Fabrication and textural characterization of nanoporous carbon electrodes embedded with CuO nanoparticles for supercapacitors

Kumaresa P S Prasad1,2, Dattatray S Dhawale1, Thiripuranthagan Sivakumar2, Salem S Aldeyab3, Javaid S M Zaidi4, Katsuhiko Ariga1 and Ajayan Vinu1

1 International Center for Materials Nanoarchitectonics (MANA), World Premier International (WPI) Research Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
2 Department of Chemical Engineering, Anna University, Gundy, Chennai 600025, India
3 Department of Chemistry, Petrochemicals Research Chair, Faculty of Science, King Saud University, PO Box 2455 Riyadh 11451, Kingdom of Saudi Arabia
4 Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

E-mail: vinu.ajayan@nims.go.jp

Received 4 March 2011
Accepted for publication 29 March 2011
Published 7 July 2011
Online at stacks.iop.org/STAM/12/044602

Abstract
We introduce a novel strategy of fabricating nanoporous carbons loaded with different amounts of CuO nanoparticles via a hard templating approach, using copper-containing mesoporous silica as the template and sucrose as the carbon source. The nature and dispersion of the CuO nanoparticles on the surface of the nanoporous carbons were investigated by x-ray diffraction (XRD), high-resolution scanning electron microscopy (HRSEM) and high-resolution transmission electron microscopy (HRTEM). XRD results reveal that nanoporous carbons with embedded CuO nanoparticles exhibit a well-ordered mesoporous structure, whereas the nitrogen adsorption measurements indicate the presence of excellent textural characteristics such as high surface area, large pore volume and uniform pore size distribution. The amount of CuO nanoparticles in the nanochannels of the nanoporous carbon could be controlled by simply varying the Si/Cu molar ratio of the mesoporous silica template. Morphological characterization by SEM and TEM reveals that high-quality CuO nanoparticles are distributed homogeneously within the nanoporous carbon framework. The supercapacitance behavior of the CuO-loaded nanoporous carbons was investigated. The material with a small amount of CuO in the mesochannels and high surface area affords a maximum specific capacitance of 300 F g⁻¹ at a 20 mV s⁻¹ scan rate in an aqueous electrolyte solution. A supercapacitor containing the CuO-loaded nanoporous carbon is highly stable and exhibits a long cycle life with 91% specific capacitance retained after 1000 cycles.

Keywords: nanoporous carbon, CuO, surface properties, supercapacitor
1. Introduction

Energy storage devices have attracted much attention in recent years as researchers look for next-generation materials for the development of alternative energy sources owing to the rapid depletion of fossil fuel reserves. Among the energy storage devices, supercapacitors or ultracapacitors are unique and have attracted much interest because they can perform better than conventional batteries and dielectric capacitors, which makes them probably the most important next-generation energy storage device [1–3]. Furthermore, the deficiencies of other power sources, such as batteries and fuel cells, could be overcome by supercapacitors, owing to their long cycle life and rapid charging and discharging at high power densities [4]. Since the discovery of electrochemical capacitors for the storage of electrical charge by General Electric [5], supercapacitors have generated considerable interest for a wide and growing range of applications in various sectors including load cranes, forklifts, electric vehicles, electric utilities, factory power backup and so on [6]. Several materials including porous carbons, transition metal oxides and conducting polymers have been widely used as electrodes in supercapacitors.

Among the supercapacitor electrode materials, porous carbons are expected to have high specific capacitance together with high power density. Despite the high specific surface area, the low conductivity of porous carbon materials limits their application in high-power-density supercapacitors. This problem can be overcome by incorporating metal or metal oxide nanoparticles to the surface of the porous carbons, which would result in remarkable physical and chemical properties originating from the spatial confinement and synergetic electronic interactions between metallic and carbonaceous components [7, 8].

