Facile Synthesis of Mesoporous Carbon Spheres Using 3D Cubic Fe-KIT-6 by CVD Technique for the Application of Active Electrode Materials in Supercapacitors

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Supporting Information

ABSTRACT: Mesoporous carbon spheres (MCS-750, MCS-800, MCS-850, MCS-900, and MCS-950) have been synthesized by a facile strategy with low temperature and rapid chemical vapor deposition technique. The synthesized MCS possess relatively large surface area (570–670 m² g⁻¹), good graphitization, remarkable porosity, and redox functionalities on the surface of the synthesized MCS. Combination of these structural and surface properties of the synthesized MCS as an electrode material (MCS-850) showed an excellent charge-storage capacity with a specific capacitance of 338 F/g at 1 mV/s, 217 F/g at 0.5 A/g. MCS-850 shows long-term cycling stability with capacitive retention of more than 96% after 2000 cycles in 6 M KOH electrolyte. In addition, a fabricated two-electrode symmetric cell obtained 86% retention after 2000 cycles. The two-electrode symmetric device exhibited a specific capacitance of 63 F/g at 5 mV/s with an energy density of 7.1 Wh/kg.

INTRODUCTION

Modern science and technology uses porous carbon materials in various fields such as water/air purification, separation, catalysis, and energy storage.¹⁻⁶ In energy-storage systems, supercapacitors play a major role as they have high power density, long life cycle, cost-effectiveness, and eco-friendly properties compared to batteries.⁷⁻¹⁰ Based on the mechanism of energy storage, supercapacitors are categorized as pseudocapacitors and electric double-layer capacitors (EDLC). Pseudocapacitors involve reversible redox or faradic charge-transfer reactions and use transition-metal oxides¹¹,¹² and conducting polymers as electrodes.¹³,¹⁴ EDLC store energy by electrochemical charge accumulation occurring at the electrode/electrolyte interface with porous carbon materials as electrodes.¹⁵,¹⁶ Hence, the electrode material becomes the deciding factor for the performance of supercapacitors.¹⁷ Among several electrode materials such as transition-metal oxides, conducting polymers and carbon materials with various morphologies are used due to their low cost, electrochemical stability, and superior electrical conductivity. In particular, mesoporous carbon spheres as electrode material improve the performance of supercapacitors due to large electrochemically active surface area and pore size, which facilitates easy access of electrolytic ions.¹⁸⁻²² The electrical conductivity of carbon material enables superior performance of supercapacitors, which is associated with the quantity of graphitization with sp² hybridization.⁹,²³ The chemical composition also contributes as a factor for supercapacitive performance.

Transition-metal atoms like Ni, Co, and Fe are used as catalyst and mesoporous molecular sieves such as MCM-41, SBA-15, and KIT-6 are used as catalytic support for the preparation of various nanostructured materials such as CNTs, spheres, rods, wires, and CMK by employing chemical vapor deposition (CVD) technique.²⁴⁻³⁰ Among the mesoporous molecular sieves, KIT-6 are potential candidates since they possess higher surface area to anchor, good dispersion of metal catalyst, and bidirectional pore modal to facilitate the reactants with the catalyst in mass level, which are the advantages of MCS growth with high yield. Carrasco et al.³¹ reported the synthesis of carbon spheres by CVD technique using NiFe-LDHs as catalyst for supercapacitor application with large reaction time, i.e., they used to feed the carbon source for 1 h. Although the carbon spheres possess higher conductivity, there is a lack in surface area. Rajagopal et al.²⁵ reported the synthesis of graphene bubbles with spherelike morphology by CVD technique using metal-supported MCM-41 for super-
capacitor application with a high reaction temperature of 900 °C.

In this work, we report for the first time the synthesis of mesoporous carbon spheres (MCS) using novel Fe-KIT-6 by simple CVD technique, which involves simple synthetic strategy, low reaction temperature, and less reaction time compared to the previous reported results. In this technique, acetylene is employed as carbon source, which was fed only for 30 min at 750, 800, 850, 900, and 950 °C to synthesize MCS. Hence, we report a simple synthetic strategy to prepare MCS with relatively high surface area and good conductivity. The supercapacitive performance of synthesized MCS as electrode material was found to be possess superior electrochemical performance with specific capacitance of 338 F/g and long-term cyclic stability with more than 96% electrochemical performance with specified conductivity. The supercapacitive performance of synthesized MCS was fed only for 30 min at 750, 800, 850, 900, and 950 °C were recorded to study the formation of well-ordered mesoporous materials with the symmetry of the body-centered cubic Ia3d space group, which was in agreement with the reported mesoporous KIT-6 materials. The lattice parameter was estimated from the SAXRD spectrum of Fe-KIT-6 using the formula $a_0 = d_{221}(6)^{1/2}$, and the value is shown in Table 1. Also we have obtained lattice parameter of the Fe-KIT-6 from TEM of about 21.65 nm, which was almost close to SAXS. The high-resolution transmission electron microscopy (HRTEM) image (Figure S2d) was used to calculate the $d$-spacing to obtain $a_0$ value.

