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Easy synthesis of porous carbon mesospheres and its functionalization with titania nanoparticles for enhanced field emission and photocatalytic activity

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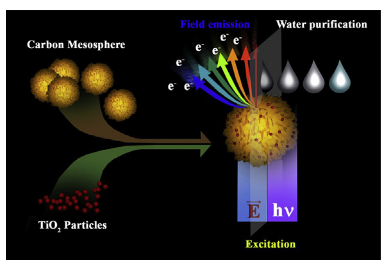
HIGHLIGHTS

- Carbon microspheres made of carbon sheet were synthesized by chemical route.
- The as synthesized carbon structure has been functionalized with TiO_2 particles.
- Hybrid samples show enhanced photocatalytic activity compared to pure sample.
- Hybrid sample shows better field emission for an optimized amount of TiO_2 particle.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple low temperature chemical approach for synthesizing porous carbon microspheres and its hybrid structure with titanium dioxide (TiO_2) nanoparticle is reported. The carbon spheres and related hybrid structures were characterized by X-ray diffraction, scanning and transmission electron microscopy, Raman and UV–Vis–NIR spectroscopy. The microscopic studies confirm the successful synthesis of hybrid structure of carbon spheres with TiO_2 nanoparticles. Also it reveals that the porous carbon spheres were actually composed of few layers thick carbon flakes. The performance of these as-synthesized pure and hybrid materials on removal of poisonous dyes from water under photon irradiation was studied. It is found that the hybrid sample shows better photocatalytic activity. It is also shown that TiO_2 nanoparticle functionalization enhances the electron field emission properties of carbon sample with reduction of turn-on field from 5.1 to 3.4 V/μm. The enhancement in the photocatalytic activity is due to the combined effect of higher surface area and the injection of electrons from carbon to TiO_2 nanoparticles whereas in case of field emission TiO_2 particles act as additional sites with lower work function and increase the roughness helping enhancement of field strength giving enhanced emission.

1. Introduction

Since the advent of nanotechnology carbon has proved to be a prime material due to its versatilities both from the fundamental as well as technological point of view. The versatilities regarding the

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properties of carbon are mainly associated with the fact that it can be found in different hybridized states that correspond to complete different properties as well as it can exist in all the possible dimensions from 0 D carbon dot to 1 D carbon nanotubes (CNTs), to 2 D graphene or 3 D diamond and other related structures. Among all these 1 dimensional CNTs and 2 dimensional graphene have gained the most attention after being discovered in the year of 1991 and 2004 by Ijima and Geim-Novoselov respectively [1,2]. Both these materials have shown their excellent ability in the different fields of applications that include hydrophobic coating, gas storage device, sensors, field effect transistor, ultra high capacitor, ultra tough paper, field emission (FE) display, reinforcing materials in different composites, drug delivery and many others [3–5]. All these specific applications cover mechanical, thermal, electrical, electronic, biomedical and other fields.

Family of carbon nanostructure is expanding continuously and some of these newly invented carbon nanostructures include carbon flowers, onions, trees, spheres, petals and many more [6–9]. In addition, the other major aspects of carbon related research are associated with the development of different hybrid materials and composites. In this process carbon nanostructures are functionalized with other suitable inorganic as well as organic or polymeric materials in order to obtain better performance in certain fields of applications. The inorganic materials include CdS, TiO_2, CdSe/ZnS, ZnO, SnO_2, ZnS and PbSe [10–17] etc. Out of these TiO_2 is very important because of its different unique properties. TiO_2 is used in heterogeneous catalysis, solar cells for the production of hydrogen and 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 and also it plays an important role in the biocompatibility of bone implants. It is also used as a gate insulator for the new generation of MOSFETs and as a spacer material in magnetic spin-valve systems; and finds applications in Li-based batteries and electro-chromic devices [18].

Though there are lots of reports regarding the enhanced photocatalytic activities of TiO_2-CNT or TiO_2 graphene composite [19–25], there is no report regarding the development of TiO_2 based hybrid material with porous carbon sphere. Previously we have reported a simple solvo-thermal synthesis of porous carbon spheres composed of carbon flakes and have shown how the water adsorption on this porous structure can considerably enhance the electron field emission properties of the material [24]. Here we report functionalization of such porous carbon mesosphere with TiO_2 nanoparticles and its usefulness as cold cathode material and also as a reagent for photo-assisted removal of poisonous organic dyes from water. These results indicate the multi-functionality of such hybrid material in true sense.

