have used capable of revealing the actual frameworks for the investigated materials. We believe that the habit plane arrangements along with the crystalline frameworks are responsible for the outstanding activity of this composite material [3].

References:

- [1] A.K.P.D. Savio, J. Fletcher, F.C. Robles Hernández, *Ceramics International*, **39** (2013) p. 2753.
 [2] A.K.P.D. Savio *et al*, *Applied Catalysis B: Environmental*, **182** (2016), p. 449.
 [3] D.L.P. F.C.R.H. wishes to thank the FEI (now Thermo Fisher Scientific) team (Dr. D. Gostovic, Dr. A. Genc, Dr. L Brock, and Dr. L. Casalena) at the Nanoport facility in Portland for facilitating the FIB (by Dr. L. Brock) and HRTEM (by Dr. A. Genc) observations.

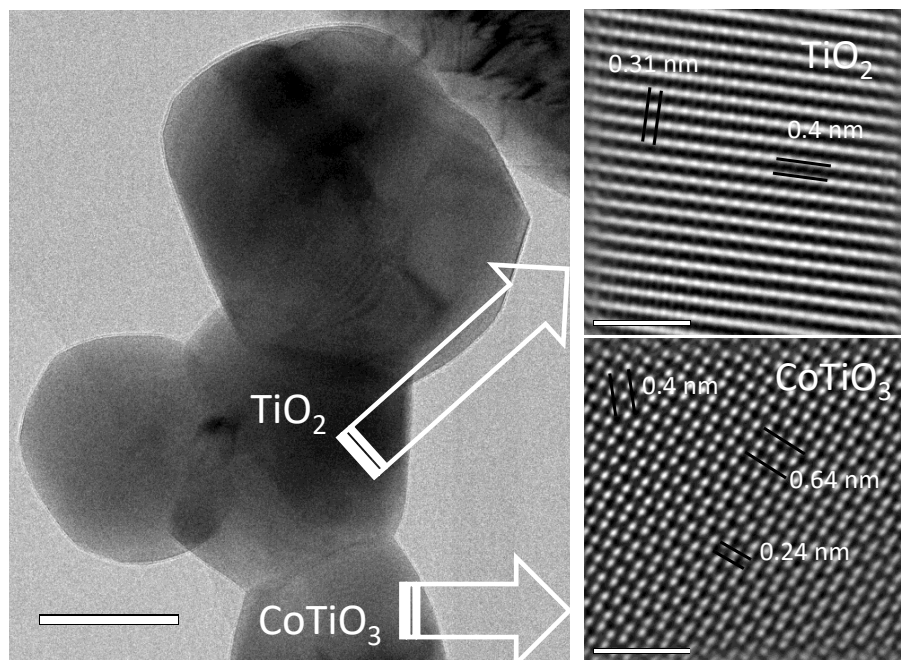


Figure 1. ACTEM images of the bulk particles and atomic resolution images revealing the crystalline structure.

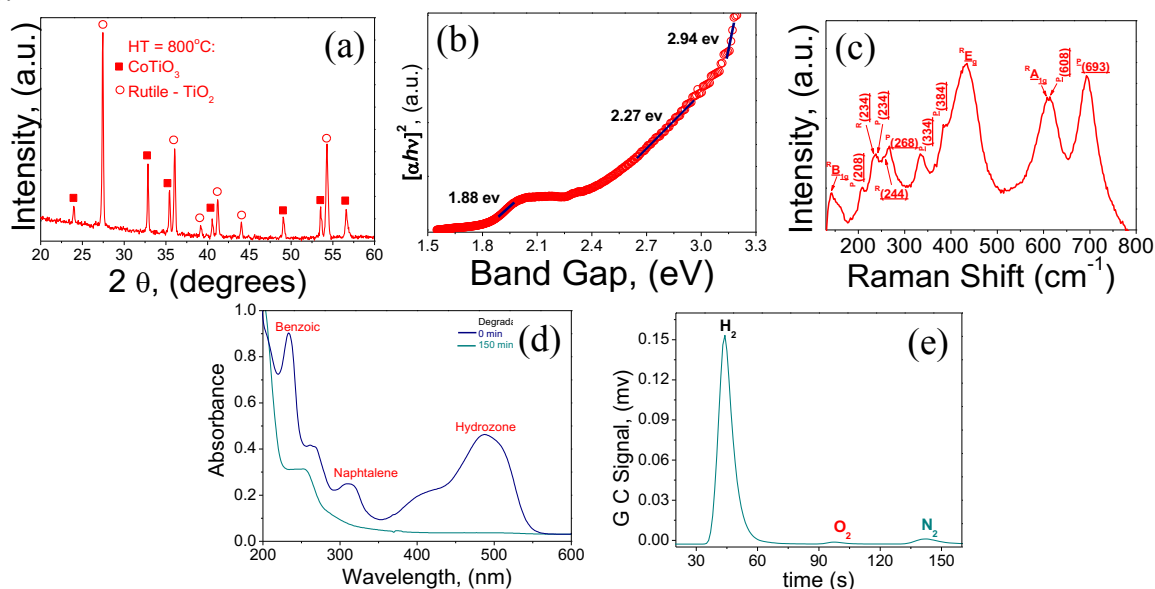


Figure 2. Characterization by means of (a) XRD, (b) Raman, (c) UV-vis, (d) dye degradation, (e) water splitting.