The nitrogen adsorption—desorption isotherm and pore size distribution of Fe-KIT-6 molecular sieve are shown in Figure 1b. As shown in Figure 1b, type IV isotherm with pronounced capillary condensation step at high relative pressure and H1 hysteresis loop indicates well-ordered mesoporous materials with large channel-like pores. The BET surface area, pore size, and pore volume of Fe-KIT-6 are listed in Table 1. The pore-size distribution of mesoporous Fe-KIT-6 molecular sieve was calculated by the Barrett—Joyner—Halenda (BJH) method, as shown in the inset of Figure 1b, which appears narrow and peak centered at about 6.62 nm.

The surface morphology of Fe-KIT-6 was investigated by scanning electron microscopy (SEM) analysis. The spongelike porous nature and agglomeration of random particles without a defined shape are shown in Figure 2a,b. The mesoporous structure of the Fe-KIT-6 catalyst was investigated by high-resolution transmission electron microscopy (HRTEM) analysis, as shown in Figure 2c,d. The HRTEM images revealed well-ordered arrays with regular 3D pore structure and fine distribution of Fe nanoparticles (as indicated by the arrow in Figure 2d) inside the pores of the 3D mesoporous KIT-6 framework. It confirmed the presence of large domains of a 3D silica—iron network, which highlights the interconnectivity in the pore structure of the Ia3d cubic phase. The HRTEM images of Fe-KIT-6 are presented as supporting data with a clear 3D cubic structure in Figure S2a,b, in which we could not find any stripes but honey combs. The enlarged HRTEM image (Figure S2c inset) shows the average pore size obtained from $N_2$ adsorption/desorption.

The wide-angle XRD patterns of MCS samples prepared at 750, 800, 850, 900, and 950 °C were recorded to study the graphitic nature of the materials. Figure 3a represents the wide-angle XRD pattern of MCS samples prepared at 750, 800, 850, 900, and 950 °C.

### RESULTS AND DISCUSSION

The growth of MCS was achieved by means of a simple CVD technique at 750, 800, 850, 900, and 950 °C using Fe-KIT-6 molecular sieves as catalytic support and acetylene as carbon source for a period of 30 min.

The Si/Fe ratio of hydrothermally synthesized mesoporous Fe-KIT-6 molecular sieve was estimated using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the results are given in Table 1. The Si/Fe ratio derived from the elemental analysis was nearly close to the gel composition as noted in the Fe-KIT-6 material. The results indicated that almost all of the metals employed during the synthesis were successfully incorporated into mesoporous materials. The small-angle powder XRD (SAXRD) pattern of mesoporous Fe-KIT-6 is shown in Figure 1a. It can be seen that the high-intense peak exhibited by Fe-KIT-6 at $2\theta = 0.9^\circ$ was due to (211) reflection, shoulder peak at $1.1^\circ$ due to (220) reflection, and the weak peaks between 1.5 and $2.2^\circ$ due to (321), (400), (420), (332), (422) and (431) reflections, indicating the formation of well-ordered mesoporous materials with the symmetry of the body-centered cubic Ia3d space group, which was in agreement with the reported mesoporous KIT-6 materials. The lattice parameter was estimated from the SAXRD spectrum of Fe-KIT-6 using the formula $a_0 = d_{221}(6)^{1/2}$, and the value is shown in Table 1. Also we have obtained lattice parameter of the Fe-KIT-6 from TEM of about 21.65 nm, which was almost close to SAXS. The high-resolution transmission electron microscopy (HRTEM) image (Figure S2d) was used to calculate the $d$-spacing to obtain $a_0$ value.

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The wide-angle XRD patterns of MCS samples prepared at 750, 800, 850, 900, and 950 °C were recorded to study the graphitic nature of the materials. Figure 3a represents the wide-angle XRD pattern of MCS samples prepared at 750, 800, 850, 900, and 950 °C.

### Table 1. Textural Property of the Mesoporous Fe-KIT-6 (75)

| Si/Fe ratio | $d_0$ from SAXRD (nm) | pore size (nm) | pore volume (cm$^3$/g) |
|-------------|----------------------|---------------|------------------------|
| Fe-KIT-6 (75) | 77                   | 22            | 846                    | 6.62                   | 1.211                  |

“$d_0$ is calculated from the gel. $a_0$ is calculated from inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. $d_0$ is calculated from $N_2$ sorption studies.”

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angle XRD patterns of MCS-750, MCS-800, and MCS-850 samples only. The XRD patterns of MCS-900 and MCS-950 samples are produced as supporting results in Figure S3. As shown in Figure 3a, the XRD pattern for all samples exhibited two well-resolved diffraction peaks with 2θ ranges of about 25.4–25.8 and 42.9–43.4°, which can be indexed to (002) and (100) diffractions of typical graphite carbon materials, respectively.34 However, the broadness of diffraction peaks of the MCS suggested a less long range of structural order in the graphitic plane.35 According to Bragg’s law, the interlayer spacings d_{002} of MCS were 0.347, 0.348, 0.349, 0.349, and 0.347 nm for MCS synthesized at 750, 800, 850, 900, and 950 °C, respectively. The values were nearly close and slightly higher than that of the pure graphitic carbon (0.335 nm), which indicated that the MCS consists of relatively well-graphitized carbon structure.23,31

