Synthesis of grape-like carbon nanospheres and their application as photocatalyst and electrocatalyst

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ABSTRACT

Carbon nanospheres of grape-like structure (CNS) with diameter ranging from 40 to 50 nm and wall thickness of 6–8 nm were synthesized by solvothermal route. The phase structure, morphology, microstructure, thermal stability, disorder and optical properties of synthesized CNS were investigated by various characterization techniques. The possible formation and growth mechanism for CNS were discussed on the basis of the in-build reaction conditions. The degradation study of organic pollutants (methylene blue) in UV light in the presence of synthesized CNS was done. The stability of the CNS in electrochemical performance was also discussed at the different potential window and compared its electrocatalytic activity with platinum supported on CNS which shows the better response for oxygen reduction reactions (ORR) at an optimized potential window (–0.2 to 1.0 V vs SCE).

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1. Introduction

In the era of nanoscience and nanotechnology, a significant amount of research has been focused on the application of catalysts used for different production processes. Catalyst is a substance that enhances the chemical reactions rate without undergoing any change in itself. There are various catalysts that have been developed for the purpose to enhance the catalysis for environmental and renewable energy applications, such as photocatalysis, electro-catalysis, hydrogen evolution, solar cells and sensor devices [1–5]. To date, most of the authors have investigated the catalytic activity using various catalysts such as metal oxides (TiO_2, ZnO, WO_3 etc.) or noble metals (Pt, Au, Pd, Ni, and Ag) individually as well as in combinations with each other, in particular, for photo catalytic and electrocatalytic applications [1–9]. However, the application of these catalysts is limited due to high cost (noble metals) and lesser active sites of metal oxide (s) for different catalytic activity [10,11]. This problem can be overcome by adding a lower cost supporting material to the conventional catalyst which has high sensitivity to enhance the chemical activity. The significance of supporting materials is to increase the dispersion of active phases, improve mechanical strength, stability and catalytic activity.

From last two decades, carbon-based nanomaterials (CNTs, graphene, carbon nanofibers, carbon black and carbon nanospheres) are widely used as the catalyst support because of their proper pore size distribution, promising thermal stability, chemical inertness, excellent electrochemical properties, ease of recovery and recyclability and lower cost than conventional catalysts [11–15]. Among different forms of carbon nano materials, carbon nano spheres (CNS) also known as graphene balls, is of great interest, because of their hierarchical and interconnected structure, that is favorable for the CNS to use as a catalyst support [16,17]. The spherical morphology of carbon in the form of CNS is normally formed when the concentric multishell fullerene clusters get stacked into each other. Moreover, the nature of carbon in these structures may be of graphitic or non-graphitic. During high-temperature treatment, the graphite sheets usually bend that follow the curvature of the sphere in order to minimize their energy with the formation of dangling bonds on their surface [17,18]. Furthermore, CNS with better thermal stability, better conductivity, low density, large void space fraction with defects in the form of dangling bonds brought about a stronger catalyst support in the adsorbents and fuel cell applications [16–22]. Much work on catalytic activity of carbon materials (CNTs, graphene, carbon black, carbon foams) is going on from last few years [11–15] whereas in case of CNS, limited work has been done.

Considering these facts, the present work is undertaken on the synthesis of CNS through solvothermal route. In addition, the photocatalytic and electrochemical performance of as-obtained CNS, for its use as a catalyst, are also discussed.

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2. Experimental

2.1. Sample preparation

In the present set of experiment, magnesium metal turnings (Mg) and acetone were used as initial ingredients to synthesize the sample. The purity of these materials was greater than 99.9%. Magnesium was used as a reducing agent and acetone as a source of carbon. Initial ingredients with the fixed amount of Mg (1.5 g) and C_3H_6O (20 ml) were put in a specially designed autoclave of 35 ml capacity. After proper sealing, the autoclave was heated up to 600 °C at a rate of 5 °C/min, held at this temperature for 5 h and cooled down to room temperature in the furnace itself. After completion of the reaction, the dark solid powder was taken out from the autoclave and washed once with (1:1) HCl to remove MgO and other impurities from the product. The powder was washed several times with high purity water to remove remaining HCl. At the end, it was washed with ethanol to eliminate the water adsorbed in the powder. The final product was dried at 100 °C for 20 h.

2.1.1. Deposition of Pt

Pt nano particles were deposited on synthesized CNS by dispersing 40 mg of CNS powder in 20 ml of ethanol in ultrasonic bath. To this solution 100 μL hexachloroplatinic acid (H_2PtCl_6) aqueous solution was added. In the mixture of metal salt and CNS support, an appropriate amount of 0.05 M NaOH/ethanol was added to maintain the pH~10. The precipitate was washed with high purity water and then dried at 80 °C.

