doi:10.1017/S1431927620022394
Microsc. Microanal. 26 (Suppl 2), 2020

Reduced Magneli Layers on Anatase TiO_2 Nanocrystals Surface Revealed by HAADF STEM Imaging

Snejana Bakardjieva[1], Robert Klie[2], Victor Y. Zenou[3], Mariana Klementová[4] and Slavomír Adamec[5]

[1]Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež, Stredocesky kraj, Czech Republic, [2]University of Illinois at Chicago, Chicago, Illinois, United States, [3]Department of Materials Engineering, Nuclear Research Center- Negev, Beer-Sheva, Tel Aviv, Israel, [4]FZU – Institute of Physics of the Czech Academy of Sciences, Prague, Hlavni mesto Praha, Czech Republic, [5]Faculty of Environment, Jan Evangelista Purkyne University, Ústí nad Labem, Ustecky kraj, Czech Republic

Titanium oxide modified by metal cations is receiving increased attention as a photocatalyst due to its important industrial applications, such as the degradation of pollutants in water and air. It is known that the photocatalytic activity depends on the structure of TiO_2 polymorphs and their interaction with dopant species, so a thorough structural characterization is essential for understanding any structure-property relationships. Previous studies using a combination of XRD and HRTEM revealed that Sc cation at low loading (1 at. %) is highly dispersed on TiO_2 surface. Reduced Magneli Ti_nO_{2n-1} layers appeared on samples having intermediate Sc loadings [1]. To date, however, no direct imaging studies of Sc distribution or its interaction with the TiO_2 matrix have been documented.

High angle annular dark field (HAADF) STEM imaging, is able to provide sub-Å spatial resolution as well as single atom sensitivity, and has been demonstrated to be a very powerful tool in the structural characterization of metal doped photocatalysts. However, no HAADF data has been reported on Sc modified TiO_2 photocatalysts because of the low Z - contrast of the Sc and Ti elements. Here HAADF imaging is used to directly observe structural configuration of Sc modified TiO_2 material obtained by coprecipitation method [1]. The images were acquired on a JEM-ARM200CF probe aberration corrected 200kV STEM/TEM.

Analysis of HRTEM images of annealed sample at 800ºC revealed more faceted nanocrystals (NCs) with a new core-shell morphology. Atomic resolution HAADF images of the core-shell NCs are shown in Fig. 1a and Fig 1b. In both NCs the shell exhibits square projected lattice structure, while the core appears composed of dumbbell-like atomic columns. The interface between these two phases is coherent. Local area Fast Fourier Transforms (FFT) of the shell/core regions indicate that the core is TiO_2 anatase along [0 1 0] crystallographic direction, and that of the shell is attributed to Ti_3O_5 viewed down [-2 0 1] zone axis.

The kinetics of decomposition of methylparation (MP) under UV light is shown in Fig. 2. Annealing at 800 ºC (TiSc4_800) leads to better photocatalytic efficiency compared with non-annealed sample TiSc4. Degussa P25 was used as a reference material. Annealing process at 800C leads to hybrid material

$[Ti_{0.96}Sc_{0.04}O_{2-\delta}][Ti_3O_5]$ with core shell structure with high concentration of oxygen vacancies and better crystallinity of anatase, which is the main reason for enhanced photocatalytic performance of TiSc4_800.