Raman spectroscopy is one of the powerful tools for the characterization of MCS (Figure 3b). In the figure, the D and G bands observed at about 1335 and 1580 cm⁻¹, respectively, are characteristic bands of carbon materials. The former, corresponding to defect-induced band, attributed to the structural defects in hexagonal graphene plane.36,37 The graphitization of carbon materials can be confirmed by I_D/I_G value. The I_D/I_G values of MCS-750, MCS-800, and MCS-850 are 0.78, 0.80, and 0.89, respectively. The I_D/I_G values of <1 obtained in our case suggests that the MCS were well-graphitized carbon structures.38 The I_D/I_G ratio increased with increasing reaction temperature in CVD technique, which is in accordance with the previously reported results.39

Figure 2. SEM images (a, b) and HRTEM images (c, d) with different magnifications of Fe-KIT-6.

Figure 3. XRD patterns (a) and Raman spectrum (b) of MCS synthesized at 750, 800, and 850 °C.
Results and Discussion

The morphology and microstructure of MCS synthesized at 750, 800, and 850 °C were investigated by SEM and HRTEM, respectively. The SEM images of MCS-750, MCS-800, and MCS-850 samples are displayed in Figure S4. The samples MCS-900 and MCS-950 were also carried out using SEM tool, and their SEM images are shown in Figure 4a–c. As shown in Figure 4a–c, all samples revealed nearly uniform formation of spherelike morphology and the increase in temperature favored the formation of spheres with high yield, as shown in Figure 4 and Table 2, respectively.

The yield of MCS-750 prepared at 750 °C is 62.5%, which is comparatively low; on increasing the reaction temperature up to 850 °C, the yield increased rapidly (174%). But beyond 850 °C, the yield of MCS-900 prepared even at 900 °C is only 137.5%, which clearly shows that the yield of MCS beyond 850 °C begins to gradually decrease.

Some of the spheres are accreted and form a chainlike structure, in agreement with previous reports.40,41 The morphological analyses of MCS-900 and MCS-950 samples were also carried out using SEM tool, and their SEM images are presented in Figure S4. The samples MCS-900 and MCS-950 also retained similar morphology to the MCS-750, MCS-800, and MCS-850 samples. Further, the microstructural study of MCS was conducted by HRTEM analysis. Figure S4a1–a2,b1–b2,c1–c2 shows the HRTEM images of MCS-750, MCS-800, and MCS-850 samples at different magnifications present to be of nearly perfect sphere with hollow structure and average size range of 810, 780, and 750 nm, respectively. The wall thickness of each carbon sphere was almost uniform, i.e., about 90 nm. In general, this kind of hollow structures could be indicated by the dark edge and pale core in HRTEM images. It is clearly shown in the HRTEM images given in Figure 5 itself that all of them have graphitic nature. The already proposed probable formation mechanism of MCS found only uniform MCS in resultants yields, indicating that C2H2 may play a crucial role in the formation of hollow-structured MCS. At the time of MCS preparation, some carbon feedstock are composed of basic structural units (BSUs). It has been reported in ref 42 that the gas/solid interface usually results in a texture of the sphere due to the random arrangement of the BSUs, which leads to the formation of sphere shape morphology with hollow structures. Moreover, the interlayer distances between layers were 0.347 (Figure 5a3), 0.348 (Figure 5b3), and 0.349 nm (Figure 5c3) for the MCS-750, MCS-800, and MCS-850 samples, respectively. The obtained results from XRD, Raman, and HRTEM studies were concurrent about the graphitic structure of MCS.

Recently, Carrasco et al.31 and Jian-Ying Miao et al.43 have reported that the probable formation mechanism of spherical carbon structures. We proposed a probable formation mechanism of MCSs, and its schematic representation is shown in Figure 6. In general, Fe particles can be incorporated in the walls of the mesoporous KIT-6 molecular sieves. As this 3D cubic KIT-6 stabilizes dispersed catalytic ions, its structural stability seems to be good.

The bidirectional and uniform pore system of KIT-6 made them well adapted for excellent catalytic supports. The factors such as nature of catalytic supports, reaction temperature, and transition-metal nanoparticles desired the growth of MCSs. In this attempt, Fe nanoparticles were well embedded in the 3D cubic mesoporous KIT-6 molecular sieves. In general, the transition-metal nanoparticles are seeds for the growth of carbon nanotubes/spheres. The continuous separation from the acetylene decomposition and deposition of graphitic carbon led to the formation of perfect carbon spheres.

The carbon radicals became good sphere-shaped carbons when C2H2 gas entered the CVD setup at a particular temperature (reaction temperature). One of the factors for the formation of MCSs temperature revealed that growth of MCSs was not observed at temperature less than 750 °C. This was obvious that appropriate sintering of the metal catalyst was necessary for the growth of MCSs. Then, further increase of temperature from 750 to 950 °C favors the formation of spheres. It is also observed that carbon deposition increased with increasing reaction temperatures. The optimized temperature was found to be 850 °C, and further increase in temperature (to 900 and 950 °C) decreased the yield. The amount of deposition of MCSs was higher at 850 °C and lower at 750 °C (Table 2).

