

## Preparation and characterization of a TiO<sub>2</sub>/carbon nanowall composite on a transparent substrate

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**Abstract**—A transparent titanium dioxide and carbon nanowall composite (B-CNW/TiO<sub>2</sub>) material was fabricated by growing boron-doped carbon nanowalls (B-CNWs) on quartz glass with a microwave plasma-enhanced chemical vapor deposition technique, followed by sol-gel deposition using titanium isopropoxide as a TiO<sub>2</sub> precursor. Different layer thicknesses were fabricated. Samples were investigated by spectroscopic ellipsometry and UV-VIS spectroscopy. The results show how the B-CNW thickness affects optical transmittance, bandgap and electrical conductivity.

The large surface-to-volume ratio and excellent field emission and electron transport properties make CNWs an ideal support for photocatalysts [1], as titanium dioxide (TiO<sub>2</sub>). TiO<sub>2</sub> has been widely used, due to its chemical stability, non-toxicity and high photocatalytic activity [2]. For these reasons, the deposition of TiO<sub>2</sub> on a B-CNW substrate is intended to benefit from the porous structure and electron mobility of carbon nanowall and wide bandgap of TiO<sub>2</sub>, for enhanced photocatalytic applications [3].

BCNWs films have been grown on quartz glass, optical grade (Continental Trade, Poland), using a gas mixture of H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> with a total flow of 328 sccm, at a pressure of 50 Torr; microwave power up to 1300 W and radiation of 2.45 GHz for 7.5, 15 and 30 min. During the process, the substrate holder was heated up to the desired temperature by an induction heater and controlled by a thermocouple. Prior to CVD growth, fused silica substrates were etched for 20 minutes, by a flow of H<sub>2</sub>, at 500°C, with the 1000W microwave power. Subsequently, the substrates were seeded by spin-coating in nanodiamond slurry [4]. The precursor solution for TiO<sub>2</sub> films was obtained using titanium(IV) tetra(2-propanolate), propan-2-ol, Triton X-100 and hydrochloric acid (37%) [5]. The sol-gel was spin coated on the B-CNW substrates and subsequently annealed in air at 450° for 5h.

The schema and photo of the samples are shown, respectively, in Fig. 1 and Fig. 2.

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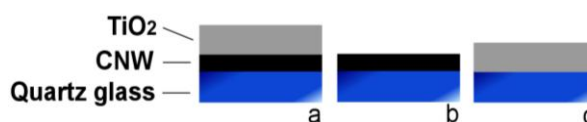


Fig. 1. Schematic of the samples (not to scale).



Fig. 2. Picture of the samples, with a different CNW growth period (from top left, clockwise: 0, 7.5, 15 and 30 min).

Raman spectra were recorded in a range of 200–3500cm<sup>-1</sup> with an integrated confocal micro-Raman system with a LabRam Aramis (Horiba Jobin Yvon, Japan) 460mm spectrometer equipped with a confocal microscope. The excitation source was a HeNe laser. Data were smoothed, baseline subtracted and normalized.

Spectroscopic ellipsometry measurements were conducted with a Jobin-Yvon UVISSEL phase-modulated ellipsometer (HORIBA Jobin-Yvon Inc., Edison, USA), in the region of 1.8 and 4.8eV.

The experiments were carried out at room temperature using an angle of incidence fixed at 60° and the compensator was set at 45°. The incidence angle resulted from Brewster's angle of a fused silica substrate.

A four-layer structural model (ambient/SRL-surface roughness layer/B-CNW/glass-substrate) was applied to the samples in order to determine the effective thickness

of SRL, and the thickness of a BCNW film and its effective complex dielectric function. The SRL has a composition of the BCNW film with spaces filled with air. Such an approach allowed for estimating the average roughness of the films.

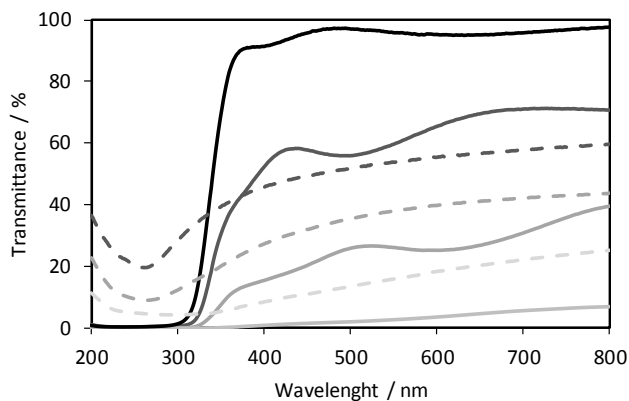


Fig. 3. Optical transmittance of BCNW (dotted lines) and BCNW/TiO<sub>2</sub> (solid lines) samples.

