Utilization of plastic wastes for synthesis of carbon microspheres: A template for nano crystalline copper (II) oxide hollow spheres

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Abstract

Catalyst and solvent free single step approach for the synthesis of carbon spheres using various municipal plastic wastes under autogenic pressure is presented. The obtained carbon spheres have been characterized with different microscopic and spectroscopic techniques. The microscopic analysis showed formation of carbon microspheres having diameters of 1-8 µm. Among the different types of plastic wastes studied, only polyethylene, polypropylene and polyacrylate could be converted into carbon spheres with 100% purity whereas the carbon particles with irregular shape was observed in case of other plastic wastes. The absence of catalyst makes the carbon spheres free from metal impurities and avoids the further purification process. The synthesis of carbon spheres from plastic wastes proceeds with the formation aromatic hydrocarbons. The CuO hollow spheres of wall thickness of ~130 nm have been prepared using plastic waste derived carbon spheres as template material under ultra-sonic treatment.

Keywords: *Plastic wastes; Carbon spheres; CuO hollow spheres*

1. Introduction

In the recent years, enormous amounts of plastic wastes have been generated due to increased usage, demand and production of plastic materials. Recycling of the waste material not only helps the generation of new resources but also reduces environmental pollution [1]. Most of the plastic materials which come to the market are recyclable but there are lots of technical as well as economical problems attached with recycling [2]. The difficulties associated with the separation and sorting of plastic wastes is the biggest problem with their recycling. The cost effective plastic materials has been recycled whereas other plastic wastes are either disposed by land filling or incinerated [3], which again creates the environmental issue due to emission of toxic pollutants.

Over the past decade carbon spheres have been attracting the interest of researcher community due to their interesting physicochemical properties and applicability as reinforcement materials for rubber [4], supports for catalysts [5], lubricating materials and in fuel cells or secondary lithium ion batteries [6]. Many techniques such as chemical vapor deposition, solvothermal synthesis [7], carbonization [8] and arc-discharge [9] have been employed for the production of carbon spheres. Many of them utilize the chemical reagent as carbon feed stock and metal as catalyst/reducing agent. One of the main disadvantages of such method is the conversion of metal catalyst into their respective metal salts during synthesis and post synthesis treatment [7], which increases the production cost as well as raises the environmental issue.

In this paper, we describe the catalyst free synthesis of carbon microspheres by the pyrolysis of a wide range of plastic wastes collected from municipal solid wastes including polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), polyacrylates (PC), polyvinyl chloride (PVC), polystyrene (PS) and PET under autogenic pressure. A single-step solvent free approach to obtain impurity free carbon spheres using different plastic wastes as carbon source is explored.

The solid carbon spheres produced from plastic wastes have been successfully utilized as the template material for the synthesis of CuO hollow microspheres with precipitation method.

2. Materials and Methods

2.1. Synthesis of carbon microspheres

Typically, for the synthesis of carbon spheres, plastic material was taken in the stainless steel autoclave. The autoclave was sealed and heated up to desired temperature at the heating rate of 20 °C/minute in the muffle furnace. The heating was cut off after attaining the preset temperature and autoclave was allowed to cool to room temperature. The product was collected, washed with benzene and dried at 100 °C for 10 h in an air oven.

2.2 Fabrication of CuO hollow microspheres

0.1 g of $CuCl_2.2H_2O$ (AR grade; S. d. fine chem., India) mixed with 1.0 g of carbon spheres (PP-700) was added in to 10 ml of Millipore water. 1.0 ml of methanol added in above mixture to dispersed carbon spheres was ultra-sonicated for 1 hr. The mixture was further sonicated after the addition of 1.0 ml of 0.1 M NaOH for 15 min and aged at 80 °C for 6 hr. Filtered and washed with excess of Millipore water followed by drying at 100 °C for 5 hr in air oven. To obtain CuO hollow spheres, the above core shell carbon sphere/CuO particles were calcined in a muffle furnace at 600 °C for 2 h with the heating rate of 1 °C/min.

