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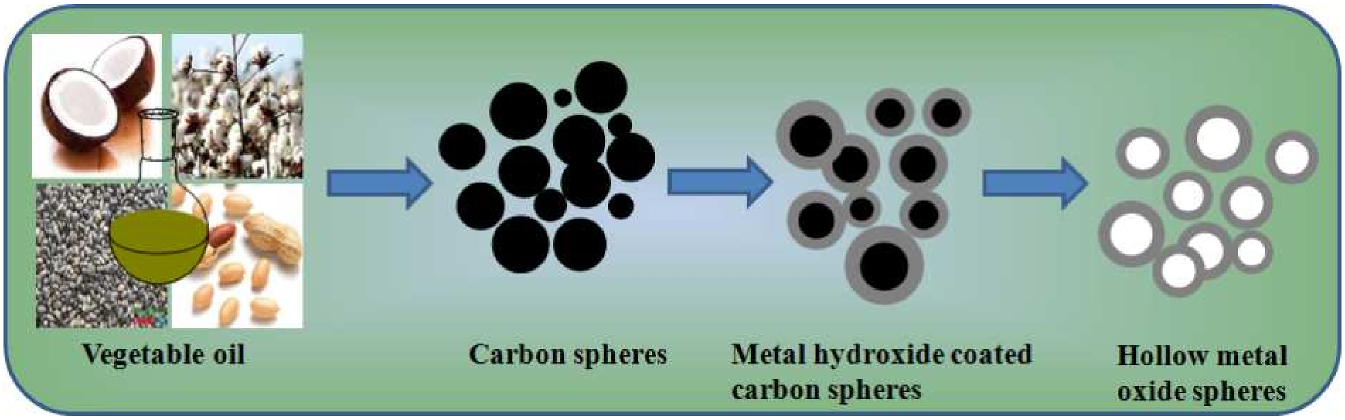

Eco-friendly, catalyst-free synthesis of highly pure carbon spheres using vegetable oils as renewable source and their application as a template for ZnO and MgO hollow spheres

Sandesh Y. Sawant[a,b], S. Senthilkumar[a], Rajesh S. Somani[a]*, Moo Hwan Cho[b]* and Hari C. Bajaj[a*]

[a]Division of Inorganic Materials and Catalysis,
Central Salt & Marine Chemicals Research Institute, (CSIR -CSMCRI),
Council of Scientific & Industrial Research (CSIR),
G. B. Marg, Bhavnagar 364002, Gujarat, India.
[b]School of Chemical Engineering, Yeungnam University,
Gyeongsan-si, Gyeongbuk 712-749, South Korea

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[*] Corresponding author: Tel: +91 278 2471793; Fax: +91 278 2567562; E-mail: rssomani@csmcri.org (Rajesh S. Somani); hcbajaj@csmcri.org (Hari C. Bajaj); Tel: +82-53-810-2517; Fax: +82-53-810-4631; E-mail: mhcho@ynu.ac.kr (Moo Hwan Cho)

The present address of Sandesh Y. Sawant is School of Chemical Engineering, Yeungnam University, Gyeongsan-si, Gyeongbuk 712-749, South Korea

Abstract

Herein we reports the eco-friendly and catalyst-free single step synthesis of solid carbon spheres, 1-10 μm in diameter, using vegetable oils derived from different bio-resources as the carbon source. The surface functionality of the synthesized carbon spheres was examined by Fourier transform infrared and charge polarized magic angle spinning nuclear magnetic resonance spectroscopy. The resulting carbon spheres were 100% pure, i.e. free of metal impurities, carbon soot and other structures; and do not require post treatments, such as extraction and purification. A detailed study showed that the synthesis of the carbon spheres proceeds through the formation and self-condensation of aromatic hydrocarbons generated from the oil precursor under an autogenic pressure. The carbon spheres were used further as a template for the synthesis of nano crystalline ZnO and MgO hollow spheres.

Keywords: Vegetable oils; Carbon sphere; Metal-free approach; ZnO/MgO hollow spheres

1. Introduction

Since the discovery of buckminsterfullerene,[1] various carbon structures have been drawing attention of research community due to their remarkable electronic and mechanical properties.[2] Initially, the carbon spheres were mainly considered as byproducts during the synthesis of carbon nanotubes. On the other hand, over the past decade, carbon spheres have been studied extensively due to their interesting physicochemical properties and low production cost compared to carbon nanotubes. Carbon spheres have applications as reinforcement materials for rubber, catalyst support[3] and lubricating materials, and can be used in fuel cells or secondary lithium ion batteries.[4]

Various approaches including chemical vapor deposition,[5] solvothermal,[6] carbonization,[7] and arc-discharge[8] have been used for the synthesis of carbon spheres. Wang et al.[9] reported the formation of carbon micro-sphere chains by the defluorination of polytetrafluoroethylene in supercritical carbon dioxide using magnesium as a catalyst. Amorphous carbon nano-spheres using polytetrafluoroethylene were reported in supercritical water with calcium hydroxide as catalyst.[10] Amorphous carbon and the catalyst trapped inside the carbon sphere are the major limitations, and resulting in the need for further purification. The cost-effective production of impurity free carbon spheres is needed to avoid post-synthesis purification.