Table 2. Influence of Reaction Temperature on Growth of MCS at Constant Reaction Condition

| Sample name | Catalyst (mg) | Carbon deposition yield (%) | MCS yield (%)(W_{ACS}/W_{Cat}) × 100 | Weight of the MCS after purification (mg) |
|-------------|--------------|-----------------------------|---------------------------------------|------------------------------------------|
| 1 MCS-750   | 200          | 126                         | 62.5                                  | 125                                      |
| 2 MCS-800   | 200          | 221                         | 165                                   | 330                                      |
| 3 MCS-850   | 200          | 223                         | 174                                   | 348                                      |
| 4 MCS-900   | 200          | 173                         | 137.5                                 | 275                                      |
| 5 MCS-950   | 200          | 159                         | 127.5                                 | 255                                      |

*Carbon source: C2H2; flow rate of C2H2: 100 SCCM; reaction time: 30 min.

The samples MCS-850 are displayed in Figure 4a. The samples MCS-800 and MCS-850 were also carried out using SEM tool, and their SEM images are shown in Figure 4b. Further, the microstructural study of MCS was conducted by HRTEM analysis. Figure S4a1–a2,b1–b2,c1–c2 shows the HRTEM images of MCS-750, MCS-800, and MCS-850 samples at different magnifications present to be of nearly perfect sphere with hollow structure and average size range of 810, 780, and 750 nm, respectively.

The wall thickness of each carbon sphere was almost uniform, i.e., about 90 nm. In general, this kind of hollow structures could be indicated by the dark edge and pale core in HRTEM images. It is clearly shown in the HRTEM images given in Figure 5 itself that all of them have graphitic nature. The already proposed probable formation mechanism of MCS found only uniform MCS in resultants yields, indicating that C2H2 may play a crucial role in the formation of hollow-structured MCS. At the time of MCS preparation, some carbon feedstock are composed of basic structural units (BSUs). It has been reported in ref 42 that the gas/solid interface usually results in a texture of the sphere due to the random arrangement of the BSUs, which leads to the formation of sphere shape morphology with hollow structures. Moreover, the interlayer distances between layers were 0.347 (Figure 5a3), 0.348 (Figure 5b3), and 0.349 nm (Figure 5c3) for the MCS-750, MCS-800, and MCS-850 samples, respectively. The obtained results from XRD, Raman, and HRTEM studies were concurrent about the graphitic structure of MCS.

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in the growth of carbon spheres by CVD protocols is still not revealed completely.

The nitrogen adsorption/desorption isotherms and the pore-size distribution curves of the MCS-750, MCS-800, and MCS-850 are shown in Figure 7a,b. All of the samples exhibited type IV isotherms, obvious condensation step, and significant hysteresis loops at high relative pressure \( P/P_0 = 0.4 - 0.9 \), which indicated the existence of a large number of mesopores.\textsuperscript{44–46} The pore-size distribution (PSD) of the MCS was calculated using the Barrett–Joyner–Halenda (BJH) method from the desorption branches of isotherms, as shown in Figure 7b. This showed that the size of mesopores in the MCS were around 3–4 nm (centered on 3.66, 2.86, and 3.11 nm for MCS-750, MCS-800, and MCS-850, respectively). Such uniform mesopores with relatively high surface area were expected to provide sufficient charge-storage space for high specific capacitance and efficient ion-transfer path. The BET surface area, pore size, and pore volume of MCS are listed in Table 3.

Moreover, high-resolution XPS technique was used to analyze the chemical composition and surface functional groups on the surface of the prepared carbon materials with the atomic percentage of the surface elements summarized in Table 3. The survey scan spectra in Figure 8a showed that the MCS contained only carbon and oxygen peaks at binding energies of about 284.7 and 533.4 eV, respectively, which

Figure 5. HRTEM images of (a1–a3) MCS-750, (b1–b3) MCS-800, and (c1–c3) MCS-850.

Figure 6. Probable formation mechanism of MCSs.

MCS formation mechanism

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suggested that the purification process removed Fe and Si of the catalytic support completely.

The XPS image of MCS in Figure 8b further demonstrated the electronic states of the surface elements. The C 1s XPS images can be deconvoluted into four individual peaks: the main peak observed at around 284.7 eV was assigned to C−C group, while the other three peaks at around 286.6, 288.4, and 290.1 eV can be assigned to the C−O, C=O, and O−C=O groups, respectively. The potential oxygen functional groups on MCS enhance the electrochemical activity and contribute to the faradic redox process occurring on the carbon surface. Comparatively, MCS-850 delivered more number of C−O (286.6 eV) groups, as indicated in Figure 8b, with high intensity. We ascribed the enhanced capacitance to the oxygen functionalities, particularly pyrone-like (C−O) groups. We illustrated the difference in oxygen content from the XPS results. And those estimated different oxygen functionalities are listed in Table S1. The relative intensities (in %) of MCS-750, MCS-800, and MCS-850 samples for C−O functionalities are 13, 16.6, and 30%, respectively. We could observe more than two times C−O functionalities in the MCS-850 sample among other samples.

