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Carbon black nanoparticle trapping: a strategy to realize the true energy storage potential of redoxactive conjugated microporous polymers[†]

Chang Wan Kang,^a Yoon-Joo Ko,^b Sang Moon Lee,^c Hae Jin Kim,^c Jaewon Choi^{*d} and Seung Uk Son^b*^a

Conjugated microporous polymers (CMPs) have significant potential as electrode materials for electric energy storage devices due to their high surface areas, conjugation features, and chemical stability. However, low conductivity has limited their electrochemical performance. To realize the maximum capability of CMPs, a synthetic strategy for enhancing their conductivity is required. This work shows that during the synthesis of CMPs, carbon black (CB) nanoparticles can be entrapped *in situ*. Moreover, redox-active benzoquinone (BQ) species could be generated at the CMP to form CMP-BQ through post-synthetic modification. The resultant CB@CMP-BQs with the entrapped CB nanoparticles showed enhanced electrochemical performance as electrode materials for pseudocapacitors, compared with CMP-BQ. They showed capacitances up to 424 and 373 F g⁻¹ at current densities of 0.5 and 1 A g⁻¹, respectively. In addition, the optimal CB@CMP-BQ3 showed excellent cycling performance for 10 000 cycles.

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Introduction

Recently, conjugated microporous polymers (CMPs) have emerged as a new class of functional materials.¹⁻⁵ The main beneficial features of CMPs are their high surface areas and chemical stability.² CMPs have been applied as adsorbents and catalysts and they have expanded application fields.³ Recently, the energy storage application of CMPs has attracted significant attention of scientists.⁴ For example, CMPs have been applied as capacitive materials for supercapacitors.⁵

However, a critical drawback of CMP-based electrode materials is their low conductivity. In the conventional engineering of electrodes, carbon black (CB) nanoparticles have been mixed with CMP-based electrode materials to enhance conductivity.⁵ Although such physical mixing with CB nanoparticles can help the electrochemical events of CMP, the utilization of the inner chemical species of CMPs is limited. To further enhance conductivity, while also improving the utilization of the inner chemical species of CMPs, further explorations are required for more efficient chemical strategies.

Recently, CMP-carbon nanotube or graphene composites have been engineered.⁶ Our research group has shown that the hollow morphology engineering of CMPs can improve their capacitive electrochemical performance, resulting in the efficient utilization of chemical species in CMPs.⁷ We speculated that the entrapment of highly conductive CB nanoparticles into the CMPs can be a more efficient strategy to further improve their electrochemical performance (Fig. 1).



Fig. 1 The conventional fabrication method and a new engineering strategy of CMP-based electrode materials on electrodes.

^aDepartment of Chemistry, Sungkyunkwan University, Suwon 16419, Korea. E-mail: sson@skku.edu

^bLaboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities (NCIRF), Seoul National University, Seoul 08826, Korea ^cKorea Basic Science Institute, Daejeon 34133, Korea

Korea Basic Science Institute, Duejeon 54155, Korea

^dDepartment of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 52828, Korea. E-mail: cjw0910@gnu.ac.kr

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Paper

To enhance the energy storage capacitance of capacitors, redox-active species have been incorporated into electrode materials, displaying combined capacitive and redox electrochemical events in so-called pseudocapacitors.8 In this regard, redox-active CMPs have been prepared by the pre-designed building block approach and post-synthetic modification methods. For example, recently, redox-active dihydrophenazine^{5a} and ferrocene^{6b} moieties were incorporated into CMPs through the pre-designed building block approach, showing the capacitances of coin cell-type pseudocapacitors up to 231 and 324 F g^{-1} ($@0.5 A g^{-1}$), respectively. Our research group has reported the synthesis of CMPs bearing redox-active diketone species through carbonylative Sonogashira coupling and post-synthetic modification, showing the capacitances of coin cell-type pseudocapacitors up to 220 F g^{-1} (@0.5 A g^{-1}).^{5c,e}

A benzoquinone (BQ) is one of the representative organic redox-active systems showing a reversible two-electron redox process.⁹ The CMP bearing benzoquinones is expected to be a promising pseudocapacitive energy storage material. Usually, CMPs have been prepared by the cross-coupling of organic building blocks through the Pd(0/+2) catalytic cycle.¹⁰ However, we found that the existence of benzoquinone derivatives in the reaction mixture hinders the Pd-catalyzed cross-coupling reactions through the regeneration blocking of zerovalent Pd species. Thus, we figured out that the benzoquinone moieties in the CMP can be generated by post-synthetic modification rather than the pre-designed building block approach. It has been known that 1,4-dimethoxybenzene (DMB) derivatives can be converted to benzoquinone moieties through the PhI(CF₃CO₂)₂based oxidation.¹¹

In this work, we report the synthesis of redox-active CMPs bearing benzoquinones and the entrapped CB nanoparticles (CB@CMP-BQs) through post-synthetic modification and their pseudocapacitive performance as electrode materials for pseudocapacitors.