Recently, we have reported the production of carbon spheres and carbon onions using different types of plastic wastes as the carbon source.[11-13] Gryglewicz et al.[14] utilized vegetable oil and their methyl esters along with bituminous coals for the synthesis of spherical-activated carbon. Vegetable oils are complex mixtures, containing fatty acids and mono-, di- and triglycerides as the major constituents, sterols, alcohols and wax esters as the minor constituents. This paper reports the eco-friendly, catalyst-free synthesis of carbon spheres by the direct pyrolysis of a wide range of vegetable oils (edible and non-edible oils), including jatropha oil, groundnut oil, mustard oil, coconut oil, cotton seed oil, and used (cooking) cotton seed oil as renewable and sustainable carbon sources. In particular, the protocol was investigated thoroughly using jatropha oil as the carbon source.

In recent years, a range of methods, including hard template (polystyrene,[15] carbon material[11, 13]), soft template (surfactants,[16] micro-droplets[17]) and template free approaches,[18] have been reported to synthesize hollow sphere structures. ZnO with different shapes and sizes has attracted considerable interest because of its important applications in photochemistry,[19, 20] sensors,[21] delivery vehicles, and catalysis.[22] MgO has been used extensively in catalysis,[23] toxic waste remediation,[24] antibacterial materials,[25] and superconductors[26]. The carbon spheres obtained from the pyrolysis of jatropha oil were used further as a template for the synthesis of ZnO and MgO hollow spheres.

2. Experimental

2.1 Synthesis of carbon sphere

The edible vegetable oils were purchased from the local market. The jatropha oil was supplied by the Division of Waste Land Research, CSMCRI, Bhavnagar, India. Typically, for the synthesis of carbon spheres, vegetable oil (5 g) was heated under closed conditions up to desired temperature in a stainless steel autoclave (50 mL capacity) at a heating rate of 20 °C/min in the muffle furnace. The heating was cut off after reaching the preset temperature, and the autoclave was allowed to cool to room temperature. The resulting product was washed with benzene and dried at 100 °C for 10 h in an air oven. The benzene wash was analyzed by gas chromatography. The nomenclature of each sample includes the vegetable oil name and reaction temperature. The reaction time is mentioned only when it was more than zero minutes after the set temperature achieved. Therefore, the nomenclature for carbon spheres prepared from jatropha oil at 700 °C for zero and 30 minutes are JO-700 and JO-700-30, respectively.

2.2 Fabrication of ZnO and MgO hollow spheres0.1 g of $ZnCl_2$ (Sigma-Aldrich) and 1.0 g of the carbon spheres (JO-700) were taken in 10 mL of Millipore water. The carbon spheres were well dispersed by the addition of methanol (1.0 mL) followed by an ultrasonication for 1 h. The mixture was aged at 80 °C for 6 h after the addition of 0.1 M NaOH (1.0 mL) as a precipitating agent. The $Zn(OH)_2$-coated carbon spheres were obtained by filtration and washing with excess Millipore water followed by drying at 100 °C for 10 h in an air oven. Finally, the ZnO hollow spheres were obtained by calcination of the above product at 600 °C for 2 h at a heating rate of 1 °C/min under static air atmosphere. For the synthesis of MgO hollow spheres, the above procedure was repeated with $MgCl_2.6H_2O$ (Merck) instead of $ZnCl_2$. The yield obtained for ZnO and MgO hollow spheres was ~23 mg (~39%) and ~11 mg (56%), respectively.

2.3 Characterization of carbon spheres

The phase and crystallography of the products were characterized by X-ray diffraction (XRD, PHILIPS X'Pert MPD, Bragg-Brentano para-focusing geometry) using $CuK_{\alpha1}$ radiation (λ= 1.54056 Å) in the 2θ range, 2–80°. The morphology of the samples was examined by scanning electron microscopy (SEM, Leo 1430 SEM) and transmission electron microscopy (TEM, JEOL JEM-2100 TEM). The surface functionality of the carbon spheres was analyzed by the Fourier Transform infrared (FT-IR) spectroscopy (Perkins Elmer Spectrum GX 2500 FT-IR spectrophotometer). The ^{13}C magic angle spinning – nuclear magnetic resonance (MAS-NMR) spectrum was recorded on a Bruker 500 MHz Advanced II spectrometer with a 5 mm MAS probe. The spectrum was acquired with cross polarization for a spinning speed 8 KHz with 2 ms and 5s as the contact and recycle time respectively. Line broadening of 200 Hz was applied with adamantane as the reference. The Fourier Transform Raman (FT-Raman) spectra of the carbon spheres were recorded using a HR800 UV Raman microscope (Horiba Jobin-Yvon, France) at ambient temperature employing diode laser at an excitation wavelength of 514 nm.

The benzene wash recovered after collecting carbon spheres was analyzed by gas chromatography coupled with mass spectroscopy (GC-MS, GCMS-QP 2010, Shimadzu) using helium as the carrier gas to better understand the reaction pathway. The surface and textural properties were measured by the N_2 adsorption-desorption method using a volumetric gas adsorption apparatus, ASAP 2020 (Micromeritics Inc. USA). Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851) was performed under a nitrogen flow (50 mL/min) at a heating rate of 10 °C/min. The elemental composition of carbon spheres was determined by energy dispersive X-ray (EDX) spectroscopy attached to the scanning electron microscope.

3. Results and discussion

3.1 Characterization of vegetable oils

The procedures used to characterize the vegetable oils are reported in the ESI†. The chemical analysis of the various vegetable oils used as a carbon precursor (Table S1, ESI†) clearly indicated that the acid values of the used oils were up to 1.27 (mg KOH/g) except for jatropha oil (12.54 mg KOH/g). The high acid value of jatropha oil revealed the presence of a large amount of free fatty acids. The saponification values of the studied oil were in the range, 160 to 220 (mg KOH/g), due to presence of short chain fatty acids. The fatty acids composition of the different vegetable oils (Table S2, ESI†) varied according to the types of oil.

