

Utilization of Plastic Wastes for Synthesis of Carbon Microspheres and Their Use as a Template for Nanocrystalline Copper(II) Oxide Hollow Spheres

Sandesh Y. Sawant,[†] Rajesh S. Somani,^{*,†} Asit B. Panda,^{†,‡} and Hari C. Bajaj^{*,†}

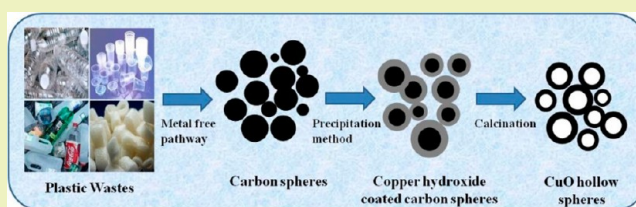
[†]Discipline of Inorganic Materials and Catalysis, Central Salt & Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar 364002, Gujarat, India

[‡]Central Glass and Ceramic Research Institute (CSIR-CGCRI), Raja S. C. Mullick Road, Kolkata-32, West Bengal, India

S Supporting Information

ABSTRACT: The metal- and solvent-free single-step approach for the synthesis of carbon microspheres using various municipal plastic wastes at 700 °C under autogenic pressure is reported. 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 carbon particles with irregular shapes were also observed in the cases 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 of aromatic hydrocarbons. The nanocrystalline CuO hollow spheres with a wall thickness of ~130 nm have been prepared using plastic waste-derived carbon spheres as the template material under ultrasonic treatment.

KEYWORDS: Polymer waste, Pyrolysis, Metal-free approach, Polypropylene, Polyethylene, Hydrocarbon



INTRODUCTION

Plastic is the common term used for a wide range of synthetic/semi-synthetic high molecular weight polymers. 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 are recyclable, but lots of technical as well as economical problems are associated with recycling.² The difficulties associated with the separation and sorting of plastic wastes is the biggest problem with its recycling. The cost-effective plastic materials has been recycled, whereas other plastic wastes are either disposed of by land filling or incinerated,^{3,4} which again creates an environmental issue due to emission of toxic pollutants.^{5,6} The conversion of plastic waste into value-added products is another way to overcome the above problems.⁷ Pyrolysis,⁸ gasification, and hydrogenation⁹ are economically and environmentally attractive techniques for plastic waste utilization. The catalytic pyrolysis and liquefaction of the plastic wastes in nitrogen or hydrogen atmosphere produces gases and oil products containing alkanes and alkenes with three to five carbon atoms.¹⁰ Aromatic and polyaromatic hydrocarbons have also been observed in oil products.⁵

In the past decade, carbon spheres have been attracting the interest of the research community due to their interesting physicochemical properties and applicability as reinforcement

materials for rubber,¹¹ supports for catalysts,¹² lubricating materials, and in fuel cells or secondary lithium ion batteries.¹³ Many techniques such as chemical vapor deposition,¹⁴ solvothermal synthesis,¹⁵ carbonization,¹⁶ and arc-discharge¹⁷ have been employed for the production of carbon spheres. Many of them utilized the chemical reagent as carbon feed stock and metal as a catalyst/reducing agent. One of the main disadvantages of such a method is the conversion of metal catalyst into their respective metal salts during synthesis and post-synthesis treatment,¹⁵ which increases the production cost as well as environmental issues. In view of the above, there is need for the catalyst-free process for the production of carbon spheres. Aliphatic and aromatic hydrocarbons have been utilized as the carbon sources for the synthesis of carbon spheres.¹⁸ Yang et al.¹⁹ and Pol et al.²⁰ have reported the synthesis of carbon spheres using poly(tetrafluoroethylene) and polyethylene terephthalate (PET), respectively. Utilization of polypropylene (PP) as carbon source for the synthesis of carbon nanotubes has also been reported.²¹

In this paper, we presented the catalyst-free synthesis of carbon microspheres by the pyrolysis of a wide range of plastic wastes collected from municipal solid wastes including PP, high density polyethylene (HDPE), low density polyethylene

Received: April 25, 2013

Revised: August 8, 2013

Published: August 12, 2013

(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 the carbon source is explored.

Inorganic materials with hollow structures have received considerable attention due to their potential applications in various fields.²² Among all the metal oxides, copper oxide (CuO) is one of the most studied materials in the literature because of its potential application for gas sensors,²³ optical switches,²⁴ electrodes, catalysis,²⁵ high-temperature superconductors,²⁶ and giant magneto-resistance materials.²⁷ Various morphologies of CuO such as nanowires,²⁸ cubes,²⁹ spheres or hollow spheres,³⁰ flower-like structures,³¹ cages, and octahedrals³² have been reported. 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.

