FLAME-SYNTHESIZED TiO_2-C NANOCOMPOSITE FILMS: UNVEILING RESISTIVE SWITCHING PHENOMENON FOR MEMORY STORAGE APPLICATIONS

Abdul Khalique*, Mario Commodo, Patrizia Minutolo**, Gianluigi De Falco**, Andrea D'Anna***
abdul.khalique@unina.it
* Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 - Napoli (Italy)
** Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili, Consiglio Nazionale delle Ricerche, P.le Tecchio 80, 80125 - Napoli (Italy)

Abstract
A composite nanostructured thin film of TiO_2-C has been fabricated through a facile one-step flame-based synthesis using a customized honeycomb burner and then collected via thermophoretic deposition. Titanium (IV) isopropoxide (TTIP) solution was used as a precursor for TiO_2 nanoparticles and ethylene/air premixed gas was the fuel source of carbon compounds. The produced nanocomposite film is analyzed with Raman spectroscopy to examine the presence of both TiO_2 and carbon peaks. The produced nanocomposite film was further investigated for optical bandgap determination through UV-Vis spectroscopy and its electrical characteristics through current-voltage (I-V) measurements. The TiO_2-C nanocomposite film exhibited capacitive coupled resistive switching behavior, unveiling great potential for non-volatile memory storage applications.

Introduction
Titanium dioxide (TiO_2) nanoparticles produced through several methods have been extensively studied for their physiochemical characteristics for the last two decades for their wide applications including biosensors, gas sensors, pigments, photocatalysts, etc [1]. Additionally, its high chemical activity under UV irradiation makes it a primary choice to be used as an active component of solar cells as well as a reaction catalyst. It is well known that TiO_2 nanoparticles exhibit significantly higher activity than the bulk material, and this is correlated with a greater active surface area. UV irradiation of TiO_2 nanoparticles produces electron-hole pairs that participate in catalytic activities on the particle surface because of photon energy absorption[2]. An inverse process is followed up with it called charge recombination. Reports suggested that such recombination of the electron-hole pairs is probably due to the energy band gap[3]. The transition of the electron from the conduction band to the valence band is directly related to the band gap, so the higher the band gap, the lesser the chance of electron transition. As a result, when TiO_2 is exposed to sunlight, the lower the band gap, the higher the proportion of usable energy because

lower energy photons are needed to excite the electrons that are present in the valence band. As of today, several techniques are being utilized for the band gap reduction of the TiO_2 including structural modification with the incorporation of carbon. The carbon doping provides enhanced absorption capacity to the crystalline TiO_2 making it a porous structure by introducing additional defects and vacancies into the TiO_2 lattice. Different methods are adopted to produce TiO_2-C nanocomposites including sol-gel method, hydrothermal method, flame aerosol synthesis, thermal decomposition and reduction method in order to obtain particles with different sizes, shapes, and crystal structures[4]. Recently, the flame-based synthesis method has been increasingly adopted for producing a variety of organic and inorganic nanoparticles thin films, and powders with different properties due to its compliant approach and industrial-level scalability.

Recently, flame-formed TiO_2-C have been reported to exhibit significant improvement in their photocatalytic performances. Besides the photocatalytic characteristics, the two-step flame-synthesized TiO_2-C thin films have revealed an interesting resistive switching effect [5]. This discovery paves the way for an interesting application of TiO_2-C nanocomposite films for non-volatile memory storage devices. The resistive switching phenomenon is attributed to the memristor, the fourth component of the circuit that was discovered in 1971 by Leon Chua[6]. This phenomenon attracted the substantial attention of the scientific community towards investigation of this symmetric fourth component of the circuit. That discovery opened the door for designing more complex integrated circuits with enhanced technical capabilities. Since then, several organic and inorganic composite materials have been produced with resistive switching behaviour along with an interesting capacitive coupled switching phenomenon.