3.2 Characterization of carbon spheres

Table 1 Effects of the experimental conditions on the preparation of carbon spheres using different vegetable oils as the carbon source

Sample code	Vegetable Oil	Temperature (°C)	Time (min)	Yield[a] (%)	Products
JO-500	Jatropha	500	0	---	No carbon product
JO-600	Jatropha	600	0	15.4 (0.771)	Agglomerated carbon spheres
JO-700	Jatropha	700	0	32.4 (1.621)	Carbon spheres
JO-700-30	Jatropha	700	30	33.2 (1.662)	Carbon spheres
JO-800	Jatropha	800	0	35.7 (1.786)	Break carbon spheres
GO-700	Groundnut	700	0	28.0 (1.402)	Carbon spheres
CCO-700	Coconut	700	0	29.2 (1.461)	Carbon spheres
MO-700	Mustard	700	0	26.4 (1.319)	Carbon spheres
CTO-700	Cotton seed	700	0	27.2 (1.361)	Carbon spheres
UCTO-700	Used cotton seed oil (cooking)	700	0	25.6 (1.282)	Carbon spheres

[a] yield was calculated on the weight basis; in parenthesis, obtained yield in g.

The effect of the experimental conditions on the formation of carbon spheres was studied using jatropha oil as the carbon source (Table 1). The formation of carbon spheres was observed at above 600 °C. The product obtained at 600 °C showed carbon spheres along with an irregular structure consisting of two or more attached spheres or capsule like structures (Fig. 1a). In contrast, at 700 °C with a zero pyrolysis time, the carbon spheres showed a perfect spherical shape with a smooth surface (Fig. 1b). Further increases in reaction time, i.e., 30 minutes at 700 °C, did not alter the morphology or yield (Fig. 1c), but cracks were observed in the carbon spheres (Fig. 1d) at 800 °C. The cracks on the surface of the carbon spheres clearly revealed their solid nature. Based on the above observations, the reaction temperature and time were selected as 700 °C and zero minute respectively, for further experiments with different vegetable oils as the carbon precursor. As compare with productivity, the yield of carbon spheres obtained using vegetable oils under present methodology (~32 %) is comparable with the yield of carbon spheres produced using different carbon sources such as various waste plastics (~34%) under similar condition[11] and starch (~40%) using hydrothermal method.[27] Whereas, Jin et al.[28] reported the synthesis of few milligram of carbon spheres (~ 250 mg) using direct pyrolysis of different hydrocarbon after 30 min reaction time (Note: the carbon precursor quantity used in this process was also low; 0.6 ml).

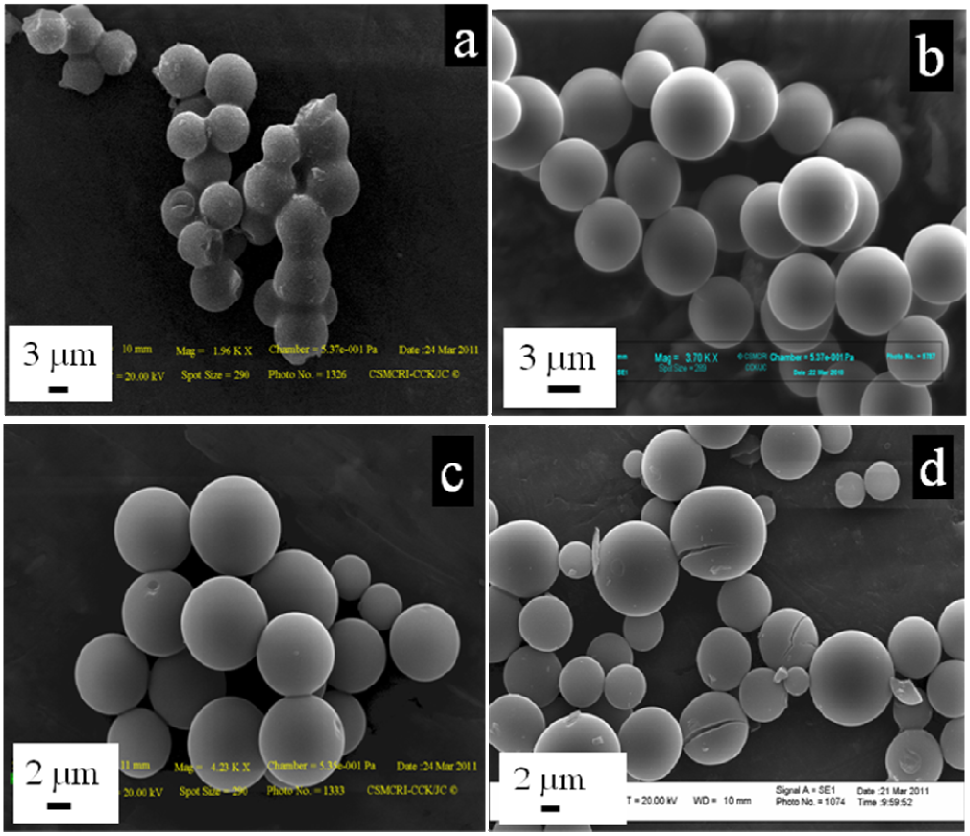

Fig. 1 SEM images of carbon spheres prepared using jatropha oil under different synthesis conditions (a) JO-600, (b) JO-700, (c) JO-700-30 and (d) JO-800.