MATERIALS AND METHODS

Synthesis of Carbon Microspheres. Plastic samples were collected from Bhavnagar municipal waste and the local market. Typically, for the synthesis of carbon spheres, plastic material (2.5 g) was taken in the 50 mL capacity stainless steel autoclave. The autoclave was sealed and heated to the desired temperature at the heating rate of 20 °C/min in the muffle furnace. The heating was cut off after attaining the preset temperature, and the 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. The nomenclature of each sample includes the abbreviation of plastic type followed by the reaction temperature. The reaction time having more than zero minutes is mentioned after the reaction temperature. Thus, for carbon spheres prepared from polypropylene at 700 °C for zero time and 1 h, the nomenclature would be PP-700 and PP-700-1, respectively. The yield obtained on the basis of the plastic used and carbon content is given in Table 1.

Fabrication of CuO Hollow Microspheres. A total of 0.1 g of CuCl₂·2H₂O (AR grade; S. d. fine chem., India) mixed with 1.0 g of carbon spheres (PP-700) was added to 10 mL of Millipore water. A total of 1.0 mL of methanol was added to the above mixture to dispersed carbon spheres and ultrasonicated for 1 h. The mixture was

further sonicated for 15 min after the addition of 1.0 mL of 0.1 M NaOH for 15 min and aged at 80 °C for 6 h. Then it was filtered and washed with the excess Millipore water followed by drying at 100 °C for 5 h in air oven. With the obtained 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.

RESULTS AND DISCUSSION

Carbon Microsphere. The plastic materials available in the market are mainly classified into seven types and assigned specific symbols by the Plastic Bottle Institute of the Society of the Plastics Industry to assist in identification and recycling of plastic (Table S1, Supporting Information). We have selected all seven categories of plastic materials as carbon feed stock. The optimization of reaction conditions has been achieved by PP as carbon source (Table 1).

The formation of carbon spheres was initiated 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 consists of agglomerated carbon spheres (Figure 1a). The increase in the reaction temperature from 600 to 700 °C produces well-dispersed carbon spheres with perfect spherical shapes and smooth surfaces, i.e., free from amorphous carbon material (Figure 1b). The further increase in reaction time, i.e., 1 h at 700 °C (Figure 1c), as well as temperature (800 °C for zero time; Figure 1d) has no effect on the morphology and yield (Table 1). On the basis of the 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. Here, we utilized the seven different types of plastic materials as carbon sources for the production of carbon spheres. The plastic materials including PP, HDPE, LDPE, and PC produced the solid carbon spheres having smooth surfaces (Figure 1b,e,f,g), whereas impurities like carbon particles along with carbon spheres was observed in the case of PVC and PS as carbon sources at 700 °C (Figure 1h,i).

Pol et al.²⁰ reported the formation of solid carbon spheres on thermal degradation of PET under autogenic pressure at 700 °C for 3 h. The utilization of PET as the carbon source in our approach produces carbon spheres along with large amounts of shiny carbon particles with irregular shapes (Figure S1a, Supporting Information). In the case of PET as the carbon source, we carried out the thermal degradation for a longer time (3 h). As a result, the yield of carbon spheres increased, but it also resulted in the carbon particles formation (Figure S1b, Supporting Information). The same results were also observed in the case of PVC and PS as carbon sources. The product obtained from PVC mainly contains the agglomerated carbon spheres with carbon particles (Figure 1h). The product containing the pure carbon sphere was black amorphous powder, whereas the presence of carbon particle impurities makes it shiny and crystalline. Hence, it could be easy to identify the pure carbon spheres product by only visualization. Polymers possess different thermal stability depending upon their monomer units and bond dissociation energies, which leads to different thermal decomposition properties. The formation of carbon particles along with carbon spheres is explained on the basis of the thermal degradation properties of the plastic wastes (polymers) utilized in the present study. Various researchers have observed that PVC, PET, and PS are difficult to pyrolyze, which leads to the considerable formation of char (due the presence of aromatic moiety), whereas PP, PE,

Table 1. Experimental Conditions for Preparation of Carbon Spheres Using Various Plastics as Carbon Source