Experimental

The experimental setup for the facile one-step flame synthesis of TiO_2-C nanocomposite thin films consists of a customized vertical honeycomb burner. Using pre-heated air as the carrier gas, a high-pressure syringe pump (Model 410 from KD Scientific, Holliston, MA, USA) was utilized to supply the atomized 0.5 Molar precursor solution of TTIP in ethanol to the reactor at a flow rate of 900 μL/min along with the spray air (60 Nl/h). The spray solution was carried to the burner with the help of secondary air through the line (60 Nl/h). The burner and its connected supply lines were heated up to 450K with the help of heating tapes to avoid the condensation of the syringe-fed TTIP solution. Furthermore, the premixed ethylene (45 Nl/h) and air (200 Nl/h) were supplied through the bottom of the honeycomb burner as the source of carbon nanoparticles. The system is capable of any variation in the concentration or the flow rate of the precursor solution or the carbon source to obtain different sizes and morphology of the produced nanocomposite films. TiO_2-C nanocomposite films are produced in this flame condition of vapor-fed 0.5M TTIP precursor solution and the premixed ethylene/air and thermophoretically collected on different substrates mounted on a rotating disk

15 cm above the burner surface rotating at a speed of 460 rpm set through a voltage regulator. Additionally, the CNP thin films have been produced with the same setup under similar conditions in the absence of TTIP precursor sending only ethanol through the syringe pump for the comparative study of the CNP film and TiO_2-C nanocomposite film.

Surface polished aluminum substrate was used for the Raman analysis of the produced nanocomposite film through a Raman microscope (model Xplora, from Horiba, Kyoto, Japan) equipped with a 100 × 0.9 NA objective and laser beam with an excitation wavelength of 532nm. For absorption analysis, UV-vis spectrophotometer (model 8453 from Agilent, Santa Clara, CA, USA) was used to obtain the spectra of produced film on quartz slides. To investigate the electrical behavior of the film the OSSILA x200 source measuring unit coupled with Linkam HFS600E-PB4 with T95 system controller was utilized. The nanocomposite films were deposited on 'Micrux ED-IDE1-Au' gold-coated electrodes.

Results and Discussions

Raman Analysis

The Raman Spectra of the CNPs thin film and TiO_2-C Nanocomposite film are shown in Fig. 1.

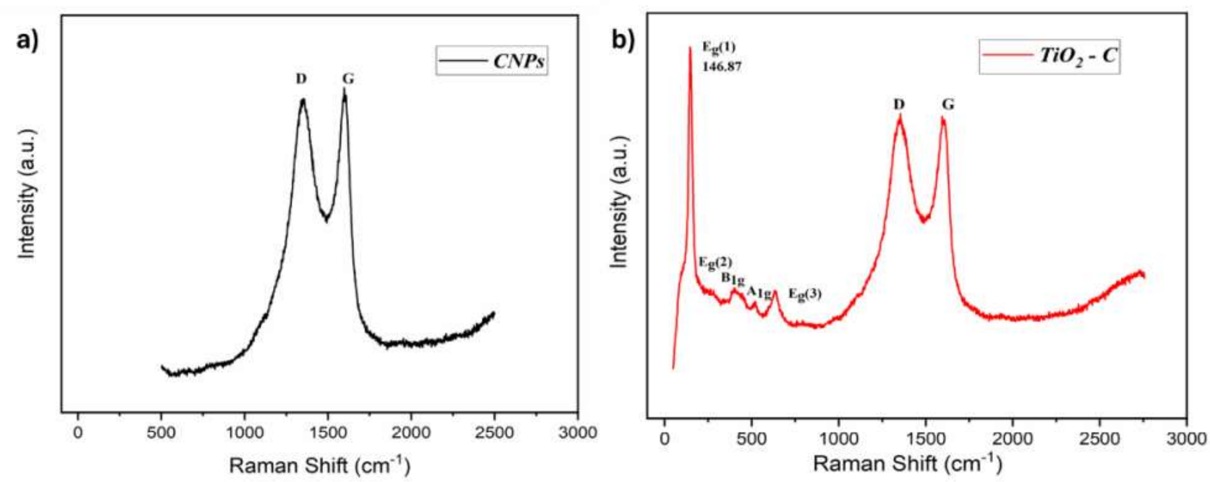

Figure 1. Raman spectrum of **(a)** CNPs thin film, and **(b)** TiO_2-C nanocomposite thin film.

The normalized Raman spectrum in Fig 1 (a) exhibits the characteristics of a standard carbon compound with D band and G band at 1350 cm^{-1} and 1600 cm^{-1} respectively with no further peak signals indicating the successful deposition of pure CNPs thin film. Fig 1 (b) shows the peaks at 146.87 cm^{-1}, 200 cm^{-1}, 402 cm^{-1}, 517 cm^{-1}, and 640 cm^{-1} attributed to the E_g, E_g, B_1g, (B_1g/A_{1g}), and E_g active anatase modes of TiO_2. There is a little positive shift of 2.87 cm^{-1} in the primary peak of TiO_2 with respect to its standard 144 cm^{-1} which suggests the blue shift due to incorporation of low band gap compound i.e., carbon. With that, the D band and G band in the spectrum corresponds to the most likely interconnection of CNPs and TiO_2 NPs, hence forming a nanostructured TiO_2-C composite thin film.