The XRD pattern of carbon spheres (Fig. S1, ESI†) revealed two peaks at 25.4° and the 43.8° 2θ, typically due to the graphitic (002) and (100) planes (JCPDS Card Files, No. 41-1487), respectively.[29] The FT-Raman spectra (Fig. S2, ESI†) of the carbon spheres prepared under optimized conditions (700 °C and zero minute) showed two characteristic peaks at 1340 (D-band) and 1600 cm^{-1} (G-band) assigned to the defect or disorder in the graphitic structure and planner configuration of the sp^2-bonded carbon structure, respectively. The normalized spectra showed more similarity with respect to the intensity and position, indicating a similar kind of graphitic arrangement in the carbon spheres regardless of the vegetable oils used for their production. A similar trend was also reported in the case of carbon spheres produced from different plastic wastes by thermal degradation.[11]

The morphology of the products synthesized from different vegetable oils was examined by SEM. Fig. S3a-e in ESI† shows the carbon spheres, produced from different vegetable oils as the carbon source, with a smooth surface in the accreted form. Jin et. al.[28] reported similar observations during the synthesis of carbon spheres by the direct pyrolysis of hydrocarbons. SEM analysis showed that the carbon spheres obtained from various vegetable oils was in the range of 1 to 10 μm in diameter (Fig. S3a-e, ESI†).

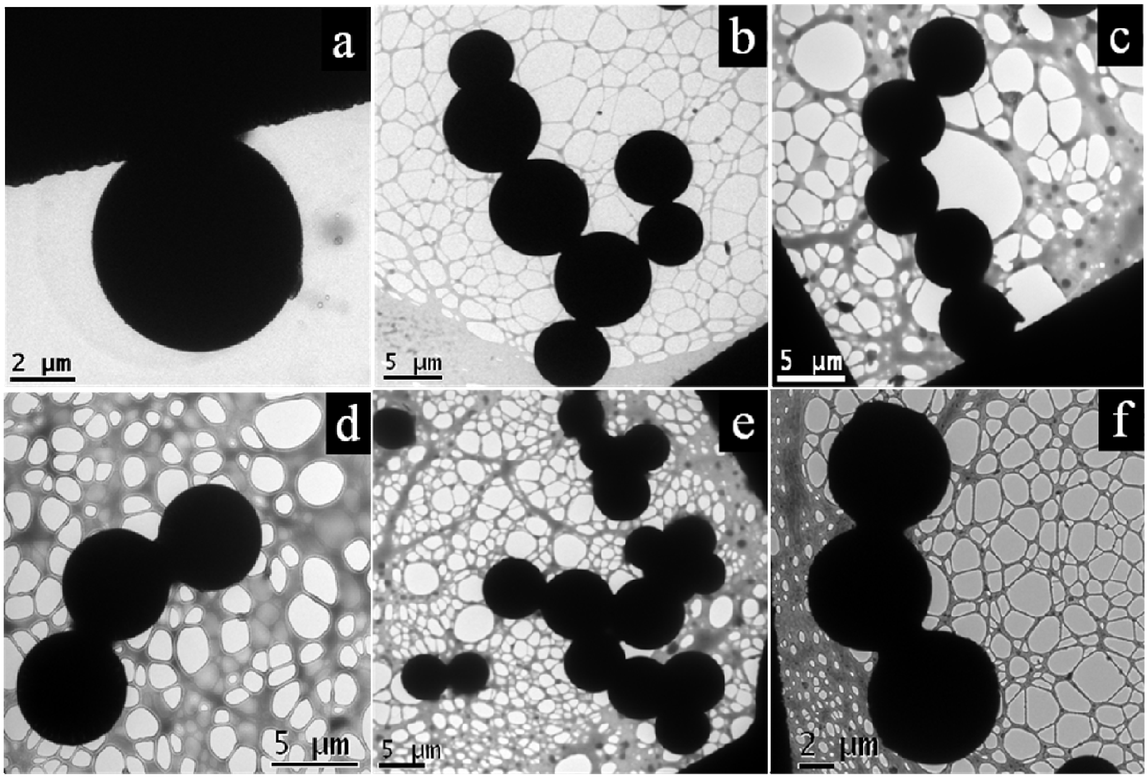

Fig. 2 TEM images of the solid carbon spheres prepared using different vegetable oils (a) JO-700 (b) GO-700, (c) CCO-700, (d) MO-700, (e) CTO-700 and (f) UCTO-700.

The TEM images (Fig. 2a-f) of the carbon spheres prepared using different vegetables oils at 700 °C revealed their perfect spherical morphology and a smooth surface. The non transparent and dark TEM images of the carbon spheres, due to the restricted transmission of the electron beam, were also indicative of their solid nature. The formation of impurities, such as carbon soot or amorphous carbon and other structures was not observed with different oil precursors. The absence of a catalyst makes it free from any metal impurities and allows the synthesis of carbon spheres with 100% purity. SEM and TEM analysis showed that the products obtained by the direct pyrolysis of different vegetable oils consisted of almost 100% carbon spheres with smooth surfaces. In particular, the present study showed that the synthesis of carbon spheres was possible not only with pure vegetable oils but also with the used oil (here cooked cotton oil was utilized). Detail analysis of the vegetable oils revealed different fatty acids content but the products obtained from these oils were only solid carbon spheres with no apparent differences. Therefore, the morphology of the carbon products was independent of the composition of the vegetable oil. The elemental composition of the carbon spheres analyzed by EDX gave a carbon content of 88-96% on weight basis (Table 2), indicating high purity carbon materials. The variation in the carbon and oxygen content of the carbon spheres produced from the different oils was attributed mainly to the initial difference in the oxygen content of the oil precursor.