The supercapacitor performances of the purified carbon materials (MCS-750, MCS-800, and MCS-850) were evaluated by cyclic voltammetry, galvanostatic charging/discharging, and electrochemical impedance spectroscopy measurements in 6 M KOH electrolyte using a three-electrode system. Figure 9a shows the CV curves of MCS-750, MCS-800, and MCS-850 electrodes at a scan rate of 50 mV/s between −1.0 and 0 V in 6 M KOH electrolyte, which exhibited rectangular-like trends with broad humps indicating the composite capacitance performance by combination of EDLC and pseudocapacitance. It was attributed to the redox reaction of the oxygen functionalities on the surface of the MCS.

Moreover, the humps are more pronounced in the case of MCS-850 than MCS-750 and MCS-800 with increased amount oxygen and its functionalities (C−O, C=O, and O−C=O), particularly pyrone-like (C−O) groups with high intensity, as shown in Table 3 and Figure 8b. It may be due to the presence of reactive dangling bonds on carbon surface as a...
result of accretion effect of MCS-850 sample. Those pyrone-like functionalities are more electrochemically active in KOH electrolyte. Due to this redox and EDLC process, the CV curve of MCS-850 electrode exhibited larger CV area and a higher specific capacitance of $338 \text{ F/g}$ than MCS-750 ($235 \text{ F/g}$) and MCS-800 ($251 \text{ F/g}$). The specific capacitance ($C_p$) of the MCS-750, MCS-800, MCS-850, MCS-900, and MCS-950 electrodes from CV curves is calculated according to eq 1:

$$C_p = \frac{\int I \, dV}{\Delta V \times \theta \times m} \quad (1)$$

where $I$ is the current density (mA/g), $\Delta V$ represents the potential window (V), $\theta$ is the scan rate (mV/s), and $m$ is the mass of the MCS (g). Figure 9c shows the CV curves of MCS-850 electrode at various scan rates, demonstrating no drastic distortion in the voltammogram even if scan rate increased up to 100 mV/s, indicating good electrolyte diffusion and efficient charge-transfer behavior at high charge and discharge rate, which could be due to well-developed mesoporosity and chainlike morphology that favors the fast access of electrolyte ions within the porous carbon spheres.

CV curves of MCS-750 and MCS-800 at various scan rates are also shown in Figure S5a,b. Moreover, the specific capacitance of the MCS-850 electrode obtained from CV curve could be compared to the published reports for carbon spheres synthesized by CVD and other techniques mentioned in Table 4. To further investigate the electrochemical performance and charge-storage capacity of the synthesized MCS, the GCD measurement was carried out. Figure 9b shows the GCD curves of MCS-750, MCS-800, and MCS-850 at various current densities.

Table 4. Comparison of Specific Capacitance of Various Porous Carbon Materials with Different Synthesis Techniques

| s. no. | material  | technique                         | specific capacitance (F/g) | electrochemical performance under ref. |
|--------|-----------|-----------------------------------|-----------------------------|----------------------------------------|
| 1      | CS        | CVD                               | 132                         | 6 M KOH @ 1 A/g                         | 31          |
| 2      | MGNB      | CVD                               | 206                         | 1 M H$_2$SO$_4$ @ 5 mV/s               | 46          |
| 3      | HMCS      | CVD                               | 120                         | 1 M H$_2$SO$_4$ @ 1 mV/s               | 50          |
| 4      | graphitic CS | catalytic graphitization           | 155                         | 0.1 M KOH @ 10 mV/s                    | 53          |
| 5      | porous CS | catalytic graphitization           | 127                         | 2 M KOH @ 0.2 A/g                      | 54          |
| 6      | porous CS | carbonization and activation       | 206                         | 2 M KOH @ 1 mV/s                       | 19          |
| 7      | MCS       | template method                    | 146                         | 2 M KOH @ 1 mV/s                       | 55          |
| 8      | carbon nanospheres | carbonization and activation      | 219                         | 0.5 M H$_2$SO$_4$ @ 1 mV/s            | 56          |
| 9      | NHCS      | template                          | 173                         | 6 M KOH @ 0.5 A/g                      | 57          |
| 10     | GNHCSs    | carbonization                      | 120                         | 6 M KOH @ 0.5 A/g                      | 58          |
| 11     | HCS       | template                          | 180                         | 6 M KOH @ 0.2 A/g                      | 59          |
| 12     | porous CS | catalytic graphitization           | 150                         | 6 M KOH @ 1 A/g                        | 60          |
| 13     | MCS       | CVD technique                     | 338                         | 6 M KOH @ 1 mV/s                       | present work|
| 14     | MCS       | CVD technique                     | 217                         | 6 M KOH @ 0.5 A/g                      | present work|

*MCS, mesoporous carbon spheres; CS, carbon spheres; MGNB, mesoporous graphene nanoballs; HMCS, hollow mesoporous carbon spheres; NHCS, N-doped hollow carbon spheres; GNHCS, graphitic N-doped hollow carbon spheres; HCS, hollow carbon spheres.*
electrodes within the potential window of −1.0−0 V at a current density of 1 A/g.