Sr. no.	sample code	temp (°C)	time (h)	yield ^a (%)	product obtained
1	PP-500	500	0	---	no product
2	PP-600	600	0	12.0	agglomerated carbon spheres
3	PP-700	700	0	34.4 (38.7)	carbon spheres
4	PP-700-1	700	1	34.8	carbon spheres
5	PP-800	800	0	42.4	carbon spheres
6	PET-700	700	0	22.4 (33.9)	carbon spheres + carbon particles
7	HDPE-700	700	0	35.6 (39.5)	carbon spheres
8	PVC-700	700	0	33.6 (83.15)	carbon spheres + carbon particles
9	LDPE-700	700	0	34.0 (37.9)	carbon spheres
10	PS-700	700	0	33.2 (33.5)	carbon spheres + carbon particles
11	PC-700	700	0	41.6 (80.1)	carbon spheres
12	PET-700	700	3	30.8	carbon spheres + carbon particles

^a% yield on basis of plastic used; in paranthesis, the % yield on the basis of the carbon content.

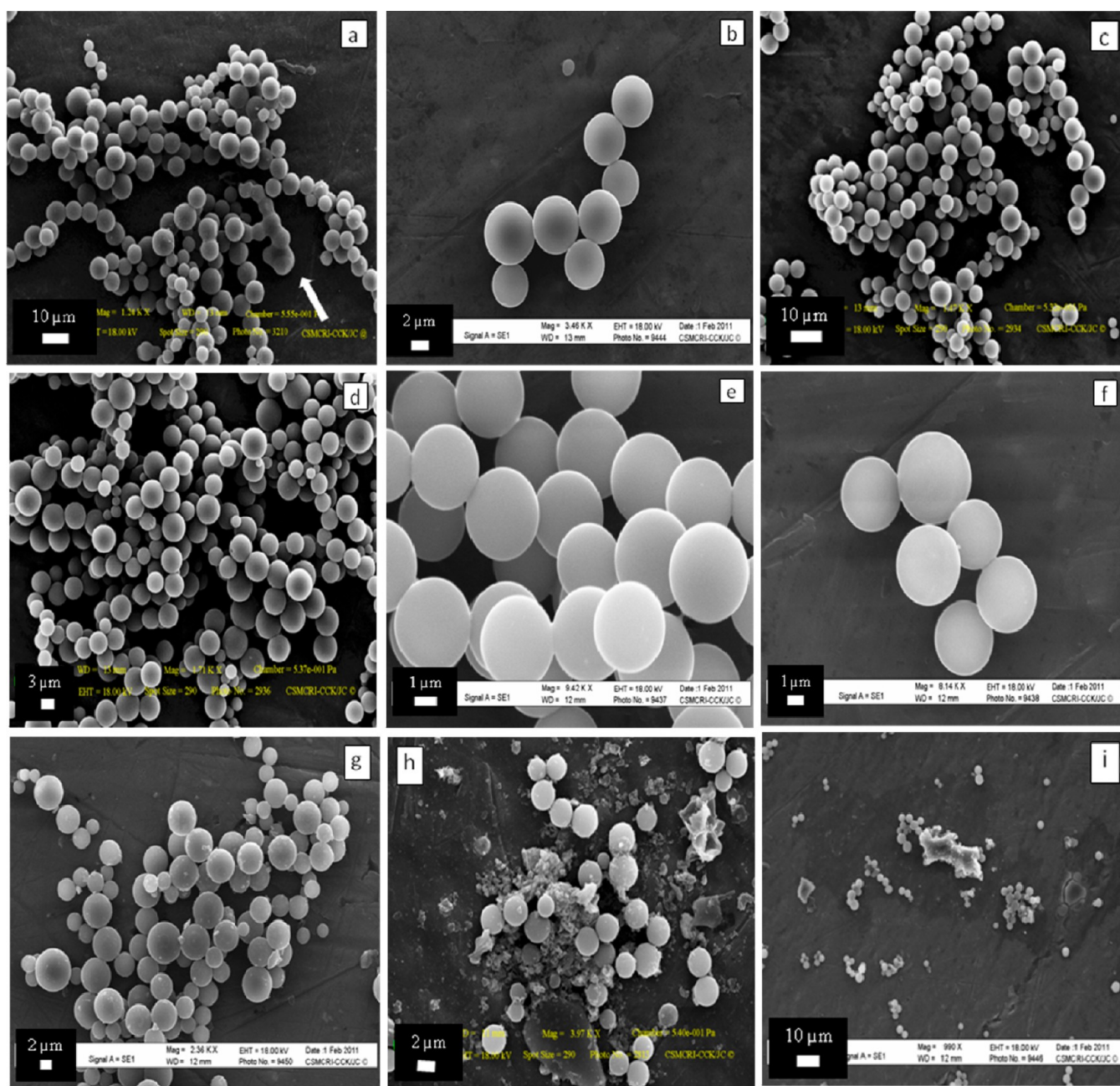


Figure 1. SEM images of carbon spheres produced by pyrolysis of different plastic materials under autogenic pressure: (a) PP-600, (b) PP-700, (c) PP-700-1, (d) PP-800, (e) HDPE-700, (f) LDPE-700, (g) PC-700, (h) PVC-700, and (i) PS-700.

and PC resulted in the 100% formation of oil and gas products.^{33–36} The carbon particles obtained, along with the carbon spheres in the case of PVC, PET, and PS, are the result of the char formation due to the presence of aromatic nuclei substituted with $-\text{OH}$, $=\text{O}$, or alkyl groups in PS and PET and formation of HCl in PVC.^{33,37} In the cases of PET, PVC, and PS, the char was produced below the temperature of carbon sphere formation ($>550\text{ }^\circ\text{C}$). This char does not take part in the spheres formation and remains as carbon particles. The other plastic materials used as carbon sources (LDPE, HDPE, PP, and PC) showed the maximum oil formation containing aromatic hydrocarbons, which results in carbon spheres formation. The char formation mechanism during thermal degradation of polymers was best explained elsewhere.³³

The products obtained from different plastic wastes were further analyzed with various physicochemical techniques. From SEM analysis, the size of carbon spheres was found to be in the range from 1 to $8\text{ }\mu\text{m}$ with all carbon precursors and was uncontrollable. Further investigation with TEM analysis (Figure 2) showed that the carbon spheres produced using various plastic precursors are solid in nature, which prevents the transmission of an electron beam through it and results in the dark spherical image of carbon spheres. The catalyst-free synthesis of monodispersed carbon microspheres is also reported by Zheng et al.³⁸ using a commercial starch solution as the carbon source. In comparison with the present methodology, both synthesis methods involved the formation of carbon microspheres under autogenic pressure conditions, but the optimized reaction temperature was different with