Experimental

General information

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) studies were conducted using a JEOL2100F. Scanning electron microscopy (SEM) was conducted using a JSM6700F. Powder X-ray diffraction (PXRD) studies were conducted using a Rigaku MAX-2200. Solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy was conducted at a CP/TOSS mode using a 500 MHz Bruker ADVANCE II NMR spectrometer. A 4 mm magic angle spinning probe was used with a spinning rate of 5 kHz. Infrared (IR) absorption spectroscopy was conducted using a Bruker VERTEX 70 FT-IR spectrometer. N2 adsorption-desorption isotherm curves were obtained at 77 K using a Micromeritics ASAP2020. The pore size distribution diagrams were obtained through analysis of the N2 sorption isotherm curves by the density functional theory (DFT) method. Combustion elemental analysis was conducted using a CE EA1110 analyzer. Thermogravimetric analysis (TGA) was conducted using a Seiko Exstar 7300. Sheet resistances were measured using a FPP-2000 sheet resistance meter.

Synthesis of CB@CMP-DMBs and CMP-DMB

For the synthesis of CB@CMP-DMB3, carbon black (Super P, Wellcos Co., 25 mg), (PPh₃)₂PdCl₂ (14 mg, 20 µmol, STREM Co.), CuI (2.0 mg, 13 µmol, Aldrich Co.), and triethylamine (20 mL, Samchun Co.) were added to a flame-dried 30 mL Schlenk flask. After sonication for 1 h, 1,3,5-triethynylbenzene (20 mg, 0.13 mmol, TCI Co.) and 1,4-diiodo-2,5-dimethoxybenzene (78 mg, 0.20 mmol, TCI Co.) in distilled DMF (10 mL) were added. After stirring at 90 °C for 24 h, the reaction mixture was cooled to room temperature. The solid was separated by centrifugation, washed with a mixture of CH2Cl2 (10 mL), acetone (20 mL), and methanol (20 mL) four times, and dried under vacuum. For the synthesis of CB@CMP-DMB1, CB@CMP-DMB2, and CB@CMP-DMB4, the same synthetic procedures of CB@CMP-DMB3 were applied except for using 100, 50, and 12.5 mg of CB, respectively. For the synthesis of CMP-DMB, the same synthetic procedures of CB@CMP-DMB3 were applied without using CB.

Synthesis of CB@CMP-BQs, CMP-BQ and CB-O

For the synthesis of CB@CMP-BQ3, CB@CMP-DMB3 (20 mg) and PhI(CF₃CO₂)₂ (0.37 g, 0.83 mmol, Alfa Aesar Co.), and methanol (5 mL) were added to a flame-dried 30 mL Schlenk flask. After sonication for 1 h, water (1 mL) was added. After the reaction mixture was stirred at room temperature for 24 h, the solid was separated by centrifugation, washed with methanol (50 mL) four times, and dried under vacuum. For the synthesis of CB@CMP-BQ1, CB@CMP-BQ2, CMP-BQ, and CB–O the same synthetic procedures of CB@CMP-BQ3 were applied except for using CB@CMP-DMB1, CB@CMP-DMB2, CMP-DMB, and CB, respectively.

Electrochemical studies

For the fabrication of working electrodes, CB@CMP-BQ3 (42 mg), CB (Super P, Wellcos Co., 12 mg), *N*-methylpyrrolidone (NMP, 0.20 g, Aldrich Co.), and a binder (46 mg, 13% PVDF in NMP) were mixed and ground in an agate mortar. The slurry was loaded onto Ti foil (0.02 mm thick, Wellcos Co.). After the Ti foil was coated with a thin layer (20 μ m thickness) using a doctor blade, it was dried at 80 °C for 1 h and at 110 °C for 18 h in a vacuum oven. Two working electrodes of circular shape were engineered using a 14 π puncher. The mass-loadings of working materials were measured to be 1.02–1.25 mg cm⁻².