The GCD curves of all of the samples deviated from regular triangular shape to a certain extent, which further demonstrated that faradic redox reactions occurred on the MCS surface during the charge/discharge process, which was consistent with CV analysis. Figure 9d shows the GCD curves of MCS-850 at the current density range of 0.5−10 A/g. With the increase in the current density, the triangular shape was closer to the ideal isosceles triangle, suggesting the superior supercapacitive performance at high current density. The GCD curves for MCS-750 and MCS-800 are also given in Figure S5c,d. The specific capacitance of MCS was calculated from the GCD curves using eq 2\textsuperscript{52}

\[
C_{sp} = \frac{I \times \Delta t}{\Delta V \times m}
\]

where \(I\) is the discharge current (A), \(\Delta t\) is the discharge time (s), \(\Delta V\) is the potential window (V), and \(m\) is the mass (g) of the active materials in the working electrode. The derived specific capacitance of optimized MCS-850 from GCD curve using eq 2 was 217 F/g at 0.5 A/g. Moreover, we have also compared the specific capacitance of MCS-850 with commercial carbon, which is higher than that of commercial carbon sphere (2 F/g at 0.2 A/g).\textsuperscript{61}

CV curves of MCS-900 (a) and MCS-950 (b) at different scan rates, GCD curves of MCS-900 (c) and MCS-950 (d) at various current densities, and specific capacitance vs scan rate of MCS-900 (e) and MCS-950 (f) are displayed in Figure S6. Both the MCS-900 and MCS-950 samples also present rectangle-like shape with smoothened hump, which indicated that the combined effect of EDLC and pseudocapacitor performance. The specific capacitances of MCS-900 and MCS-950 are 189 and 151 F/g at a scan rate of 1 mV/s and 54 and 51 F/g at a scan rate of 100 mV/s, respectively. The specific capacitance values of MCS-900 and MCS-950 electrodes are provided in Table S2 using CV and GCD measurements. It is believed that the electrolyte allowed penetrating at low scan rate into pores more thoroughly and to make greater contact with internal surface of the electrode material and hence yield larger specific capacitance. At higher scan rates, it delivered lower specific capacitance due to insufficient time for electrolyte diffusion and adsorption process. These results...
can be seen in Figure S6e for MCS-900 and Figure S6f for MCS-950 samples.

It was also found that the increase in reaction temperatures from 750 to 850 °C results in the increase in oxygen functionalities and oxygen contents on the surface of MCSs due to which we claimed that the MCS-850 sample exhibited a better capacitive performance than the other samples. But unfortunately, we found lower capacitive behavior with further increase in reaction temperature beyond 850−950 °C, as evidenced by EDX analysis. The EDX micrographs are shown in Figure 10a−e. Table 5 represents EDX spectra of MCS synthesized at various temperatures and their corresponding carbon and oxygen contents in weight (%).

Table 5. EDX Spectra Results of Carbon and Oxygen Contents in Weight (%)

| element | weight (%) |
|---------|------------|
|         | 750 °C | 800 °C | 850 °C | 900 °C | 950 °C |
| C K     | 92.98  | 91.47  | 89.20  | 94.34  | 95.64  |
| O K     | 7.02   | 8.53   | 10.80  | 5.66   | 4.36   |

To further demonstrate the excellent capacitive performance of the MCS-850, EIS was carried out. The Nyquist plots of MCS-750, MCS-800, and MCS-850 electrodes are shown in Figure 11a. The semicircle in the high-frequency region provides charge-transport resistances at electrode/electrolyte interfaces (R_{ct1}). The intersect of the semicircle arcs in the real axis provides charge-transport resistances. In addition, the high-frequency intercept at real axis provides the solution or series resistance (R_s). From Table S3, it noted that series resistance R_s seems to be same for all of the samples due to the surface resistance of nickel foam used in the analysis. From Table S3, it noted that the R_{ct} value of MCS-850 (0.69 Ω) is much lower than that of MCS-750 (1.96 Ω) and MCS-800 (2.59 Ω). It could be related to its well-developed porosity and electrochemically active functionalities on the surface that tend to render the interface between the electrolyte and the electrode material an efficient charge transportation. In the low-frequency region, MCS-850 exhibited a nearly vertical line parallel to imaginary axis, which implies better capacitive behavior than MCS-750 and MCS-800. The existence of Warburg-type impedance further confirms the fast diffusion of ions in it. Figure 11b demonstrates the relationship between specific capacitance and current density. It is noted that the specific capacitance gradually decreased when the current density increases from 0.5 to 2 A/g. However, the capacitance was maintained well even at a high current density (2−10 A/g) in the range of 114−100 F/g for MCS-850, 60−20 F/g for MCS-800, and 32−10 F/g for MCS-750.

The excellent rate capability of MCS-850 was owing to the existence of suitable mesoporous structure, which provides shorter ionic diffusion distance and rapid mass-transport path. The change in specific capacitance as a function of scan rate is shown in Figure 11c. It can be clearly revealed that as the scan rate increases, specific capacitance decreases. Consequently, it can be seen that the CV delivered larger capacitance at lower scan rates, while smaller capacitance at higher scan rates. It is believed that the electrolyte allowed penetrating at low scan rate into pores more thoroughly and to make greater contact with internal surface of the electrode material and hence yield larger specific capacitance. At higher scan rates, it delivered lower specific capacitance due to insufficient time for electrolyte diffusion and adsorption process.