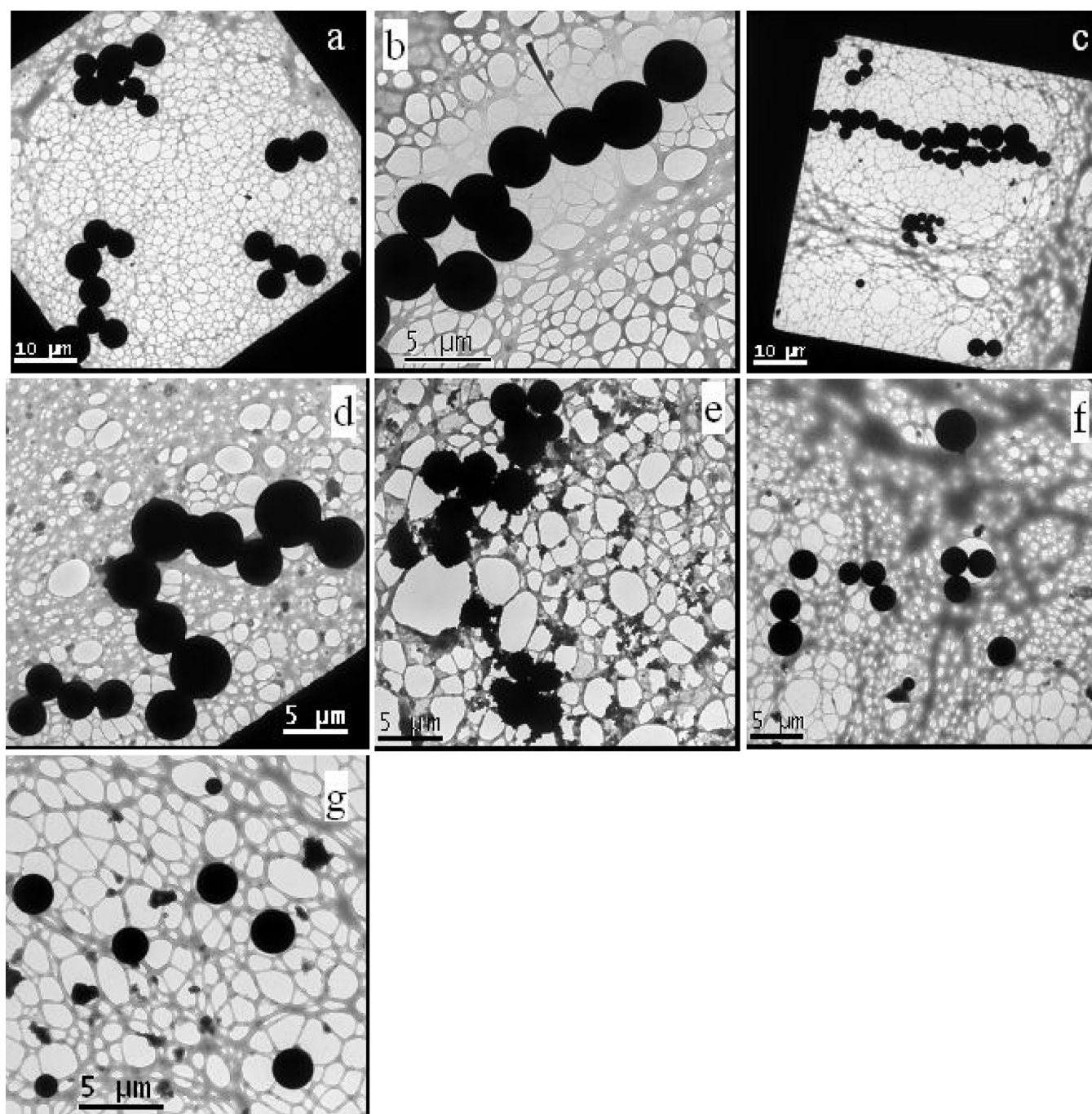


Figure 2. TEM images of solid carbon spheres prepared using different plastics as carbon sources: (a) PP-700, (b) HDPE-700, (c) LDPE-700, (d) PC-700, (e) PVC-700, (f) PS-700, and (g) PET-700.

different reaction times. The earlier reported methodology (Zheng et al.³⁸) for the synthesis of carbon spheres from starch involved the comparatively lower reaction temperature (600 °C), but the required time for the complete formation was a minimum of 6 h, much more than the present methodology. Although starch is cheap and commercially available, the utilization of plastic wastes for the production of valuable carbon spheres provided an advantage over the reported methodology with “waste to wealth” strategy.

The powder XRD technique was used to examine the crystallinity and phase of the prepared carbon products from different plastic wastes. The carbon materials mainly showed two diffraction peaks: one at $2\theta = 24\text{--}26^\circ$ and other at $2\theta =$

$43\text{--}44^\circ$ due to 002 and 100 graphitic planes, respectively.³⁹ The intensity and base area (broadening) of the peaks depends upon the crystallinity of carbon materials. The carbon products obtained from different plastic materials depicted two peaks at 2θ values of 25.4° and 43.8° (JCPDS card file no. 41-1487) in their XRD profile (Figure 3). The intensity of the 002 peaks clearly indicated that the graphitization in the carbon products prepared from waste plastics varies with the plastic precursor and product obtained. No correlation was observed with the carbon morphology or types of precursor with the degree of graphitization. The pure carbon spheres product obtained from PP, HDPE, and PC excluding LDPE showed more degree of graphitization than the products containing carbon particles

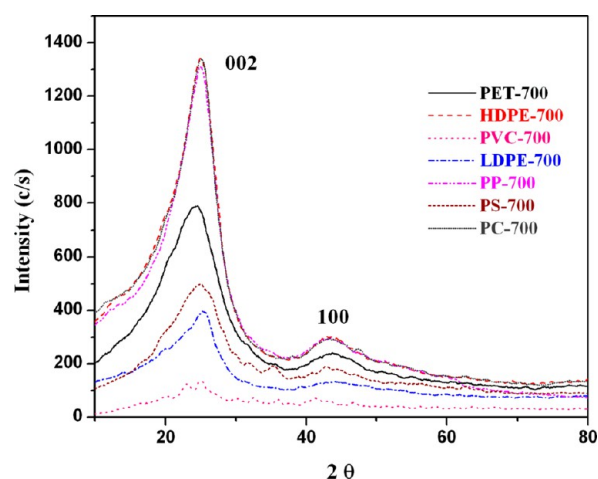


Figure 3. XRD pattern of carbon spheres prepared using pyrolysis of plastic wastes under autogenic pressure at 700 °C for zero time.