Absorption

Absorption of the TiO_2-C nanocomposite thin film is studied to investigate the energy band gap variation with respect to the pure TiO_2. Titania has remained a primary choice among semiconductor metal-oxides for various application due to its stable energy bandgap of 3.2 eV that is often engineered through incorporation of different organic and inorganic compounds to get desired behavior and performance for different applications. Employing the Tauc model, the optical band gap is experimentally determined from the UV-visible absorption spectrum:

$$\sqrt{\alpha h\upsilon} = B\left(h\upsilon - E_g^{opt}\right) \quad (1)$$

Here in Fig. 2, TiO_2-C nanocomposite thin film is reported with a reduced energy bandgap with respect to the pure TiO_2.

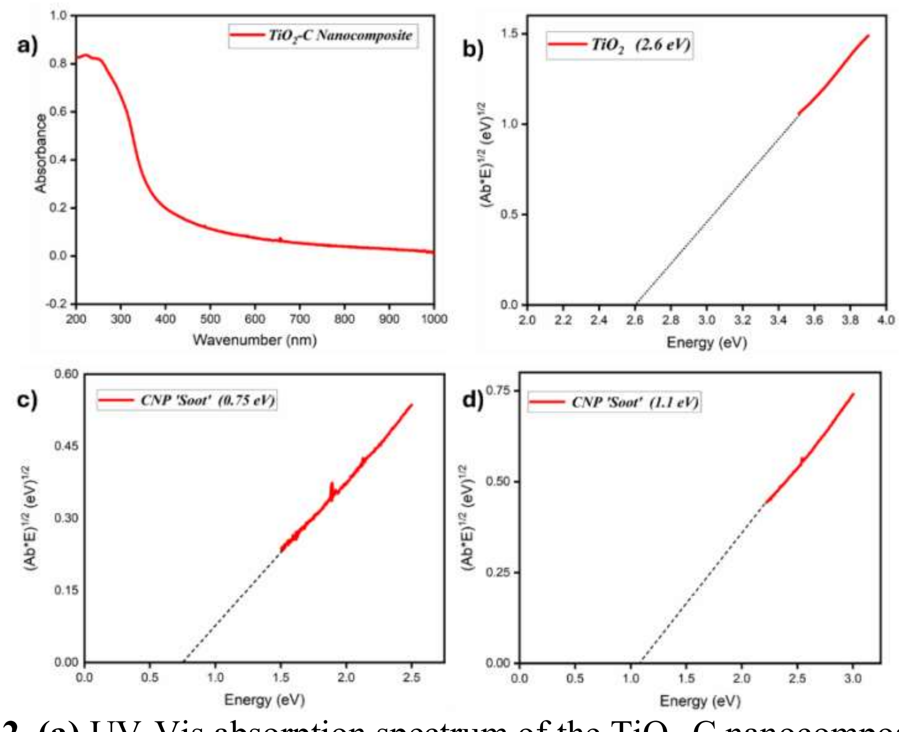

Figure 2. (a) UV-Vis absorption spectrum of the TiO_2-C nanocomposite thin film,**(b-d)** Tauc plot of the produced film to determine bad gape.

Fig. 2 (a) shows the complete absorption spectrum of the TiO_2-C nanocomposite film measured on the quartz. Employing the Tauc model, Fig. 2 (b-d) shows the Tauc plot visualized in different ranges of the spectrum for determining the optical bandgap. It is evident from the Fig. 2(b) that there is a significant reduction in the bandgap of TiO_2 from standard 3.2 eV to 2.6 eV apparently due to the CNPs incorporation. Whereas, in Fig. 2 (c-d) the Tauc plot corresponds to the bandgap of 0.75 eV and 1.1 eV attributed to the presence of CNPs.

Electrical 'Current-Voltage' Measurement (I-V)

As the memristor was introduced, the idea of a fourth circuit element has garnered a lot of interest as it allows for the creation of increasingly intricate integrated circuits using memristors to meet increasingly demanding technical specifications. Herein, an interesting resistive switching phenomena is observed in the produced TiO_2-C nanocomposite thin film. In Fig. 3 the curves measured at a voltage scan rate VSR of 0.2 v/s are shown.