2. Experimental

The preparation of porous carbon microspheres have been reported elsewhere [26]. Briefly, appropriate amount of ferrocene and sulfur was thoroughly mixed in a mortar and the mixture was then taken in a 100 ml Teflon coated stainless steel autoclave which was filled with 90% benzene and was sealed well. The whole system was then put into an oven maintained at 200 ^{O}C for 48 h followed by a subsequent natural cooling resulted a blackish product that was collected after filtration. The final product was obtained after thoroughly washing the black residue by diluted HCl, distilled water and ethanol and then overnight drying it in an oven at 60 °C. A part of it was kept as-synthesized and the other part was divided into three parts and different amount of commercially purchased TiO_2 nanoparticle (Merck) were added and composites were developed by ultrasonication. The samples were named as C1 (pure carbon sphere), CT1 (hybrids with 2 g TiO_2 in 0.5 g carbon), CT2 (hybrids with 3 g TiO_2 in 0.5 g carbon) and CT0 (hybrids with 0.5 g TiO_2 in 0.5 g carbon). 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 were done with the help of Witec Raman spectrometer (excitation wavelength $\lambda_{ex} = 532$ nm). Shimadzu UV-3600 UV–Vis–NIR spectrometer was uses to record the absorption spectra of different dyes dissolved in water (For photocatalytic study).

The photocatalytic activities of the as-prepared samples were studied with a standard photocatalytic set up with two dyes, rhodamine B(RhB) and methyl orange (MO). For a typical experiment, RhB and MO stock solution of 0.01 g ml^{-1} was prepared. 10^{-5} M test solution was then prepared by adding required amount of de-ionized water to the stock solution. 0.03 g of all the samples C1, CT0, CT1 and CT2 were added to this test solution separately and stirred in same speed in dark condition for 3 h. Thereafter the solutions containing each powder sample were kept under UV irradiation using two 40 W UV tube (Phillips) which emits wavelength of 254.6 nm (UV C). The tube to suspension surface distance was kept at 15 cm. The above mentioned solutions were retained under UV emission for different time durations and parts of the solutions were collected in different time intervals for absorption study. The time evolution of the absorption spectra were recorded with the solutions collected in different time intervals.

A home-made high vacuum field emission set up was used to study the electron field emission characteristics using a diode configuration. The sample under test was used as a cathode and a stainless steel tip was used as anode (conical shape with a 1 mm tip diameter) electrode. A base vacuum of 10^{-6} mbar was achieved with the help of a liquid nitrogen trapped rotary-diffusion pump with an appropriate chamber baking arrangement. The whole arrangement was made visible through the chamber view port to assure that no electric discharge was taken place and the current obtained was only due to cold field emission of electron from the sample.

3. Results and discussion

3.1. XRD analysis and microscopic study

Fig. 1 shows the XRD patterns of all the pure and hybrid samples, using Cu K_α radiation ($\lambda = 0.15406$ nm) operated at 40 kV, 40 mA with a normal $\theta - 2\theta$ scanning. It is seen that C1 sample has a

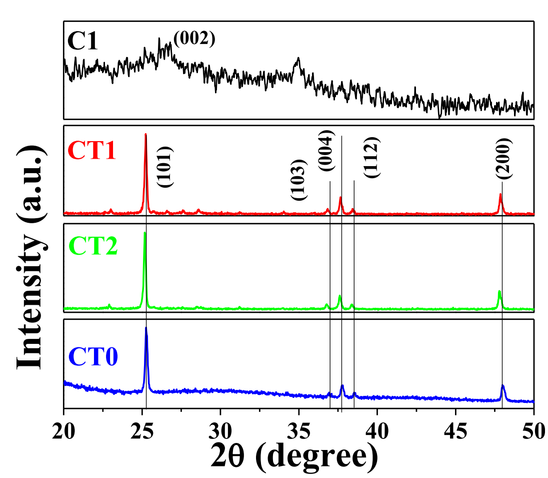

Fig. 1. XRD patterns of all the samples.