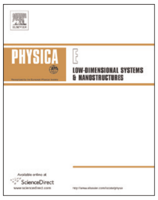
Physica E 74 (2015) 244–250

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe



# Unique combination of zero–one–two dimensional carbon–titania hybrid for cold cathode application

D. Banerjee [a,1], D. Kumar [a], N.S. Das [a], S. Sarkar [b], K.K. Chattopadhyay [a,b,*]

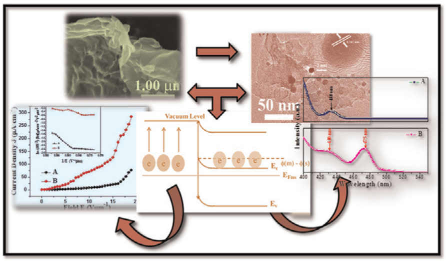
[a] *School of Material Science and Nanotechnology, Jadavpur University, Kolkata 700032, India*
[b] *Thin Film and NanoScience Laboratory, Department of Physics, Jadavpur University, Kolkata 700032, India*

## HIGHLIGHTS

- An easy chemical route was proposed to synthesis amorphous CNT–graphene composite.
- The as synthesized composite has been functionalized with $TiO_2$ nanoparticle.
- The PL of as prepared carbon system got enhanced after being functionalized by $TiO_2$.
- The field emission property of $TiO_2$ functionalized a-CNTs–a-Gs was enhanced.

## GRAPHICAL ABSTRACT

Synthesis and Characterization of Amorphous Carbon Nanotubes–Graphene–$TiO_2$ Hybrid for Cold Cathode Application.



## ARTICLE INFO

*Article history:*
Received 17 June 2015
Received in revised form
7 July 2015
Accepted 9 July 2015
Available online 10 July 2015

*Keywords:*
Amorphous materials
Composite materials
Nanostructured materials
Scanning electron microscopy
Tunnelling

## ABSTRACT

A unique multi-dimensional hybrid system has been developed by incorporating titania nanoparticle into chemically synthesized amorphous carbon nanotubes (a-CNTs)-amorphous graphene composites. The as-synthesized samples were characterized by x-ray diffraction, scanning and transmission electron microscopy; Raman spectroscopy and photoluminescence spectroscopy. The microscopic studies confirm the attachment of the $TiO_2$ nanoparticles on carbon structures. The performance of the both the pure and hybrid samples as cold cathode emitter has been investigated and it has been found that cold emission performance of the pure carbon system improves considerably after $TiO_2$ nanoparticles being added to it giving a turn on field as low as 2.1 V/µm and enhancement factor 2746. The enhancement of field emission characteristic after $TiO_2$ addition was justified from the 'ANSYS- Maxwell' software based simulation study.

## 1. Introduction

Carbon nanotubes (CNTs), after being discovered by Iijima in the year of 1991 [1], have gained considerable attention of the present researchers due to its unique electronic, mechanical and physical properties. CNTs with their various potential applications like gas sensors, gas storage devices, drug delivery reagent, hydrophobic coating, field effect transistor etc., are also considered to be an ideal candidate for the field emission (FE) display devices by virtue of their high aspect ratio (length to diameter), sharp tip-curvature, chemical inertness and mechanical strength [2,3]. There are uncountable reports regarding the FE property of CNTs [4–6]. Soon it was realized that regarding FE, it is possible to get better

---

[*] Corresponding author at: Thin Film and NanoScience Laboratory, Department of Physics, Jadavpur University, Kolkata 700032, India. Fax: +91 33 2414 6007.
*E-mail address:* kalyan_chattopadhyay@yahoo.com (K.K. Chattopadhyay).
[1] Present Address: Academy of Technology, G.T. Road (Adisaptagram), AEDCONAGAR, Hooghly 712121, India.

http://dx.doi.org/10.1016/j.physe.2015.07.007
1386-9477/

performance from CNTs if their walls can be decorated with either suitable organic functional groups [7–9] or by other inorganic nanostructures. The inorganic semiconductor includes CdS, $TiO_2$, CdSe/ZnS, ZnO, $SnO_2$, ZnS and PbSe [10–13]. However, most of these works were performed on crystalline CNTs which are difficult to synthesize with high yield. All the established methods (mainly chemical vapor deposition CVD) for large scale synthesis of crystalline CNTs require reaction temperature as high as 800–1100 °C with different catalyst and other complicated parameters like inert atmosphere etc which are not easy to achieve. In this point of view amorphous carbon nanotubes (a-CNTs) can be a good substitute for crystalline CNTs.

Also recently after being discovered by Geim and Novoselov in the year of 2004 [14], graphene, another sp$^2$ hybridized 2 dimensional allotrope of carbon gained main attention of the researchers due to its versatile applications like high performance transistors, transparent electrodes, ultra-capacitors, ultra-tough paper, gas adsorbent, sensors and also in many others [15–17]. Apart from these applications point of views this material got its importance due to some of its interesting properties like zero band gap, thermodynamic stability, extremely high charge-carrier mobility or the quasi-particles in it being described as massless Dirac fermions [18,19]. There are some established methods for synthesizing graphene that includes drawing method, epitaxial growth on silicon carbide, different chemical vapor deposition (CVD) methods, growth from metal-carbon melts, graphite oxide reduction and others [20–22] of which un-zipping of CNTs is very common technique [23]. Here we have used the same technique using prolong ultrasonication to unzip a-CNTs in order to produce amorphous graphene (a-Gs). The ultrasonication basically produces a-CNTs–a-Gs composite structure due to incomplete unzipping of a-CNTs.

