doi:10.1017/S1431927613009720
Microsc. Microanal. 19 (Suppl 2), 2013

Characterization of Carbon-Coated Anatase Titania (TiO_2) Nanoparticles (NPs) with Transmission Electron Microscopy (TEM)

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Anatase phase of TiO_2 is proved to be a good catalyst material and in NP form it has been shown to be quite useful for photocatalytic splitting of water [1]. Doping of carbon in anatase TiO_2 NPs is thought to enhance their photocatalytic performance even further by absorbing more light in the visible range [2]. In this report, we investigated carbon-coated anatase TiO_2 NPs with TEM technique to determine the quality of carbon-coating on them and their optical properties. The preparation of these TiO_2 NPs and their carbon-coating was accomplished with a multi-element diffusion-flame burner (MEDB) whose experimental details can be found elsewhere [3].

Bright-field TEM (BF-TEM) analysis was applied first to investigate the quality of carbon-coating of TiO_2 NPs. Figure 1 contains a typical BF-TEM electron micrograph that provides an insight into the size and structure of TiO_2 NPs. It shows that TiO_2 NPs were either having uniform mass-thickness contrast (labeled as "A" for amorphous phase) or having non-uniform diffraction contrast (labeled as "C" for crystalline phase). A couple of regions, one from an A-labeled NP (in red) and the other one from a C-labeled NP (in yellow), were picked in the Figure 1 and were then shown to the right of the micrograph by zooming those areas about three times than their original size. After doing this, it was found that only crystalline TiO_2 (c-TiO_2) NPs were coated with carbon layer of about 5 nm in thickness. Carbon-coating of only c-TiO_2 NPs suggests a solid-state mechanism for its growth as supposed to gas-phase reaction growth mechanism [4]. These findings suggest that carbon diffuses into TiO_2 NPs first and then diffuses outward once the NPs get saturated with carbon. Since the crystalline materials, due to crystal imperfections, typically have higher diffusion coefficients than their amorphous counter-parts and hence it explains why only the c-TiO_2 NPs were coated.

Valence electron energy-loss spectroscopy (VEELS) in high-resolution TEM-mode was employed next to investigate the optical properties of an amorphous TiO_2 (a-TiO_2) NP, a c-TiO_2 NP, and a carbon-coated c-TiO_2 NP. Figure 2 contains the HRTEM micrographs of these NPs and their corresponding optical parameters namely real part or epsilon 1 ($\varepsilon 1$) and imaginary part or epsilon 2 ($\varepsilon 2$) of dielectric function $\varepsilon(\omega)$. These optical parameters were calculated by applying Kramer-Kronig Analysis (KKA) to their VEELS spectra in Digital Micrograph™ software. Figure 2 shows that $\varepsilon 1$ crosses the energy-loss axis around 4 eV for the case of a-TiO_2 NP and around 12 eV for the cases of c-TiO_2 as well as carbon-coated c-TiO_2. It implies that electron beam excited volume plasmons and single-particle transitions in different manner for amorphous NPs than crystalline TiO_2 NPs. This behavior of $\varepsilon 1$ is possibly due to their different band-structures. Figure 2 further shows that $\varepsilon 2$ of carbon coated NP is more peaked around 2.2-4 eV energy range than other two NPs. It is assumed that the enhanced electron energy absorption in the range of 2.2-4 eV was due to the replacement of some oxygen vacancies by carbon atoms near the surface region of TiO_2 NPs as shown by Khan et al. [2]. It is concluded from the study that carbon doping most likely changed the band structure of anatase TiO_2 NPs and hence enabled these NPs to absorb more electron energy near the energy range of visible light.