Cycling performance was another important factor in determining the supercapacitance of electrode for many practical applications. The cycling stability of MCS-850 electrode was tested using GCD cycling at a current density...
of 2 A/g, as shown in Figure 11d. At the end of 2000 cycles, the specific capacitance was almost same with minor loss, retaining nearly 96% of capacitance, which indicated good cycling performance.

The two-electrode symmetric supercapacitor was fabricated and tested in 6 M KOH aqueous electrolyte. The image of the manufactured two-electrode cell is embedded in Table S4. The specific capacitances of the two-electrode symmetric cell calculated by CV method using eq 1 and by GCD method using eq 3 are listed in Table S4.

\[
C_{sp} (F/g) = \frac{2I\Delta t}{m\Delta V} \tag{3}
\]

where \(I\) is the discharge current (A), \(\Delta t\) is the discharge time (s), \(m\) is the mass of the active material in a single electrode (g), and \(\Delta V\) is the potential difference (V). It is well known that the energy density of supercapacitor depends on the square of potential window (eq 4). A significant improvement in energy and power density can be obtained if the cell can operate at larger potential range. For that, we tried to improve cell voltage of prepared symmetric supercapacitor as follows. Figure S7a,b reveals the CV and GCD curves of the symmetric cell at various potential windows. When the cell voltage increased from \(-0.8\) to \(1.0\) V, the CV curves still retained their nearly quasi-rectangular shape, which is indicative of good capacitive and reversibility behavior. However, while the voltage increased from \(-0.8\) to \(1.2\) V, the current increased rapidly because the electrolyte was being decomposed. Therefore, the potential window of 1.8 V was selected to evaluate the electrochemical performance of the symmetric cell.

Figure 12a demonstrates the typical CV curves of the symmetric cell of MCS-850 electrode at different scan rates from 5 to 100 mV/s with the potential window of \(-0.8\) to 1.0 V. The CV curves showed a quasi-rectangular shape, which seems to be the combination of EDLC, and pseudocapacitive behaviors confirmed the contribution of pseudocapacitance, which is derived from the surface oxygen functional groups. Moreover, the shape of the CV curves did not change even at a high scan rate of 100 mV/s, exhibiting excellent rate capability and fast ion transportation. The GCD curves in Figure 12b show a nearly triangular shape, suggesting good electrochemical charge and discharge reversibility. Furthermore, the calculated specific capacitance values of the symmetric cell (MCS-850 used as electrode) from CV and GCD curves are listed in Table S3.

Figure 12c shows that the specific capacitance of fabricated symmetric cell as a function of scan rate. The specific capacitances of 63 and 48 F/g were obtained at scan rates of 5 and 100 mV/s, respectively. The difference in specific capacitance found between 63 and 48 F/g is comparatively low, demonstrating good rate capability. The cycling performance of symmetric two-electrode cell was tested for about 2000 continuous cycles at a current density of 1 A/g between \(-0.8\) and 1.0 V, using the GCD method, and is displayed in Figure 12d. After 2000 cycles, the capacitive retention of MCS-850 remained about 86% of the initial capacitance. This cyclic stability test illustrates that the MCS-850 electrode has a significant cycling stability behavior. We also calculated the energy density (Wh/kg) and power density (W/kg) using eqs 4 and 5. The Ragone plot for two-electrode symmetric cell in 6 M KOH aqueous electrolyte is presented in Figure 13, showing that the high specific energy density of the cell was 7.1 Wh/kg, which delivered a power density of 277 W/kg. This result is higher and comparable to that of the previously reported carbon-based symmetric supercapacitor in aqueous electrolyte.\(^{62,63}\)

\[
E = \frac{1}{8}C_{sp}(\Delta V) \left(\frac{1000}{3600}\right) \tag{4}
\]

\[
P = 3600 \frac{E}{\Delta t_d} \tag{5}
\]
and stirred at 35 °C for complete dissolution. The obtained white precipitate was filtered, dried at 100 °C for 8 h, and calcined for 5 h at 550 °C in air.

**Synthesis and Purification of Mesoporous Carbon Spheres.** MCS was synthesized by the CVD technique using Fe-KIT-6 as catalytic support. A simple CVD horizontal tube furnace setup containing quartz tube (45 mm i.d., and 960 mm long) and gas flow control units (Figure S1) was used to produce MCS. In a typical experiment, about 200 mg of Fe-KIT-6 was placed in a quartz boat inside a quartz tube. Argon gas was purged to the catalyst at a flow rate of 100 SCCM (SCCM — standard cubic centimeter per minute) for 30 min to remove water molecules, i.e., pretreated catalyst, and hydrogen gas was purged at a flow rate of 110 SCCM for 30 min to reduce the metal particles. The reaction was carried out using acetylene as the carbon source at 750, 800, 850, 900, and 950 °C at a flow rate of 100 SCCM for 30 min. The furnace was cooled to ambient temperature under argon atmosphere. The black powder collected from the quartz boat was weighed, purified, and then used to further characterization studies. The catalytic decomposing of acetylene was calculated in terms of percentage of the carbon deposition by eq 6.

\[
\text{yield of MCS (\%)} = \frac{m_{\text{tot}} - m_{\text{cat}}}{m_{\text{cat}}} \times 100
\]  

where \(m_{\text{tot}}\) is the total mass of carbon product and catalyst and \(m_{\text{cat}}\) is the mass of catalytic support.