Metal oxide nanocrystals have been extensively studied for their unique magnetic, catalytic and electronic properties [9, 10]. In recent years, transition metal oxides, such as RuO$_2$ [11, 12] and MnO$_2$ [13], have become promising materials for supercapacitors owing to their high pseudocapacitance. The most success was achieved for RuO$_2$; however, the high cost and low abundance of RuO$_2$ limit its large-scale application. Therefore, there is a strong need to develop low-cost alternatives. Copper oxide, CuO, is a metal oxide with favorable redox properties, and thus thin CuO films synthesized by electrodeposition [14] and chemical bath deposition [15] have been used in supercapacitors. However, the highest specific capacitances obtained in those studies are only 37 and 43 F g$^{-1}$, respectively. The low capacitances may be due to the film morphology with low accessible surface area. It is also difficult for the ions and electrons to diffuse through a submicron-thick film. To avoid the above-mentioned drawbacks, it is necessary to incorporate CuO nanoparticles into a porous support with high surface area in order to create well-dispersed active sites interacting with ions and the electrolyte.

Nanoporous materials have attracted significant attention owing to their interesting textural parameters [16–29], which make them an excellent support for the fabrication of nanoparticles. Several reports on the fabrication of transition-metal-oxide-supported nanoporous materials are available in the literature [30–35]. However, most of the methods involve the post synthetic impregnation of the metal oxide nanoparticles inside the mesochannels of the support, which has a limited efficiency. Recently, Vinu et al have reported the direct incorporation of a high amount of metal ions in the SBA-15 framework by simply adjusting the water-to-hydrochloric acid molar ratio of the synthesis medium [24] without destroying the mesoporous structures. They also showed that small nanoparticles are located inside the nanochannels of the mesoporous silica SBA-15 materials. Although several metal-substituted mesoporous SBA-15 materials have been reported, the information on the Cu-incorporated mesoporous silica is rather limited.

Here, we report on the preparation of mesoporous silica SBA-15 with different Cu contents using pluronic P123 as surfactant, tetraethyl orthosilicate (TEOS) as silica source and copper nitrate as Cu source. We demonstrate that mesoporous silica with a high Cu content can be converted into nanoporous carbons decorated with well-dispersed CuO nanoparticles via a hard templating approach [36, 37], proposed by Ryoo et al using sucrose as a carbon source. It is assumed that the copper in the wall structure of the SBA-15 and inside the mesochannels of the SBA-15 is completely transformed inside the porous structure and the walls of the nanoporous carbons during the replication process. Finally, the nanoporous carbons supported by CuO nanoparticles have been applied as electrodes for supercapacitors. Among the materials studied, the nanoporous carbons loaded with a small amount of CuO showed the best supercapacitor performance.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate, sucrose and triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO$_{20}$PO$_{70}$EO$_{20}$) were obtained from Aldrich. Copper(II) nitrate trihydrate was purchased from Wako.

2.2. Preparation of SBA-15 containing different amounts of Cu

CuSBA-15 materials with various Si/Cu molar ratios were prepared by the following procedure. Amphiphilic triblock copolymer Pluronic P123 (4 g) was dispersed in 30 g of water and stirred for 4 h. Then, 70 ml of 0.29 M HCl was added and stirred for 2 h (pH ~ 2.2). Then, 9.0 g of TEOS and an appropriate amount of copper nitrate were added directly into the homogeneous solution under stirring. The resulting gel was aged at 40 °C for 24 h and finally baked at 100 °C for 48 h. The samples were labeled CuSBA-15 – x, where x denotes the Si/Cu molar ratio in the synthesis gel. After synthesis, the obtained solids were calcined in flowing air at 540 °C to decompose the triblock copolymer.
2.3. Preparation of CuO-encapsulated nanoporous carbons

CuO-encapsulated nanoporous carbons were prepared using CuSBA-15 \( - x \) (\( x \) = 2.5, 5 or 10) as the template and sucrose as the carbon source. In a typical synthesis, 1 g of CuSBA-15 was added to a solution obtained by dissolving 0.9 g of sucrose and 0.1 g of \( \text{H}_2\text{SO}_4 \) in 5 g of water and keeping the mixture in an oven for 6 h at 100 °C. Then the oven temperature was raised to 160 °C for another 6 h. To obtain fully polymerized and carbonized sucrose, 0.75 g of sucrose, 0.0840 g of \( \text{H}_2\text{SO}_4 \) and 5 g of water were added to the pretreated sample and the mixture was subjected to the thermal treatment described above. The template–polymer composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 5 h to carbonize the polymer. The nanoporous carbons loaded with CuO nanoparticles were recovered after the dissolution of the silica framework in 5 wt% hydrofluoric acid by filtration, washed three times with ethanol and dried at 100 °C. The thus-produced samples were labeled as Cu-NC-x, where \( x \) denotes the initial Si/Cu ratio in the CuSBA-15 gel.