Table 2 Elemental composition of the carbon spheres prepared using different vegetable oils

Sample	Elemental composition (wt.%)	
	C	O
JO-600	90.76	9.24
JO-700	88.41	11.59
JO-700-30	91.23	8.77
JO-800	89.64	10.36
GO-700	95.38	4.62
CCO-700	89.06	10.94
MO-700	89.44	10.56
CTO-700	92.20	7.80
UCTO-700	89.76	10.56

TGA of the prepared carbon spheres under a nitrogen atmosphere showed a maximum 7–8% weight loss (Fig. S4, ESI†). The TGA plot showed insignificant weight loss in the range 200-400 °C possibly due to adsorbed water or decomposition of polyaromatic hydrocarbons, such as naphthalene, anthracene, etc., which may not be converted to the desired carbon structure. The second weight loss at 500-600 °C was associated with the decomposition of oxygen functionality present on the carbon spheres. The produced carbon spheres revealed a highly hydrophobic nature with good thermal stability under an inert atmosphere.

The nitrogen sorption isotherm of JO-700 at 77 K (Fig S5, ESI†) indicated weak adsorbate-adsorbent interactions and a nonporous nature with a very low surface area (3.9 m^2/g). The measured isotherm was Type III as per the International Union of Pure and Applied Chemistry classification, wherein a steep increase in the amount of adsorbed nitrogen in the higher partial pressure region with no distinct hysteresis behavior indicated that nitrogen adsorption occurs mainly on the external surface of the non-porous carbon spheres. The carbon spheres produced using different vegetable oils, e.g. GO-700, CCO-700, MO-700, CTO-700, and UCTO-700, also exhibited very low surface areas, i.e. 2.51, 1.94, 2.39, 1.63, and 1.34 m^2/g, respectively, owing to their non-porous nature.

The surface functionality of the carbon spheres was determined by FTIR spectroscopy. No sharp peaks were observed in the FTIR spectrum (Fig. S6, ESI†) of all the carbon spheres synthesized at 700 °C, possibly due to the absence of surface functionality or the high carbon content in the products. Therefore, the samples were subjected to ^{13}C CP-MAS NMR analysis to better understand the surface functionality. The ^{13}C CP-MAS NMR spectrum of the carbon spheres (Fig. S7, ESI†) prepared from the different vegetable oils displayed a peak at ~ 60 ppm assigned to the epoxide and hydroxide groups. The resonance peak at ~ 130 ppm was attributed to sp^2 hybridized carbon atoms. The presence of carbonyl groups was also detected by the peak at 180-190 ppm.[30] The variation of the chemical environment of the carbons atoms induced the peak broadening.

3.3 Growth mechanism

The formation of carbon spheres was independent of the chemical composition of the carbon precursor. The different vegetable oils, despite their different chemical compositions; produced carbon spheres with a smooth surface of the same size range under similar pyrolysis conditions. Analyzing the intermediate products associated with formation of carbon spheres could be helpful in understanding the possible pathway for the formation of carbon spheres.[31] The benzene washes of the carbon spheres were analyzed by GC-MS to identify the intermediate structure formed during synthesis.

GC-MS analysis (Table 3) of the benzene wash of the carbon spheres synthesized at 700 °C with different vegetable oils revealed the presence of polyaromatic hydrocarbons (PAHs). On the other hand, PAHs along with the different aliphatic alkanes including octane, nonane, decane, and their higher analogues, which were further converted to aromatic compounds or carbon particles with increasing reaction temperature, were also observed in the benzene wash of JO-600. Toluene and naphthalene derivatives were the major content of the filtrate in all the samples (Table 3) along with pyreneas a maximum number of carbon atoms PAH. It has been reported that the pyrolysis of vegetable oils and fats produces the hydrocarbons products.[32] Therefore, the thermal degradation of vegetable oil resulted in the formation of aromatic hydrocarbons from fatty acids followed by their self condensation into higher carbon analogues. Finally, the thermal dissociation of these aromatic hydrocarbons/carbon analogues followed by solidification under autogenic pressure produced the carbon spheres.

Table 3 Chemical composition of the benzene wash of carbon spheres prepared from the different vegetable oils determined by GC-MS analysis

Chemical Intermediates	Wt % Composition					
	JO-700	GO-700	CCO-700	MO-700	CTO-700	UCTO-700
Toluene	32.27	33.69	30.83	36.27	44.70	48.57
Naphthalene	22.03	38.35	40.55	39.27	22.22	31.27
Methyl naphthalene	11.13	7.05	4.58	5.69	6.93	8.04
Anthracene or Phenanthrene	4.26	9.39	8.37	7.35	3.94	5.38
Pyrene	5.89	4.80	5.43	4.06	1.58	1.40
Biphenyl	---	2.91	6.64	3.56	---	---
Fluorene	---	2.34	3.60	---	---	---
2-Methyl-1,1`-biphenyl	---	1.47	---	---	---	---
Ethyl benzene	7.21	---	---	3.80	8.16	2.46
Xylene	12.43	---	---	---	9.95	2.88
Ethyl methyl benzene	4.76	---	---	---	2.53	---