The BCNW film has been assumed to be an isotropic, homogeneous material and its dispersion was fitted to a new amorphous model derived on the basis of the Forouhi-Bloomer formulation. DeltaPsi software (v. 2.4.3) was employed to determine the spectral distributions of the refractive index  $n(\lambda)$  and the extinction coefficient  $k(\lambda)$  of the carbon nanowall film.

UV-vis spectroscopy was conducted in the 200÷1000nm range, scan step 1nm, scan filter =10. In order to evaluate the band gap energy of the samples, a Tauc method was adopted.

The intrinsic optical transmittance of B-CNW with a different BCNW thickness is reported by the dotted lines in Fig. 3, while the solid one represents the composite (TiO<sub>2</sub>/B-CNW). The B-CNW layer thickness is obviously related to the deposition time, which negatively affects optical transmittance.

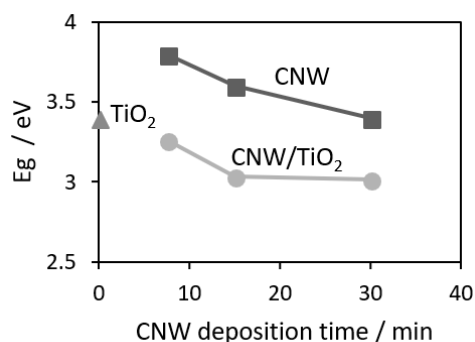


Fig. 4. Optical bandgap estimated by Tauc plot.

Optical bandgaps, estimated by a Tauc plot [6], plotted in Fig. 4, show their decrease by increasing the thickness of the BCNW layer, both in the BCNW - only sample and the composite. TiO<sub>2</sub> is found to be in an anatase form by the Raman spectra and exhibits an initial bandgap of 3.4eV.

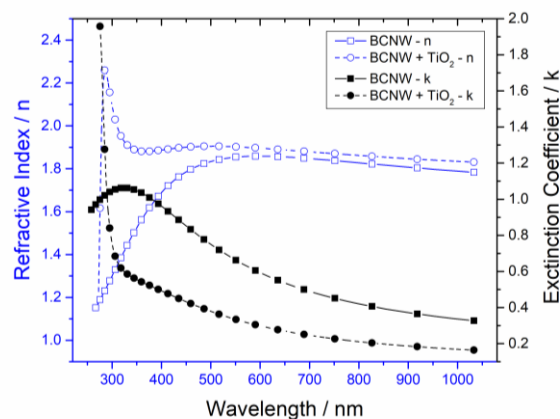


Fig. 5. Variation of optical constants of bare BCNW film and that of BCNW/TiO<sub>2</sub> composite.

Figure 5 illustrates the refractive index (left axis), and extinction coefficient (right axis) of the BCNW and BCNW/TiO<sub>2</sub> evaluated by spectroscopic ellipsometry, as a function of wavelength.

The refractive index of the BCNWs interfacial layer shows normal dispersion in the visible range. The  $n$  values of BCNW/TiO<sub>2</sub> present a deep drop in the low range of VIS. Next, they are shifted slightly towards a longer wavelength exhibiting the resonance peak at approx. 300nm.

The achieved values of  $n$  were high, ranging from 1.7 to 2.3 for BCNW films (Fig. 5). In general, the refractive index decreases when BCNW films are covered by TiO<sub>2</sub>. The observed effect is attributed to TiO<sub>2</sub> incorporation in the BCNW structure.

The  $k$  values as illustrated in Fig. 5 (right axis) are below 0.6 and 0.3 at 550nm for bare BCNW and BCNW/TiO<sub>2</sub>, respectively. The coverage by TiO<sub>2</sub> results in a drop of the extinction coefficient below 0.3, indicating much lower light absorption over the pristine BCNW film. That parameter is critical for optical application of deposited BCNW films.

In conclusion, optical properties of BCNW and BCNW/TiO<sub>2</sub> composite were investigated. Optical transmittance is mainly affected by the BCNW thickness, rather than the TiO<sub>2</sub> coverage. A thicker BCNW layer lowers the composite bandgap. The additional coverage of BCNW by a highly transparent material like TiO<sub>2</sub> enables

to achieve highly conductive transparent electrodes.

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## References

- [1] H. Wang, X. Quan, H. Yu, S. Chen, *Carbon* **46**, 1126 (2008).
- [2] A. Fujishima, X. Zhang, D.A. Tryk, *Surf. Sci. Rep.* **63**, 515 (2008).
- [3] M. Pierpaoli, C. Giosuè, M.L. Ruello, G. Fava, *Environ. Sci. Pollut. Res.* **24**, 12638 (2017).
- [4] M. Sobaszek *et al.*, *J. Phys. Chem. C* **121**, 20821 (2017).
- [5] A. Lewkowicz *et al.*, *Opt. Mater.* **36**, 1739 (2014).
- [6] J. Tauc, *Mater. Res. Bull.* **3**, 37 (1968).