2.4. Electrode preparation

A bare glassy carbon electrode (GCE) was mirror-polished with 0.05 M \( \text{Al}_2\text{O}_3 \) slurry and rinsed with double-distilled water. The electrode materials Cu-NC-x (10 mg ml\(^{-1}\)) were dispersed in an aqueous solution of methanol forming a slurry and sonicated for 10 min. Then 20 \( \mu \)l of slurry was spread onto the GCE electrode surface using a micropipette. After the solvent was evaporated, the electrode surface was covered with 5 \( \mu \)l of Nafion solution, and the electrodes were dried at 70 °C for 1 h to evaporate the solvent.

2.5. Characterization

Powder x-ray diffraction (XRD) patterns of nanoporous carbon materials encapsulated with different amounts of CuO were recorded with a Rigaku diffractometer using \( \text{CuK}_\alpha \) (\( \lambda = 0.154 \text{ nm} \)) radiation, in the 2\( \theta \) range of 0.8–10°, with a step of 0.01° and integration time of 10 s. Nitrogen adsorption and desorption isotherms were measured at −196°C with a Quantachrome Autosorb 1 sorption analyzer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size was obtained from the adsorption and desorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method. The surface morphology and composition of the studied materials were studied with a Hitachi S-4800 field-emission scanning electron microscope (HRFESEM, accelerating voltage 5.0 kV) equipped with an energy-dispersive x-ray spectroscopy (EDS) setup. High-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2000EX2 microscope operated at 200 kV. Powders for the HRTEM analysis were sonicated in ethanol for 2–5 min and deposited on a copper grid.

Electrochemical measurements were conducted with a CHI 760C workstation, in a standard three-electrode cell. Cu-NC-x, platinum foil and Ag/AgCl were used as working, counter and reference electrodes, respectively. The measurements were carried out in a 1 M \( \text{Na}_2\text{SO}_4 \) aqueous electrolyte solution by cyclic voltammetry technique by varying the potential between −1.0 and 1.5 V (versus Ag/AgCl) at a rate of 20–100 mV s\(^{-1}\). The charge-discharge current densities ranged from 1 to 3 mA cm\(^{-2}\) at a potential of −1.0 to 1.5 V.

3. Results and discussion

3.1. Characterization of CuO-encapsulated nanoporous carbons

Figure 1(A) shows small-angle powder XRD patterns of nanoporous carbon samples encapsulated with different amounts of CuO. All the samples show a peak at about 1.2°, confirming the presence of a uniform mesostructure. These results also reveal that the structural order of the support materials is retained even after the encapsulation of a large amount of CuO nanoparticles inside the mesochannels of the support. As expected, the intensity of the small-angle XRD peak increases with decreasing amount of CuO in the sample.
Among the samples studied, Cu-NC-2.5 exhibited the lowest intensity, indicating a large number of CuO nanoparticles in the mesochannels of the nanoporous carbon. It is interesting to note the peak shift towards the higher angles with increasing amount of CuO in the nanoporous carbons, revealing a reduction in the unit cell constant. This may be attributed to the partial collapse of the carbon nanostructure upon CuO encapsulation. During the high-temperature treatment, CuO nanoparticles tend to agglomerate and require a large space to accommodate them in the confined channel. As a result, part of the wall structure of the carbon may collapse. This explanation is consistent with the XRD peak broadening for the Cu-NC-2.5 sample.