3. Results and Discussion

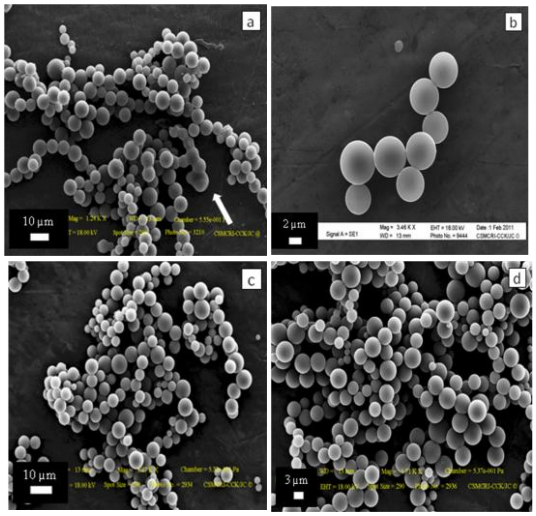

Fig. 1. SEM images of carbon spheres produced by pyrolysis of different plastic materials under autogenic pressure; (a) PP-600, (b) PP-700, (c) PP-700-1, (d) PP-800.

The formations of carbon spheres begin above 600 °C whereas an oily sticky mass was obtained below 600 °C. Even though the carbon spheres formation begins at 600 °C, the obtained product consist of agglomerated carbon spheres (Fig. 1a). The increase in the reaction temperature from 600 °C to 700 °C produces well dispersed carbon spheres with perfect spherical shape and smooth surface i.e. free from amorphous carbon material (Fig. 1b). The further increase in reaction time i.e. one hour at 700 °C (Fig. 1c) as well as temperature (800 °C for zero time; Fig. 1d) has no effect on the morphology and yield. On the basis of above observations, the reaction temperature and time were selected as 700 °C and zero hour respectively, for further experiments with different plastic materials as carbon precursor.

The carbon spheres were initially uniformly coated with copper hydroxide under ultra-sonic treatment. To obtain the CuO hollow spheres the carbon copper hydroxide core shell structure was calcined under static atmosphere at 600 °C for 2 hr at the heating rate of 1 °C/min. The HR-TEM analysis (Fig. 2a) depicts the formation of CuO hollow microspheres by utilizing carbon spheres as template. Fig. 2b shows the porous CuO hollow sphere composed of CuO nanoparticles with

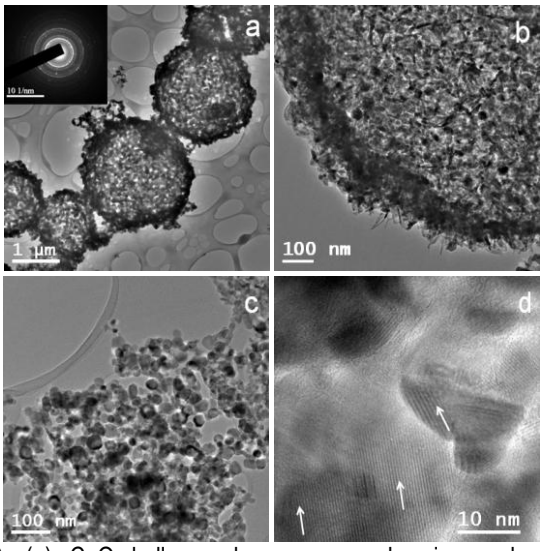

Fig. 2. (a) CuO hollow spheres prepared using carbon spheres (PP-700) as template (inset electron diffraction pattern of CuO hollow sphere); (b) surface of hollow spheres composed with CuO nanoparticles; (c) building block CuO nanoparticles observed in system and (d) crystal lattice of CuO nanoparticles

wall thickness of ~130 nm. CuO nanoparticles of ~25 nm in size have also been observed along with microspheres (Fig. 2c). Inset of Fig. 2a showed the typical electron diffraction pattern for CuO hollow microspheres whereas Fig. 2d showed the crystal lattice of CuO microsphere.

4. Conclusions

The reported protocol allowed catalyst and solvent free approach towards the large scale production of carbon micro spheres using various plastic wastes. Plastic materials such as PP, LDPE, HDPE and PC resulted in the carbon spheres with 100% purity i.e. absence of amorphous carbon material and foreign morphologies. Without any post treatment, the obtained carbon spheres have been successfully utilized as the template for the synthesis of nano crystalline CuO hollow spheres.

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