The as prepared composite structure has further been modified by $TiO_2$ nanoparticles as $TiO_2$ is widely used in heterogeneous catalysis; as a photocatalyst; in solar cells for the production of hydrogenand electric energy; as a gas sensor; as a white pigment (e.g. in paints and cosmetic products); as a corrosion-protective coating, as an optical coating; in ceramics; in electric devices such as varistors; is important in earth sciences; plays a role in the biocompatibility of bone implants; is being discussed as a gate insulator for the new generation of MOSFETs and as a spacer material in magnetic spin-valve systems; and finds applications in nanostructured form in Li-based batteries and electrochromic devices [24]. Though there are so many reports regarding synthesis and different applications of CNT–$TiO_2$ or graphene–$TiO_2$ hybrid structure but so far the authors are concerned, there are no report regarding the synthesis and applications of a-CNTs or a-Gs-$TiO_2$ hybrid material. Keeping this in mind we have reported here the synthesis of a-CNTs–a-Gs-$TiO_2$ hybrid structure and have studied the performance of this system cold cathode material. *The reason for choosing $TiO_2$ for making hybrid material with CNTs is mainly due to the fact that it has a lower work function with respect to CNTs and hence it may improve the field emission property of the composite both in terms of turn-on field and current density. $TiO_2$ nanoparticles can act as additional emitting sites. Also simulation study supported such prediction as discussed in* Section 2. It has been seen that the as prepared amorphous CNT-graphene system shows good performance as cold cathode material which has been even enhanced after the inclusion of oxide nanoparticle into the system.

## 2. Experimental and characterization

The synthesis of a-CNT has been reported previously [25,26], briefly, ammonium chloride and ferrocene, all with analytical grade purities, were taken in 2:1 weight ratio and thoroughly mixed in a mortar followed by an open atmosphere heating in an oven at 250 °C. The naturally cooled black product was then washed by diluted hydrochloric acid and deionized water several times to remove the remaining amount of iron if any. The black residue was finally dried at 80 °C for 24 h. The as synthesized a-CNTs were functionalized by conventional acid treatment [27].

For production of a-Gs certain amount (5 wt%) of acid treated a-CNTs were dispersed into 60 ml ethanol and ultrasonicated for 2 h.

A part of it was kept as-synthesized and to another part certain amount of commercially purchased $TiO_2$ nanoparticle (Merck) were added and ultrasonication assisted composites were developed. The samples were named as A (pure carbon i.e. a-CNTs–a-Gs composites), B (carbon–$TiO_2$ system).

All the pure and hybrid samples were characterized by x-ray diffraction (XRD Bruker, D8 Advance). The morphology of the as prepared samples was studied by field emission scanning electron microscope (FESEM, Hitachi, S-4800) and high resolution transmission electron microscopy (HRTEM, JEOL-JEM 2100). Raman spectroscopic study has been done with the help of Witec Raman spectrometer (excitation wavelength $\lambda_{ex}=532$ nm). Photoluminescence (PL) spectrophotometer (Elico S-4600) was used to record the PL spectra of the as prepared sample.

The field emission study has been carried out in our home-made high vacuum field emission set up using a diode configuration consisting of a cathode (sample under test) and a stainless steel tip anode (conical shape with a 1 mm tip diameter) mounted in a liquid nitrogen trapped rotary-diffusion high vacuum chamber with an appropriate chamber baking arrangement. The measurements have been performed at a base pressure of $10^{-6}$ mbar. The tip-sample distance has been adjusted to a few hundred of μm by means of a μm screw. The whole surface of the sample can be made visible through the chamber view port, which has enabled us to recognize the electron emission or discharge, if any. It has been confirmed that there was no discharge and the current observed due to cold field emission of electron from the sample.

## 3. Results and discussions

### 3.1. X-ray diffraction analysis and microscopic study

Fig. 1 shows the XRD patterns of all the samples, where the spectra has been taken by irradiating the as-prepared sample by Cu $K_\alpha$ radiation ($\lambda=0.15406$ nm) operated at 40 kV, 40 mA with a normal $\theta$–$2\theta$ scanning. It is seen that sample A has no distinct peak throughout the region and thus it can be concluded that this is amorphous in nature and this amorphousness comes mainly

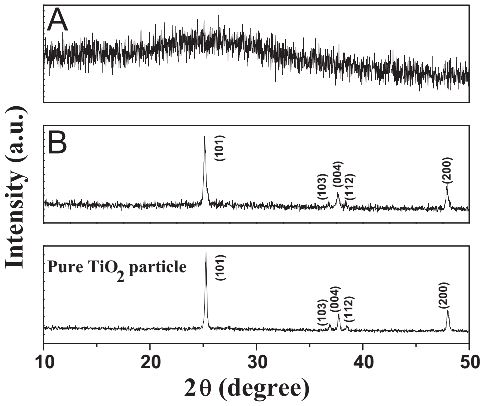


**Fig. 1.** XRD spectra of all the samples.