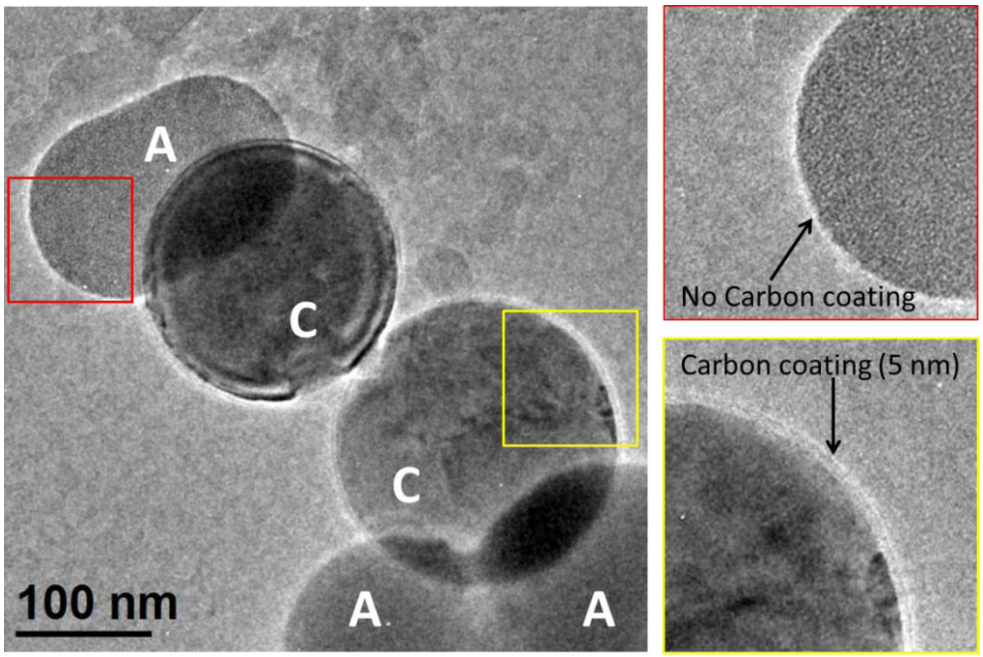

Figure 1: A BF-TEM electron micrograph of a specimen from carbon-coated TiO_2 NPs. NPs labeled as "A" are amorphous in the micrograph while the ones labeled as "C" are "crystalline".

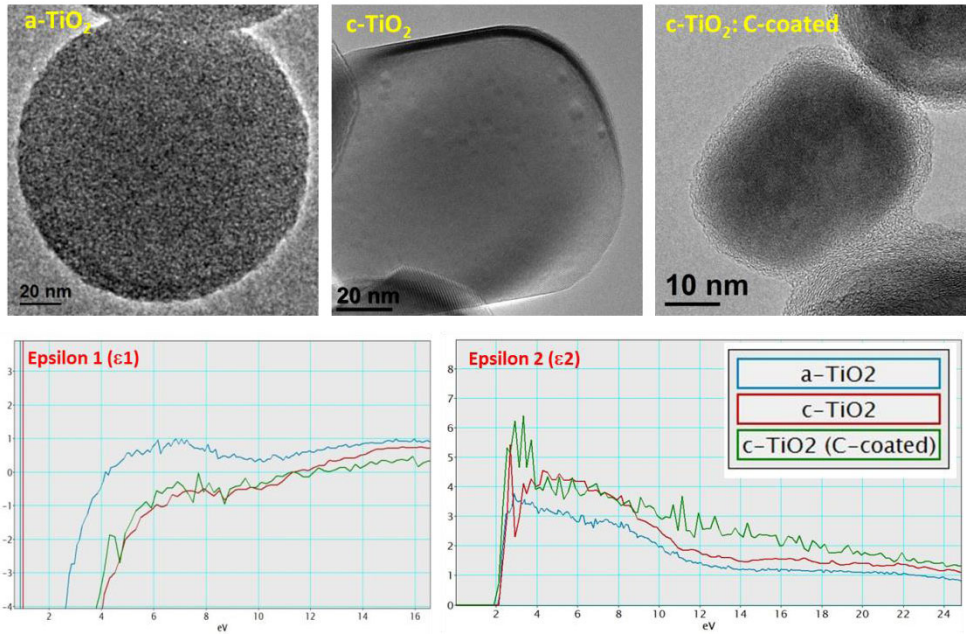

Figure 2: HRTEM micrographs and optical parameters (epsilon 1 & epsilon 2) of a-TiO_2, c-TiO_2 and carbon-coated c-TiO_2 NPs.

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https://doi.org/10.1017/S1431927613009720 Published online by Cambridge University Press