The dispersion of the CuO nanoparticles on the surface of the nanoporous carbons was characterized by powder XRD measurements performed in a wide angular range (see figure 1(B)). No peaks are observed for Cu-NC-10 and Cu-NC-5 samples confirming that CuO nanoparticles are highly dispersed either on the surface or inside the pore walls of the carbons. This result also confirms the absence of agglomerated CuO nanoparticles in these samples, and it is reasonable to assume that the size of the CuO nanoparticles is limited by the pore size of the nanoporous carbon support. The high dispersion of the CuO particles inside the nanochannels of the nanoporous carbon support can be explained as follows: we previously reported that the amount of metal oxide species in the pore channels of the nanoporous silica is quite small when a small amount of the metal source is added in the synthesis gel [24]. We consider that the CuO nanoparticles in the Cu-NC-10 and Cu-NC-5 samples are generated from the disintegration of the copper silicate framework of the template during the high-temperature carbonization treatment. On the other hand, the Cu-NC-2.5 sample showed several high-angle XRD peaks indicating the presence of large CuO crystallites. They might originate from the CuO agglomeration during the high-temperature treatment. The CuO crystallite size in this sample is much larger than the pore diameter of the nanoporous carbons, indicating that most of the agglomerated CuO nanoparticles are situated on the external surface of the support.

The textural characteristics of the CuO-supported nanoporous carbon were evaluated on the basis of the nitrogen adsorption isotherm measurements. Figure 2 shows the results for samples prepared from CuSBA-15–x templates, and the textural parameters data are given in table 1. All the samples exhibit type IV isotherm with a sharp capillary condensation step and a broad H1 hysteresis loop, which is a characteristic of well-ordered mesoporous materials with large pores and narrow pore size distribution. It is worth noting that the shape and position of the capillary condensation step of the isotherms are similar in the CuO-supported and pure nanoporous carbons. This observation confirms that the prepared materials possess a well-ordered mesoporous structure even after the encapsulation of CuO nanoparticles inside the pore channels. The amount of adsorbed nitrogen decreases with increasing amount of CuO in the nanoporous carbons. Among the samples studied, the specific surface area was the lowest in Cu-NC-2.5 and the highest in Cu-NC-10.

The low specific surface area of Cu-NC-2.5 can be attributed to the presence of large CuO crystals in the pore channels; these crystals block the pores not allowing the molecules to access the adsorption sites. A high CuO amount in Cu-NC-2.5 also results in a higher density of this material. The reduction of the textural parameters may also be attributed to a loss of the structural order in Cu-NC-2.5.

Figure 3 shows the HRSEM-EDS spectra of CuO-encapsulated nanoporous carbons. All the samples show C, Cu and O peaks confirming the presence of CuO, and the intensities of the Cu and O peaks increase with increasing amount of CuO in the samples. The highest CuO amount was measured in Cu-NC-2.5 and the corresponding values

![Figure 2](image2.png)

![Figure 3](image3.png)
Figure 4. SEM images of CuO-encapsulated nanoporous carbons: (A, D) Cu-NC-10, (B, E) Cu-NC-5 and (C, F) Cu-NC-2.5.

are given in table 1. It should be mentioned that the amount of CuO is much lower in the final nanoporous carbons than in the nanoporous CuSBA-15 template materials. This is mainly because much Cu is lost in the conversion of copper silicate into CuO during the high-temperature treatment and in the washing procedure where HF was used to remove the nanoporous silica template. Figure 4 shows HRSEM images of the CuO-encapsulated nanoporous carbons. All the materials show a rodlike morphology with uniform length and width. This morphology is similar to that of the pure nanoporous carbons and the nanoporous silica SBA-15 template, confirming the success of the replication process. Agglomerated particles with different shapes and sizes were present in some parts of the Cu-NC-2.5 sample. Well-ordered
mesoporosity was clearly observed for all the samples, as shown in the high-resolution images, which is consistent with the XRD and nitrogen adsorption data.