prepared using PET, PS, and PVC. The trend obtained in the degree of graphitization of the carbon product is HDPE \geq PC \geq PP > PET > PS > LDPE > PVC. On the basis of the XRD results, the graphitization degree of carbon spheres was not high; hence, the micro-Raman spectra was recorded for the detailed structural characterization. The Raman spectra of carbon spheres (Figure 4) synthesized at 700 °C using different

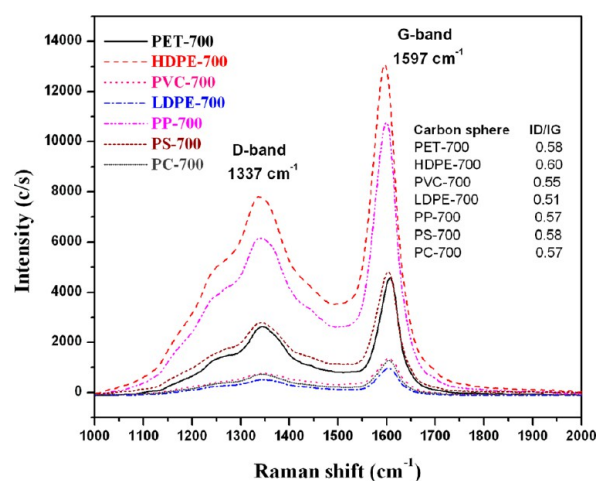


Figure 4. Raman spectrum of carbon spheres with their I_D/I_G ratio in inset.

plastic wastes showed the two bands, namely, the G-band at 1597 cm^{-1} , attributed to the E_{2g} mode of sp^2 hybridized carbon atoms in the hexagonal graphitic structure, and the D-band at 1337 cm^{-1} , a measure of the disorder due to vibrations of carbon atoms with dangling bonds. Instead of different intensities, the value of the I_D/I_G ratio for the Raman spectra of carbon spheres was nearly the same and in the range of 0.50–0.60 (inset of Figure 4). The broadening of the D-band and I_D/I_G ratio showed the existence of some of the amorphous phase and the defects in the graphitic structures of the obtained carbon spheres.³⁸

The absence of catalyst makes the carbon spheres free from any metal impurities and allows the synthesis of carbon spheres with 100% purity. The SEM and TEM observations demonstrate that the products of direct pyrolysis of plastic materials, including PP, HDPE, LDPE, and PC, produced

almost 100% carbon spheres with smooth surfaces and without foreign morphology. The elemental composition of carbon products analyzed by CHN/O analysis is shown in Table 2. All

Table 2. Elemental Composition of Carbon Products Prepared Using Waste Plastics under Autogenic Pressure

sample code	elemental composition (wt%) by CHN/O analysis			
	C	H	N	O
PP-700	96.35	1.16	1.17	1.32
PET-700	94.72	2.56	2.09	0.63
HDPE-700	95.01	2.70	1.44	0.85
PVC-700	95.03	2.31	0.00	–
LDPE-700	95.65	2.17	0.75	1.43
PS-700	93.12	1.27	0.74	4.87
PC-700	96.21	0.03	1.83	1.93

of the carbon particles and spheres obtained from different waste plastic materials showed 93–97% of carbon content on weight basis. The elemental composition of produced carbon spheres showed a small amount oxygen atoms calculated by summarizing and subtracting the total weight percentage of carbon, hydrogen, and nitrogen from 100%.

The nitrogen adsorption–desorption at 77 K on carbon spheres (PP-700) obtained by the pyrolysis of polypropylene exhibits a type III isotherm (Figure S2, Supporting Information), indicating its nonporous nature with a very low surface area (2.1 m^2/g). The carbon spheres obtained from different plastic waste, including PET, HDPE, PVC, LDPE, PS, and PC, possess very low surface area, i.e., 0.1, 1.8, 4.9, 3.2, 7.0, and 2.1 m^2/g , respectively, representing their dense and solid nature. There was no sharp adsorption peaks in the FTIR spectrum (Figure S3d–g, Supporting Information) of carbon spheres obtained using PP, HDPE, LDPE, and PC at 700 °C, which reveals the lack of surface functionality with high carbon content in products. Whereas the FTIR spectrum (Figure S3a–c, Supporting Information) of carbon products obtained from PET, PS, and PVC showed that the characteristic transmission bands of –OH groups at 3400 and 1630 cm^{-1} corresponds to the presence of C=C groups. The carbon products were further analyzed with ^{13}C CP-MAS NMR analysis for a clear illustration of surface functionality. The ^{13}C CP-MAS NMR spectrum of all carbon products (Figure S4, Supporting Information) prepared from different plastic resources displayed a strong peak at 130 ppm corresponding to the sp^2 hybridized carbon. The resonance peak at 180–190 ppm was attributed to the presence of carbonyl groups. Epoxides and hydroxide groups were also detected by peak at 60 ppm.⁴⁰