The formation mechanism of carbon spheres from various hydrocarbon sources under autogenic pressure was well elaborated by Pol et. al.,[33] in which carbon spheres resulted from the solidification in the carbon-rich core of the drops in the presence of the remaining supercritical fluid products (H_2, CH_4, free radicals: –H, –CH_3). The above results showed that the production of carbon spheres by the direct pyrolysis of vegetable oil under autogenic pressure was a multistep process, wherein initially, the higher fatty acids decompose and rearrange to aromatic analogues followed by their dissociation and solidification to carbon spheres. Fig. 3 shows the various steps involved in the formation of the carbon spheres under autogenic pressure. The formation of carbon spheres followed the same pathway observed in the formation of carbon black,[34] whereas the size of the carbon spheres formed in present methodology was larger (few micrometers) due to the aggregation of small carbon particles under autogenic pressure . Here, the chemical composition of the vegetable oils had no effect on the formation of carbon spheres because it proceeded through the pyrolysis of common hydrocarbons.

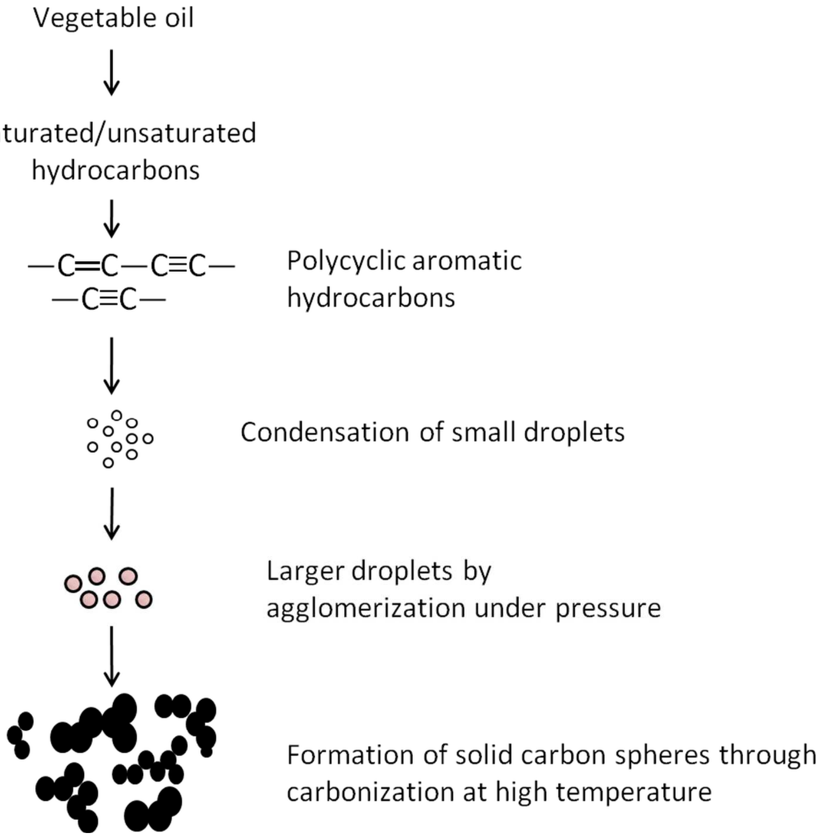

Fig. 3 Probable steps involved in the synthesis of carbon spheres under autogenic pressure using vegetable oil as the carbon source.

3.4 ZnO and MgO hollow spheres

Carbon spheres obtained from pyrolysis of jatropha oil (JO-700) was further used as a template for the synthesis of ZnO and MgO hollow spheres. In the present methodology, the coating of zinc hydroxide or magnesium hydroxide was carried out using their chloride salts and a 0.1 M NaOH solution as the precipitating agent in an ultra-sonication bath. The appropriate amount of methanol was added to improve the dispersion of carbon spheres in water because of their highly hydrophobic nature.

3.4.1 Effect of amount of metal precursor

Deng et al.[35] utilized polystyrene spheres as the template material for the synthesis of hollow metal oxide spheres by the absorption of metal salts on their charged surface. As shown by FT-IR analysis, the obtained carbon spheres possessed an inert surface with less surface functionality. Therefore, the concentration of metal ion precursors plays a vital role in the structure formation. The effect of metal ion precursor was studied by varying the amount of precursor (0.05, 0.1, 0.15, and 0.2 g) for 1 g of carbon spheres. A uniform coating of zinc hydroxide and magnesium hydroxide were observed (Fig. S8a-d, ESI†) with precursor amounts of 0.05 and 0.1 g. In contrast, the formation of zinc hydroxide and magnesium hydroxide particles (Fig. S9a-d, ESI†) with trapped carbon spheres were observed with increasing precursor concentration (0.15 and 0.2 g).

3.4.2 Preparation of ZnO and MgO hollow spheres

The carbon/zinc hydroxide and carbon/magnesium hydroxide core shell structures were calcined under a static air atmosphere to produce the zinc oxide and magnesium oxide hollow spheres, respectively. As shown by SEM, calcination at 600 °C for 2 h at a heating rate of 1 °C/min resulted in ZnO (Fig. S10a, ESI†) and MgO (Fig. S10b, ESI†) hollow spheres. Whereas, breakage in the ZnO (Fig. S11a, ESI†) and MgO hollow spheres (Fig. S11b, ESI†) was observed with further increases in the calcination temperature (700 °C for 2 h), possibly due to thermal shock.