Figure 5 shows HRTEM images of CuO-encapsulated nanoporous carbons. A well-ordered nanoporous structure is observed in all the samples. It consists of equidistant, parallel nanopore arrays revealing that the structure of the nanoporous carbon is stable despite the encapsulation of a high amount of CuO in the nanochannels. Lattice fringes of CuO nanocrystals are clearly visible in the HRTEM image of Cu-NC-2.5, indicating that the CuO particles formed inside the channels of nanoporous carbon are highly crystalline and may offer excellent characteristics for redox or coupling reactions. Black spots observed in all the samples may be attributed to the CuO nanoparticles inside the nanopore channels. No large particles were observed in Cu-NC-2.5, suggesting that they are not homogenously dispersed in this sample.

3.2. Supercapacitance behavior of CuO-loaded nanoporous carbons

Cyclic voltammetry (CV) is a suitable tool for estimating the difference between the non-Faradic and Faradic reactions. Figure 6 shows the CV curves obtained for Cu-NC-2.5, Cu-NC-5 and Cu-NC-10 electrode cells at a voltage scan rate of 20 mV s\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) electrolyte using a Pt wire as the auxiliary electrode and Ag/AgCl as the reference electrode.

The capacitance was calculated as

\[ C = \frac{I_{\text{max}}}{\frac{dV}{dt}}, \]  

where \( I \) is the average current and \( \frac{dV}{dt} \) is the voltage scanning rate. The interfacial capacitance \( C_i \) (F cm\(^{-2}\)) was calculated as

\[ C_i = \frac{C}{A}, \]  

where \( A \) is the area of active material dipped in the electrolyte. The specific capacitance \( C_s \) (F g\(^{-1}\)) of the electrodes was calculated as

\[ C_s = \frac{C}{W}, \]  

where \( W \) is the active weight of the material.
A supercapacitor is an electrochemical storage device that can store the charge electrostatically using the reversible adsorption of ions of the electrolyte onto active materials that have a high and accessible specific surface area [38]. Therefore, the selection of the electrolyte ions is crucial and is a key to generating high specific capacitance [39]. As can be seen from figure 6, the supercapacitance of the CuO-encapsulated nanoporous carbon increases with decreasing CuO amounts, namely, it is 235 F g\(^{-1}\) for Cu-NC-2.5, 265 F g\(^{-1}\) for Cu-NC-5 and 300 F g\(^{-1}\) for Cu-NC-10. All the samples show a pair of redox peaks in the voltammetric diagrams revealing an irreversible process of charge transfer in CuO, which is due to the hindering of the mass transfer in the framework of the crystalline oxide. CuO is an ideal material for the supercapacitor. The small CuO particles encapsulated in the nanochannels of the nanoporous carbon, as well as their support, exhibit high surface area, and thus the resultant composite is expected to have a high specific capacitance. The low supercapacitance for Cu-NC-2.5 could be due to the presence of the large aggregated CuO nanocrystals, as confirmed by XRD, and the lower surface area of the nanoporous carbon support (see table 1). In addition, the restoration of the conjugated carbon can be hindered by a high amount of large CuO nanoparticles. Further characterization was carried out for the Cu-NC-10 sample, which showed the highest supercapacitance.

An important requirement for the electrode material of a supercapacitor is its stability to high, pulsed discharge power. This property is a strong function of the electrochemical kinetics of redox transitions within the electroactive materials. It was investigated for Cu-NC-10 at different scan rates using cyclic voltammetry. Figure 7 shows the CV curves in 1 M Na\(_2\)SO\(_4\) electrolyte recorded at scan rates from 20 to 100 mV s\(^{-1}\) within the voltage range of \(-1.5\) to \(1.0\) V. An increase in current with increasing scan rate is observed indicating an ideal capacitive behavior [40]. At 20 mV s\(^{-1}\), the CV curve has a nearly rectangular shape characteristic of a capacitor. The shape distorts at higher scan rates mainly owing to the significant contribution of the equivalent series resistance that is associated with the capacitor. This behavior has also been observed in other porous electrode materials such as mesoporous carbons [41]. The CV measurements were also used to calculate the specific and interfacial capacitances. Figure 8 shows the capacitances of the Cu-NC-10 electrode in 1 M Na\(_2\)SO\(_4\) at different voltage scan rates. With increasing the scan rate from 20 to 100 mV s\(^{-1}\), both specific capacitance and interfacial capacitance significantly decrease, from 300 to 120 F g\(^{-1}\) and 3.82 to 1.52 F cm\(^{-2}\), respectively. The maximum specific and interfacial capacitances at a scan rate of 20 mV s\(^{-1}\) were measured for Cu-NC-10 and could be ascribed to the high surface area of the carbon and CuO support. According to Xing et al [42], at a high scan rate, the ions do not have sufficient time to diffuse inside the mesochannels and access all the adsorption sites. As a result, the capacitance of nanoporous carbon encapsulated with CuO nanoparticles decreases with increasing sweep rate. The specific capacitance is much higher for the CuO-encapsulated than the unfunctionalized nanoporous carbon, mostly because of the high accessibility by the electrolyte ion, effective use of the specific surface area and pore diameter and the conduction through the CuO nanoparticles in the encapsulated carbon.