Formation Mechanism of Carbon Microspheres. In the past decades, production of nanometer-, micrometer-, and submicrometer-sized carbon materials from various hydrocarbon sources such as benzene, toluene, methane, etc. is well elaborated by various researchers.^{41,42} The self-assembly approach of hydrocarbons into higher polyhydrocarbons resulted in the formation of carbon materials. Jin et al.¹⁸ reported the formation of carbon spheres using various aromatic hydrocarbons as the carbon source. The pyrolysis of the plastic material for the production of aromatic hydrocarbon under a reducing environment at high pressure is gaining impetus. As mentioned earlier, the production of carbon spheres from aromatic hydrocarbons and degradation of plastic materials to the mixture of hydrocarbons are well-known processes. The production of carbon spheres using pyrolysis of

various plastic materials proceeds via hydrocarbon production followed by their self-assembly to carbon spheres under autogenic pressure. To test the above hypothesis, a benzene wash of product was analyzed with GC-MS (Table 3) to

Table 3. Composition (wt %) of Washing Filtrate of Carbon Spheres Prepared from Various Plastic Precursor Determined by GC-MS Analysis^a

chemical intermediates	wt % composition					
	PET-700	HDPE-700	LDPE-700	PP-700	PS-700	PC-700
toluene	30.3	7.3	9.8	17.2	6.7	16.1
naphthalene	36.9	31.2	51.3	53.5	32.6	6.8
methyl naphthalene	—	2.5	—	—	—	—
anthracene or phenanthrene	13.4	15.6	18.7	18.2	13.2	6.4
pyrene	7.1	8.9	5.8	11.1	6.9	2.3
biphenyl	9.0	20.0	11.4	—	20.2	43.3
fluorene	3.2	5.6	—	—	7.7	6.6
other	—	8.9	3.0	—	12.7	18.4

^aThe PVC-700 filtrate showed the presence of 1,2-diphenyl-2-butene only and polymer product with base m/z 105.05.

identify the intermediate structures associated with formation of carbon spheres. The weight of the obtained product before and after the benzene wash was measured to know the purity of the material, but there was no significant weight loss observed. A presence of different hydrocarbons mainly aromatic in nature was detected by GC-MS analysis confirming the formation of carbon spheres under closed conditions involving two steps: the degradation of plastic materials into various hydrocarbons below 500 °C followed by their self-assembly to carbon spheres above 500 °C under autogenic pressure. The different aromatic products present in the benzene wash of carbon product obtained at 700 °C were in trace amount and detected only by chromatography. The oily sample obtained at 500 °C having a petroleum odor also reveals the degradation of plastic materials into hydrocarbons.

CuO Hollow Microspheres. Polystyrene spheres have been widely used as a template for the synthesis of metal oxide hollow spheres.⁴³ Carbon microspheres obtained from pyrolysis of polypropylene (PP-700) were further utilized as the template for the synthesis of CuO hollow microspheres using cupric chloride as the copper precursor and 0.1 M NaOH solution as the precipitating agent in ultrasonication bath. The appropriate amount of methanol was added to the reaction mixture for the thorough dispersion of highly hydrophobic carbon spheres.

The carbon spheres were initially uniformly coated with copper hydroxide under ultrasonic treatment (Figure S5a, Supporting Information). To obtain the CuO hollow spheres (Figure S5b, Supporting Information), the carbon copper hydroxide core-shell structure was calcined under static atmosphere at 600 °C for the 2 h with the heating rate of 1 °C/min. The HR-TEM analysis (Figure 5a) depicts the formation of CuO hollow microspheres by utilizing carbon spheres as the template. Figure 5b shows the porous CuO hollow sphere composed of CuO nanoparticles with a wall thickness of ~130 nm. CuO nanoparticles of ~25 nm in size have also been observed along with microspheres (Figure 5c). The inset of Figure 5a shows the typical electron diffraction pattern for CuO hollow microspheres, whereas Figure 5d shows the crystal lattice of CuO microsphere.