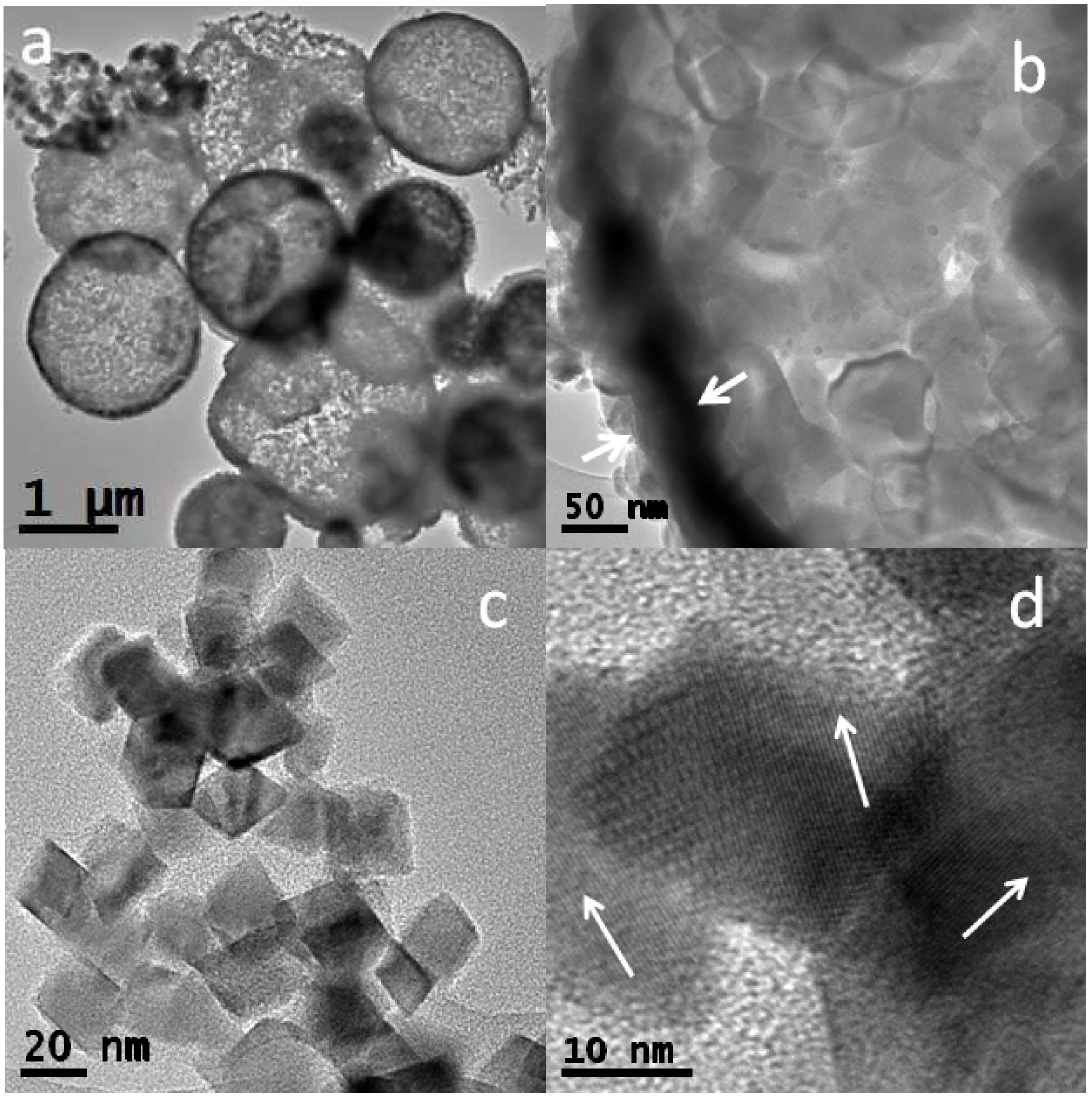

Fig. 4 TEM images of (a) ZnO hollow spheres prepared using carbon spheres (JO-700) as a template, (b) surface of ZnO hollow spheres composed of nanoparticles; (c) building block ZnO nanoparticles, and (d) crystal lattice of ZnO nanoparticles.

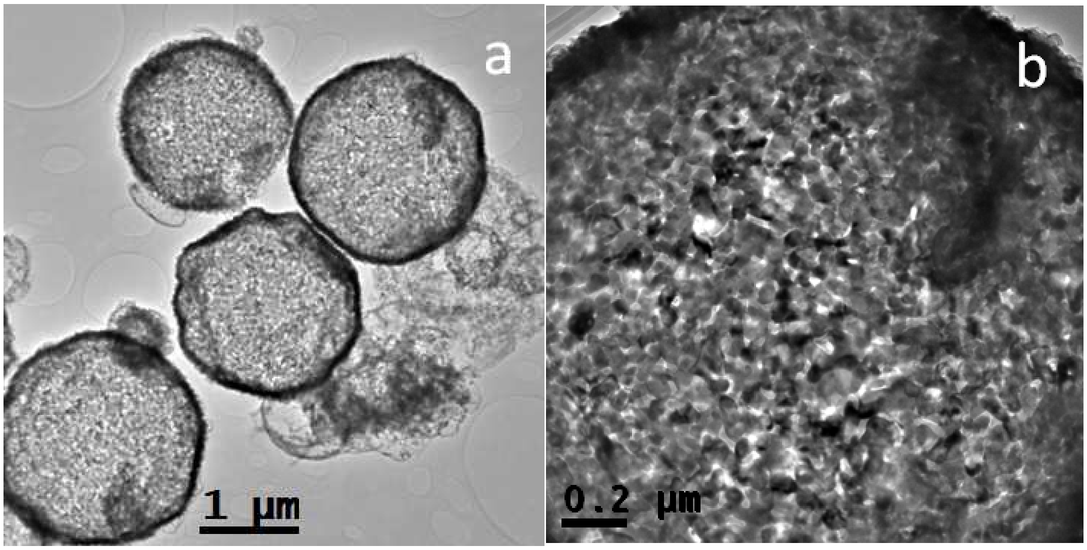

Fig. 5 TEM images of (a) MgO hollow spheres prepared using carbon spheres (JO-700) as a template and (b) porous surface of MgO hollow spheres composed of nanoparticles.