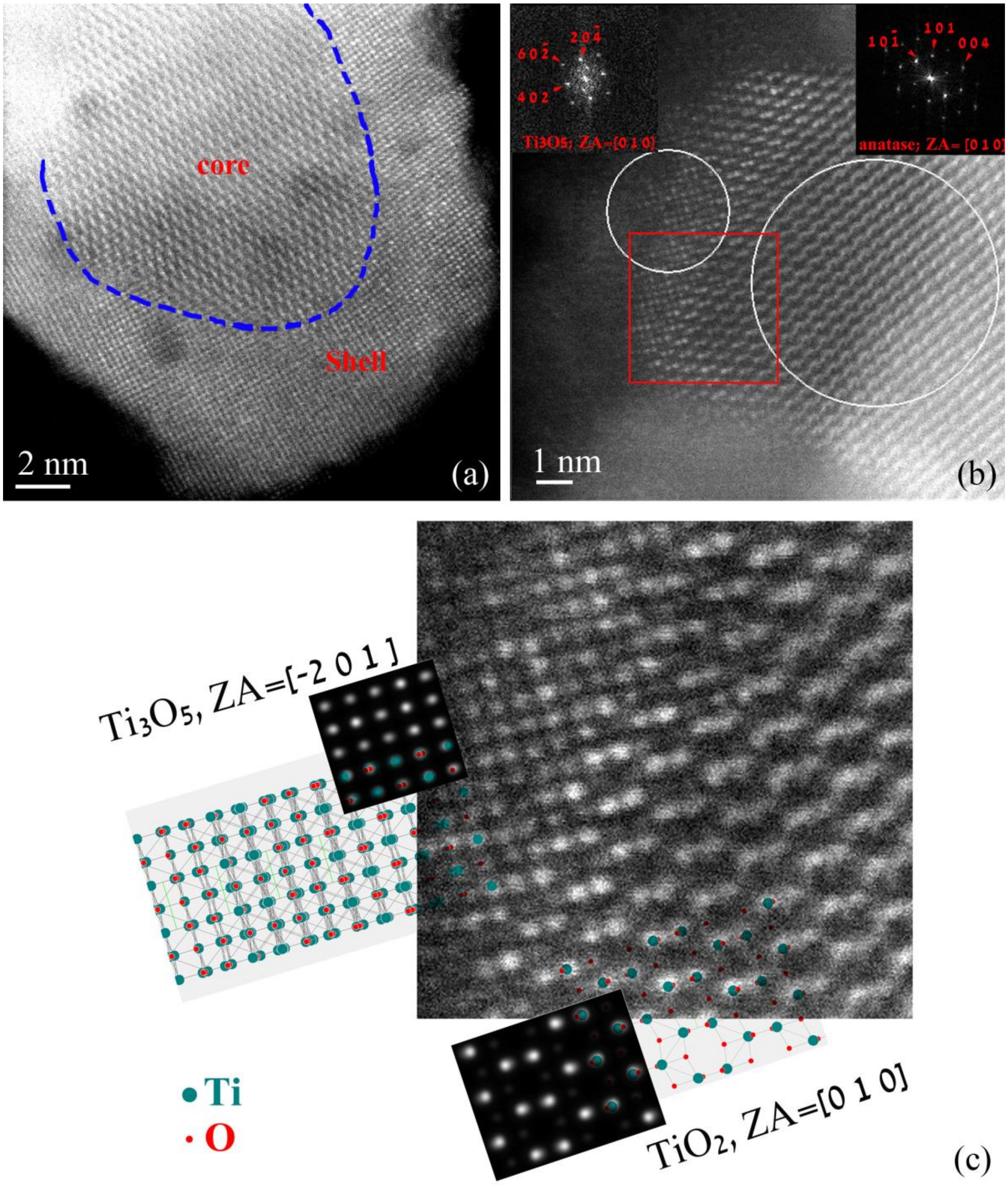

Figure 1. (a) TEM micrograph of TiSc4 at low magnification. (b) SAED taken from the green boxed area shows presence of (203), (402) and (-602) planes of monoclinic Ti3O5 and the corresponding intensity profile of anatase (inset).

https://doi.org/10.1017/S1431927620022394 Published online by Cambridge University Press

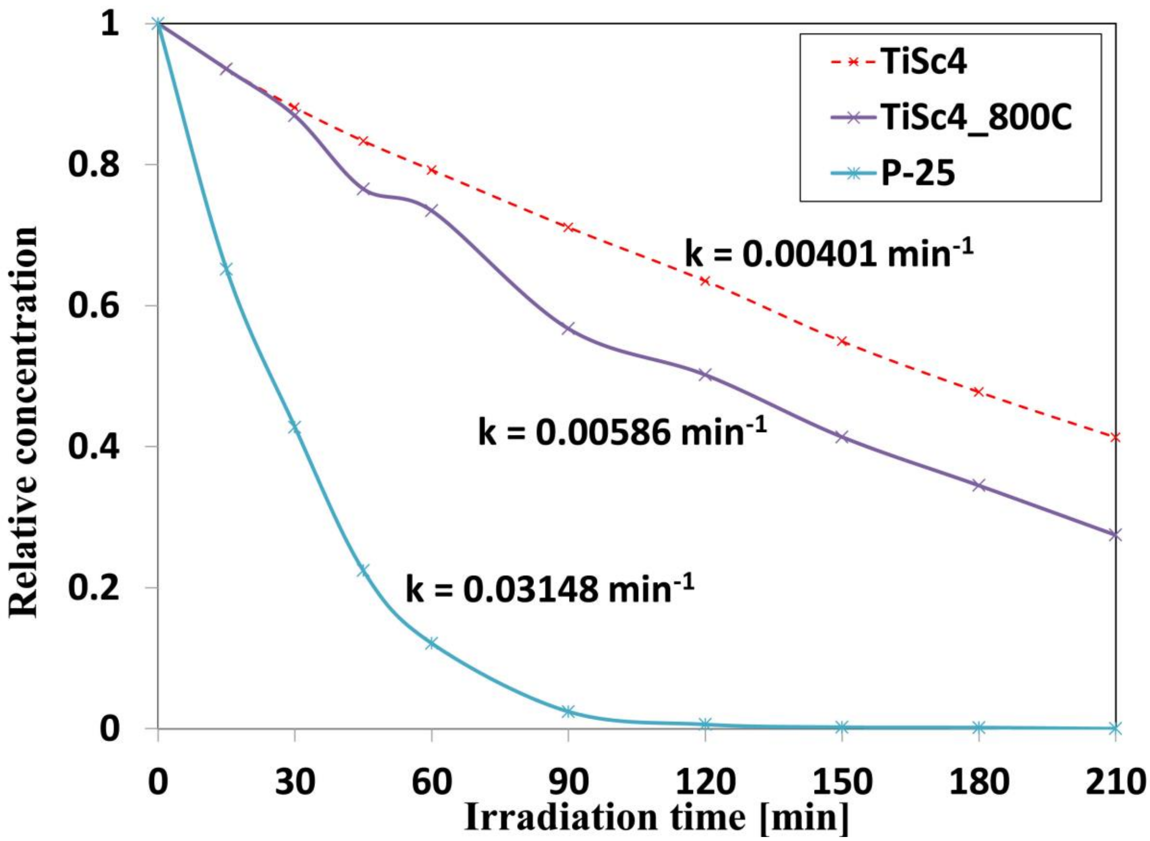

Figure 2. Decomposition of methylparation under UV light on TiSc4 and annealed TiSc4-800 samples, and standard P25.

References

[1] V. Y Zenou and S. Bakardjieva, Mater. Characterization, 144 (2018), p.287.

[2] The authors acknowledge funding from the Czech Science Foundation (Project GACR 18-15613S).
[3] The authors acknowledge Core of UICs Research Resource Center (NSF 0959470/1626065).

https://doi.org/10.1017/S1431927620022394 Published online by Cambridge University Press