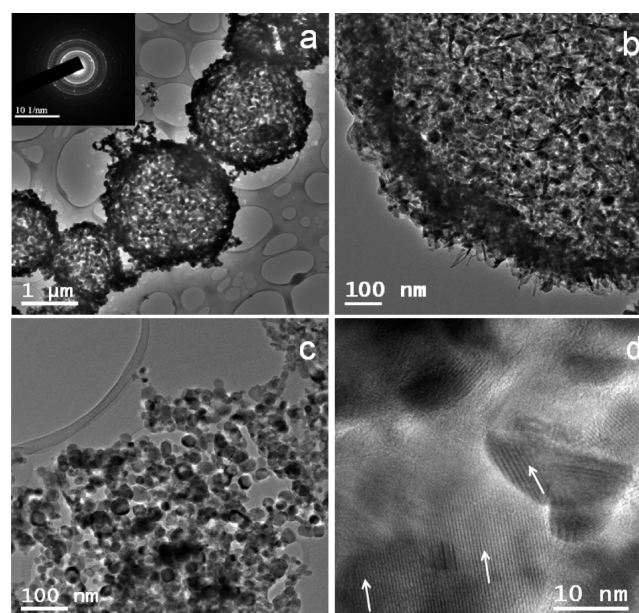


Figure 5. (a) CuO hollow spheres prepared using carbon spheres (PP-700) as the template (inset: electron diffraction pattern of CuO hollow sphere). (b) Surface of hollow spheres composed with CuO nanoparticles. (c) Building block CuO nanoparticles observed in the system. (d) Crystal lattice of CuO nanoparticles.

The hollow microsphere is composed of CuO rather than Cu₂O as confirmed by XRD analysis. The XRD patterns of hollow spheres (Figure S6, Supporting Information) show the characteristic peaks for CuO at 2θ of 35.5° (002), 38.7° (111), 48.7° (202), 53.4° (020), 58.4° (202), 61.5° (113), 66.2° (311), 68.1° (220), and 75.2° (222); no characteristic peak for Cu₂O was observed. The crystallite size determined the diffraction peak of the (002) CuO plane, and the Scherrer formula was ~32.8 nm, showing the nanocrystalline composition of CuO hollow spheres.

CONCLUSION

Utilization of waste plastic materials for the production of carbon microspheres is explored. The reported protocol allowed a catalyst- and solvent-free approach toward the large scale production of carbon microspheres using various plastic wastes. Plastic materials such as PP, LDPE, HDPE, and PC resulted in carbon spheres with 100% purity, i.e., absence of amorphous carbon material and foreign morphologies. The carbon microspheres produced under autogenic pressure have very poor surface functionality, i.e., highly hydrophobic in nature. Without any post-treatment, the obtained carbon spheres have been successfully utilized as the template for the synthesis of nanocrystalline CuO hollow spheres.

ASSOCIATED CONTENT

Supporting Information

Characterization of spheres. Table S1: Waste plastic materials used as carbon source for production of carbon spheres with classification codes (given by the Plastic Bottle Institute of the Society of the Plastics Industry) and collecting source. Figure S1: SEM images of carbon spheres produced from PET as carbon source (a) PET-700 and (b) PET-700-3. Figure S2: N₂ isotherm of carbon spheres prepared from polypropylene as carbon source (PP-700) at 77 K. Figure S3: FT-IR spectra of

solid carbon spheres (a) PVC-700, (b) PS-700, (c) PET-700, (d) PP-700, (e) LDPE-700, (f) HDPE-700, and (g) PC-700. Figure S4: ^{13}C CP-MAS NMR spectra of solid carbon spheres derived from different plastic wastes at 700 °C for zero time. Figure S5: (a) Carbon spheres (PP-700) uniformly coated with copper hydroxide under ultrasonic treatment and (b) CuO hollow spheres obtained after calcinations at 600 °C for 2 h. Figure S6: P-XRD pattern of carbon spheres templated nanocrystalline CuO hollow spheres. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel: +91 278 2471793. Fax: +91 278 2567562. E-mail: rssomani@csmcri.org (R.S.S.); hcbajaj@csmcri.org (H.C.B.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for financial support under Network project CSC-0120. Sandesh Y. Sawant acknowledges CSIR, New Delhi for the award of Senior Research Fellowship.

ABBREVIATIONS

PP, polypropylene; PET, polyethylene terephthalate; HDPE, high density polyethylene; LDPE, low density polyethylene; PVC, polyvinyl chloride; PS, polystyrene; PC, polyacrylate

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