2.2. Characterization

The sample was characterized by X-ray diffraction (XRD) using Philips PANalytical X'Pert-PRO with CuKα radiation ($\lambda = 1.54$ Å) obtained from the copper target using an inbuilt Ni filter. During XRD experiment, scan speed was 5°/min. The field emission scanning electron microscopy (FESEM) of the sample was done using Zeiss Supra 55 equipment. Microstructural features and growth mechanism was examined by TECHNAI G transmission electron microscope (TEM) at an applied voltage of 200 kV. For TEM study, the synthesized sample was suspended in ethanol. One drop of suspension was dropped on carbon-coated copper grid and ethanol was allowed to evaporate. Energy dispersive spectroscopy (EDS) was done by Oxford Instruments INCA-Act Energy 200. Differential thermal analysis (DTA) and thermo-gravimetric analysis (TG) were carried out at a heating rate of 5 °C/min in the temperature range of 50–1000 °C in air atmosphere using Perkin-Elemer, diamond TG thermal analyzer. Raman measurements were carried out using Ar+ excitation source of 514.5 nm wavelength with a Renishaw-Invia micro-Raman spectrometer. Optical absorption spectrum was recorded with double beam UV–vis absorption spectrophotometer (Hitachi, Model-U-3900H) in the range 200–600 nm. Photoluminescence (PL) emission spectrum of the sample was recorded by Edinburgh Instruments FS920 spectrometer having 450 W Xe arc lamp and a single photon counting photo-multiplier (Hamamatsu R2658P).

2.3. Photocatalytic study

Photocatalytic activity of the CNS was investigated for the degradation of methylene blue dye (MB) as a model organic contaminant under UV–vis light irradiation. Experiments were conducted in a photoreactor having a cylindrical glass vessel of 1 L capacity in the presence of 125 W UV lamp as the light source. A 0.05 g of CNS as the catalyst was added to the 50 ml of the MB dye solution having concentration 12.5 μM in a cylindrical vessel. Prior to the UV light illumination, the reaction mixture was stirred for 30 min in the dark to ensure the adsorption–desorption equilibrium between the catalyst surface and the dye solution. The reaction mixture was then irradiated under the UV light source. The temperature inside the reactor was maintained constant with the recycled water. After specific intervals of time, the sample was collected from the bulk solution and centrifuged to separate out the dye solution from the catalyst. The absorption spectra of the MB solution was then recorded by UV–vis spcetrophotpmeter at $\lambda_{max} = 664$ nm during the photo-degradation process.

2.4. Electrochemical measurements

Electrochemical measurements were performed on the Bio-Logic EC Lab SP 300 instrument using three electrode cell comprising of a glassy carbon electrode (GCE) as working electrode, Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in 0.5 M H_2SO_4 at room temperature. The amount of catalyst (4 mg) was mixed with 1 ml of ethanol and sonicated for 20 min. 10 μL of the as-prepared catalyst suspensions were dropped onto the glassy carbon electrode and dried at room temperature. After evaporation for 30 min, 10 μL of Nafion® 117 solution (Sigma-Aldrich) was dropped on the top surface of the electrode to cover and stabilize the CNS structure.

3. Results and discussion

3.1. XRD analysis

To determine the structure of as-obtained CNS, the XRD measurements were conducted as shown in Fig. 1. The main peak at $2\theta = 25.6°$ corresponds to the (002) diffraction plane of hexagonal graphite [17,18]. The broadening of the peaks in X-ray diffraction pattern of CNS indicates the disorder and turbostratic structure of the graphite [18,21,23]. Moreover, the indistinguishability of the (100) and (101) peaks centered at 43.7° also reflects the presence of disorderness in the structure [18]. This can also be associated with the presence of some oxygen atoms, which are not detected in XRD because of the negligible amount (< 5%) in the powder sample.

3.2. Microstructural analysis and formation mechanism

The structural features of the synthesized CNS were studied using FESEM and is shown in Fig. 2. Low magnification micrograph
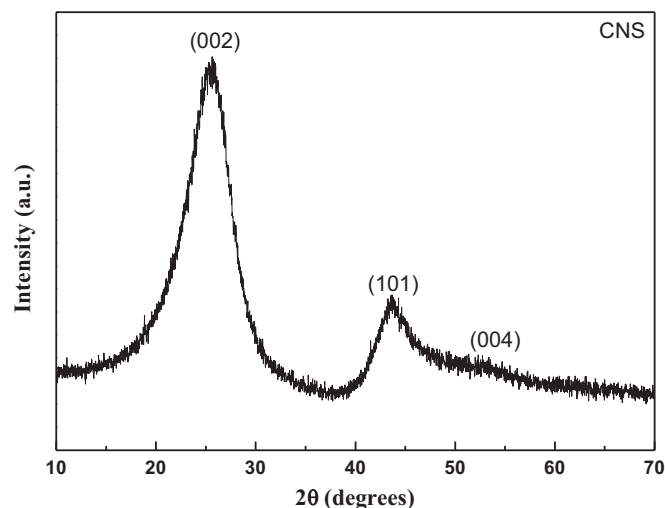

Fig. 1. XRD pattern of as-obtained carbon nanospheres (CNS).