A galvanostatic charge-discharge method was also applied to evaluate the capacitive behavior of the Cu-NC-10 electrode. Figure 9 shows a plot of potential versus time at various current densities. A sharp change in voltage due to the equivalent series resistance of the electrochemical capacitor cell is observed at the beginning of the charge and discharge profiles, even at a high current density of 3 mA cm\(^{-2}\). The associated electrical parameters such as specific power, specific energy and coulombic efficiency (\(\eta\), \%) were calculated as 7.2 kW kg\(^{-1}\), 12.96 kWh kg\(^{-1}\) and 60%, respectively, at 3 mA cm\(^{-2}\).

The electrochemical stability of the supercapacitor made of Cu-NC-10 was evaluated through CV measurements, which were carried out at a 100 mV s\(^{-1}\) scan rate, in the potential range of \(-1.5\) to \(1.0\) V, for 1000 cycles. The specific capacitance of the electrode as a function of cycle number is shown in figure 10. There is a small capacitance decrease in the first 100 cycles, which is due to the consumption of
Figure 9. Charge–discharge profiles of the Cu-NC-10 electrode at different current densities.

Figure 10. Specific capacitance as a function of cycle number for the Cu-NC-10 supercapacitor electrode at a scan rate of 100 mV s⁻¹.

The electrolyte caused by the irreversible reaction between the electrodes and electrolyte [43], followed by saturation. The Cu-NC-10 electrode exhibits high stability, retaining 91% of the initial capacity even after 1000 cycles. This property is rather important for the fabrication of high-performance hybrid supercapacitors. All these results reveal that the fabricated CuO-encapsulated nanoporous carbon is a suitable supercapacitor material with high stability and specific capacitance (300 F g⁻¹), which is much higher than that of other porous carbon supports.

4. Conclusions

Nanoporous carbons encapsulated with different amounts of CuO nanoparticles can be synthesized using CuSBA-15 with an appropriate copper content via a hard templating approach. The CuO nanoparticles can be finely distributed along the nanochannels of the nanoporous carbon with a well-ordered porous structure. Aggregates of CuO nanoparticles were formed in the CuSBA-15 sample prepared using a high Cu content. The amount of CuO in the nanoporous carbons can be finely controlled by simply varying the amount of Cu in the nanoporous silica template. The specific surface area of the samples decreases with increasing CuO nanoparticle content in the nanoporous carbon samples. Among the samples studied, Cu-NC-10 showed the highest specific surface area and pore volume. The supercapacitance behavior of the samples containing different amounts of CuO was investigated. Cu-NC-10 material showed a high supercapacitance of 300 F g⁻¹ at low scan rates, which significantly exceeded the value of unfunctionalized nanoporous carbons. CuO-encapsulated nanoporous carbons showed high stability even after 1000 cycles of measurements. These findings open a new direction in developing novel supercapacitors, and the synthetic process can be extended to nanoporous carbons encapsulated with other metal oxide nanoparticles. These functionalized materials are expected to find applications in sensing and redox catalysis for the synthesis of fine chemicals.

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