The as-synthesized materials were treated with 40% HF (hydrofluoric acid) solution to remove the Si phase. The obtained sample was treated with HCl solution to remove Fe particles and washed with deionized water repeatedly and dried. After drying, the sample was oxidized at 400 °C for 2 h in atmospheric air to remove carbonaceous impurities like microcrystalline carbon and amorphous carbon to yield the final mesoporous carbon spheres, which were designated as MCS-750, MCS-800, MCS-850, MCS-900, and MCS-950. After purification, the percentage of the MCSs on the mass of the catalytic support was also calculated by eq 7, and the values are listed in Table 2.

\[
\text{MCS Yield (\%)} = \frac{W_{\text{MCS}}}{W_{\text{cat}}} \times 100
\]  

where \(W_{\text{MCS}}\) is the weight of the MCS after purification (in mg) and \(W_{\text{cat}}\) is the weight of the catalyst in mg.

**Structural Characterizations.** Inductive coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer OPTIMA 3000) was used to determine the amount of metal loading into KIT-6. The X-ray diffraction (XRD) pattern was recorded with PANalytical XPert diffractometer equipped with liquid nitrogen-cooled germanium solid-state detector using Cu Kα radiation. Scanning electron microscopy (SEM, JEM-5600LV) was used to analyze surface morphology. High-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL JEM 2100 electron microscope operated at 200 kV. Raman measurements were carried out using a laser Raman microscope-RAMAN 11i with 532 nm line of an Ar ion laser as an excitation source. \(N_2\) adsorption—desorption
isotherm measurement was performed at 77 K with a Quanta Chromatograph. The specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller (BET) equation. The pore-size distribution (PSD) was measured by the Barrett–Joyner–Halenda (BJH) method from the adsorption branches of the isotherms. X-ray photoelectron spectroscopy (XPS) was employed on XPS-Omicron Nanotechnologies.

**Electrochemical Characterization.** Electrochemical experiments were carried out in electrochemical workstation (Autolab PGSTAT) using a three-electrode system in 6 M KOH aqueous electrolyte. The three-electrode cell was assembled with the prepared MCS cast on precleaned Ni foam, which acts as the working electrode, Pt wire as the counter electrode, and saturated Ag/AgCl (3 M KCl) as the reference electrode. The working electrode was prepared as follows: the prepared MCS (80%), carbon black (10%), and PVDF (10%) were mixed with a few drops of dimethylformamide (DMF) using agate mortar to get a paste. The resulting paste was cast onto a precleaned nickel foam and pressed at 10 MPa pressure. The as-prepared working electrode was dried overnight at 80 °C. Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS) techniques were employed for the measurements of electrochemical performance. The CV and GCD measurements were performed with a potential window between −1.0 and 0 V at different scan rates from 1 to 100 mV/s and current densities from 0.5 to 10 A/g. EIS was conducted in the frequency range of 100 kHz to 0.01 Hz with 5 mV AC amplitude at the open-circuit potential.

**Fabrication of Two-Electrode Symmetric Device.** The two-electrode symmetric supercapacitor was fabricated and tested in 6 M KOH aqueous electrolyte. The working electrode was prepared by mixing carbon as active material (MCS-850), carbon black as conductive medium, and PVDF as binder in a weight ratio of 8:1:1, respectively. The above resulting paste of electrode materials in equal amount was cast on precleaned Ni foam, which acts as the working electrode, Pt wire as the counter electrode, and saturated Ag/AgCl (3 M KCl) as the reference electrode. The working electrode was prepared as follows: the prepared MCS cast on precleaned Ni foam, which acts as the working electrode, Pt wire as the counter electrode, and saturated Ag/AgCl (3 M KCl) as the reference electrode. The working electrode was prepared as follows: the prepared MCS (80%), carbon black (10%), and PVDF (10%) were mixed with a few drops of dimethylformamide (DMF) using agate mortar to get a paste. The resulting paste was cast onto a precleaned nickel foam and pressed at 10 MPa pressure. The as-prepared working electrode was dried overnight at 80 °C. Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS) techniques were employed for the measurements of electrochemical performance. The CV and GCD measurements were performed with a potential window between −1.0 and 0 V at different scan rates from 1 to 100 mV/s and current densities from 0.5 to 10 A/g. EIS was conducted in the frequency range of 100 kHz to 0.01 Hz with 5 mV AC amplitude at the open-circuit potential.

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**ASSOCIATED CONTENT**

- Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02160.

Schematic of the CVD synthesis of MCS; HRTEM images with 3D cubic structure of Fe-KIT-6 at different magnifications; XRD spectrum, SEM images, and electrochemical analysis of MCS-750, MCS-800, MCS-900, and MCS-950; relative intensities (in terms of %) of different oxygen functionalities of MCS-750, MCS-800, and MCS-850; and CV and GCD curves of symmetric device at different potential windows and specific capacitances of symmetric device derived from CV and GCD profiles (PDF)

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**Notes**

The authors declare no competing financial interest.

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