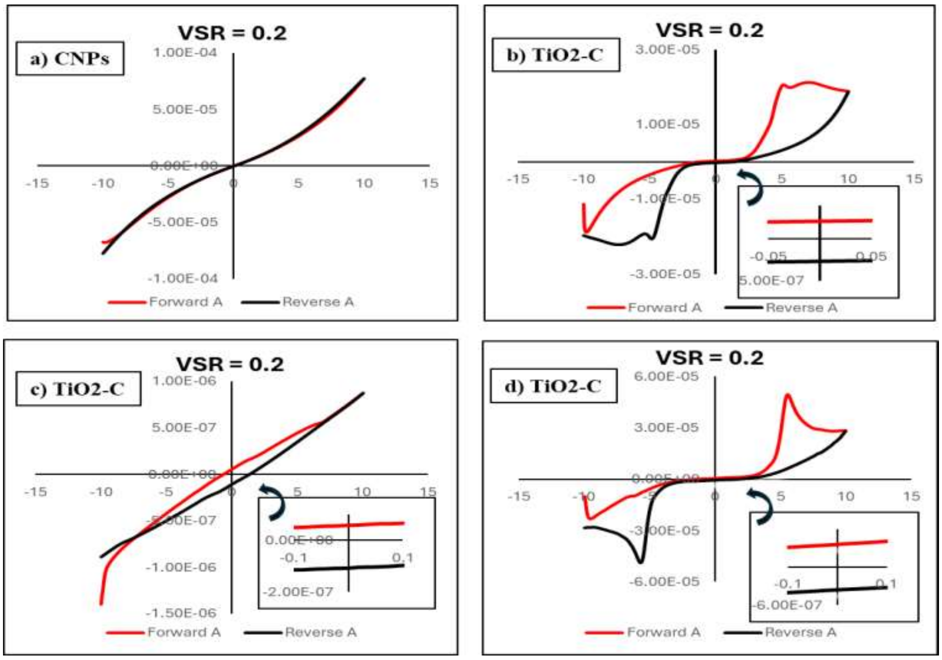

Figure 3. Current-Voltage ***(I-V)*** curves of the **(a)** CNPs thin film, **(b)** TiO_2-C nanocomposite on the synthesis day, **(c)** TiO_2-C nanocomposite after putting them in dark 'deactivation', **(d)** TiO_2-C nanocomposite after exposure to the solar light irradiation 'reactivation'.

The I-V measurements of TiO_2-C nanocomposite film unveiled the capacitive coupled resistive switching phenomenon that is observed in the non-zero crossing I-V curves, generally termed as non-pinched I-V hysteresis. Fig. 3 (a) shows a typical non-ohmic I-V curve attributed to the carbon compound of the 0M flame that produced pure CNPs film. Whereas the I-V curves of the TiO_2-C nanocomposite films in fig. 3 (b-d) exhibit an interesting activation and deactivation phenomenon of the switching behavior under exposure to the solar light irradiation and dark condition respectively. Fig. 3 (b) represents the I-V measurement taken on the synthesis day showing substantial bipolar switching. Fig.3 (c) shows the I-V measurements taken after a span of 05 days under dark. The switching phenomenon completely disappeared with a significant reduction of the current by up to 02 order of magnitude as illustrated in the Fig.3 (c) suggesting deactivation of the nanocomposite film due to the presence of TiO_2. Furthermore, upon exposure to the solar light irradiation for 05 days the switching behavior re-appeared again with an increase in the current value equivalent to the initial measurement of the nanocomposite film as shown in Fig. 3 (d). Such activation/deactivation behavior in the produced film hints toward its great potential to be utilized for sensors and non-volatile memory storage devices.

Conclusion

The TiO_2-C nanocomposite films were successfully produced through a facile one-step flame synthesis technique. Raman analysis revealed its composite formation and a noticeable blue shift in the primary peak of anatase attributed to the incorporation of low bandgap carbon compound. Substantial reduction in the optical band gap was observed due to the presence of CNPs. The extensive investigation of the I-V revealed the capacitive-coupled memristive effect along with an interesting activation/deactivation phenomenon of the switching mechanism under solar light irradiation/darkness. Such fascinating electrical properties of the produced nanocomposite film pave the way for deep insights into exploring its advance applications.

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