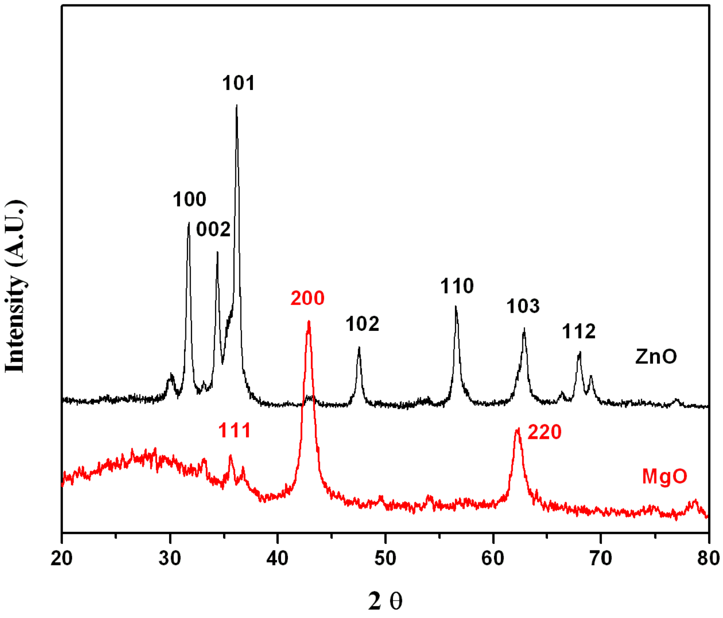

Fig. 6 XRD pattern of the ZnO and MgO hollow spheres prepared using carbon spheres as a template.

The ZnO and MgO hollow spheres prepared using 0.1 g of the metal salt precursor was analyzed further by TEM. Fig. 4a and 4b shows a TEM image of the ZnO hollow spheres (1-2 µm) with a wall thickness of ~50 nm consisting of nanoparticles as building blocks. Agglomerates of the cubic shaped ZnO nanoparticles, ~20 nm in size, were also observed along with the hollow spheres (Fig. 4c). Fig. 4d showed the crystal lattice of the ZnO nanoparticles. TEM analysis of the MgO hollow spheres (Fig. 5a and 5b) showed a hollow and porous spherical structure composed of nanoparticles with a wall thickness of ~100 nm. The XRD patterns of the ZnO and MgO hollow spheres (Fig. 6) were in good agreement with the JCPDS file of ZnO (JCPDS No. 36-1451) and MgO (JCPDS No. 45-0946). The crystallite size of the ZnO and MgO hollow spheres, determined from the main diffraction peak (101 for ZnO and 200 for MgO) using Scherrer formula, was approximately 21 and 8.0 nm, respectively, indicating their nano crystalline nature. The effect of instrumental broadening was nullified using Si (111) as standard.

3.4.3 Effect of precipitating agent

With the use of ammonium hydroxide (1 mL) as the precipitating agent (in the case of 0.1g of metal precursors) instead of a NaOH solution, the formation of solid ZnO rods, ~ 1 µm in width and few µm in length, along with ZnO hollow spheres was observed (Fig. S12, ESI†). The effect of the precipitating agent was not observed in the case of the MgO hollow spheres. ZnO rods may be formed due to the formation of a soluble zinc ammonium complex, which later precipitated as zinc hydroxide rods during aging.

4. Conclusion

Vegetable oils derived from different bio-resources were utilized successfully as renewable and sustainable carbon sources for the metal free synthesis of carbon spheres. The methodology adopted was simple and provided an efficient way of producing carbon spheres in high yield. The resulting carbon spheres showed a smooth surface with 100% purity, i.e., free of metal impurities, amorphous carbon and other structures. With the help of the experimental and analytical characterization evidence, the mechanism of carbon sphere formation was disclosed. The synthesis of carbon spheres proceeds through the formation of aromatic/aliphatic hydrocarbons followed by their decomposition to carbon spheres. The prepared solid carbon spheres were successively applied as a template for the synthesis of nano crystalline ZnO and MgO hollow spheres without surface modification. Due to the high yield as well as easy operation, the present methodology can be scalable for the synthesis of carbon sphere. Whereas the comparable low yield of ZnO and MgO hollow spheres limits the process for large scale production.

Acknowledgments

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† **Electronic supplementary information (ESI) available:** The characterization procedures, chemical characteristics and fatty acids composition of vegetable oils. XRD, FT-Raman, SEM, TGA, FT-IR, and ^{13}C CP-MAS NMR analysis of carbon spheres synthesized using different vegetable oils. N_2 Sorption isotherm of JO-700 at 77K. SEM images of carbon spheres coated with zinc hydroxide and magnesium hydroxide using different concentration of precursor. SEM

images of ZnO and MgO hollow spheres obtained at different calcination temperatures. SEM image of ZnO hollow sphere and rod obtained with ammonium hydroxide as precipitating agent.

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