For the assembly of symmetric CR2032 coin cell-type supercapacitors, the working electrode was loaded on one cap of a CR2032 coin cell. After a separator (No. 20 filter paper, Hyundai Micro Co.) was loaded on the working electrode, a gasket was added. After the separator was wetted by electrolyte solution (1 M H₂SO₄, 0.10 g), the other working electrode was loaded. After a space disk (Sus, 1T thick) and the other cap were loaded, the cell was crimped. After additional wetting time of 24 h, electrochemical measurements were conducted using an electrochemical workstation (WonATech ZIVE SPI). The specific capacitances (C_s) were obtained as follows. Cell capacitance (C_{cell}) was calculated using the following equation: $C_{cell} = I/[(\Delta V/$

 Δt) × m] in which I = applied current (A), $\Delta V/\Delta t$ = the slope of discharge curves after IR drop, m = the total mass of electrode materials (g), and $C_{\rm s}$ of a single electrode = $4C_{\rm cell}$.¹²

Results and discussion

Fig. 2 shows a synthetic route of CB@CMP-BQs. First, a CMP with *p*-dimethoxybenzene moieties (CMP-DMB) was prepared by the Sonogashira coupling of 1,3,5-triethynylbenzene with 1,4diiodo-2,5-dimethoxybenzene in the presence of CB nanoparticles. We gradually reduced the amount of CB nanoparticles from 100 mg to 50 and 25 mg with a fixed amount of 1,3,5triethynylbenzene and 1,4-diiodo-2,5-dimethoxybenzene. The resultant materials were denoted as CB@CMP-DMB1, CB@CMP-DMB2, and CB@CMP-DMB3, respectively. The oxidation of the CB@CMP-DMBs with PhI(CF₃CO₂)₂ (PIFA) generated benzoquinone moieties in the materials to form CB@CMP-BQ1, CB@CMP-BQ2, CB@CMP-BQ3, and respectively.

As a control material, CMP-BQ was prepared by the PIFAbased oxidation of CMP-DMB. Another control material, denoted as CB–O, was prepared by the treatment of CB nanoparticles with PIFA (Fig. 2).

TEM and SEM showed that CB nanoparticles have sizes of \sim 45 nm (Fig. 3a, S1 and S2 in the ESI†). The HR-TEM analysis showed that the CB nanoparticles have a layered graphite structure (Fig. 3d). In comparison, the TEM and SEM images of CB@CMP-DMB3 showed the coating of CB nanoparticles with



Fig. 2 Synthetic schemes of CB@CMP-DMBs, CB@CMP-BQs, and a control material CB-O.



Fig. 3 TEM images of (a and d) CB, (b and e) CB@CMP-DMB3, (c and f) CMP-DMB, (g and j) CB-O, (h and k) CB@CMP-BQ3, and (i and l) CMP-BQ. Refer to Fig. S2 in the ESI† for the TEM images of CB@CMP-DMB1, CB@CMP-DMB2, CB@CMP-BQ1, and CB@CMP-BQ2.

CMP-DMB (Fig. 3b and S1 and S2 in the ESI⁺). The sizes of CB@CMP-DMB3 increased to ~125 nm, indicating that the thickness of the CMP-DMB3 coating corresponds to \sim 40 nm. The HR-TEM analysis indicated the amorphous feature of CMP-DMB layers in CB@CMP-DMB3, matching with the conventional properties of CMP materials in the literature (Fig. 3e).¹⁻⁵ As the relative amounts of CB in CB@CMP-DMBs increased, the coating thicknesses of CMP-DMB layers in CB@CMP-DMB2 and CB@CMP-DMB1 were reduced to \sim 23 and \sim 10 nm, respectively (Fig. S2 in the ESI[†]). When the amounts of CB were reduced from 25 mg to 12.5 mg with the fixed amounts of 1,3,5-triethynylbenzene (0.13 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (0.20 mmol), the formation of CMP-DMB without entrapped CB nanoparticles was observed (Fig. S3 in the ESI[†]). The control CMP-DMB that was prepared without using CB nanoparticles showed quite big particles with a size range of 150-500 nm (Fig. 3c and f).

After the post-oxidation of CB, CB@CMP-DMBs, and CMP-DMB, TEM analysis indicated that the resultant CB–O, CB@CMP-BQs, and CMP-BQ maintained the original morphologies (Fig. 3g–l, S1 and S2 in the ESI†).

The surface areas and porosity of the CMP and CB materials were investigated through the analysis of N₂ sorption isotherm curves based on the Brunauer–Emmett–Teller (BET) theory and the DFT method (Fig. 4a–c and Table S1 in the ESI†). First, while the CMP-DMB showed a high surface area (SA) of 609 m² g⁻¹



Fig. 4 (a–c) N₂ adsorption–desorption isotherm curves (obtained at 77 K) and pore size distribution diagrams (based on the DFT method), (d) IR spectra, and (e) solid state ¹³C NMR spectra of CMP-DMB, CMP-BQ, CB@CMP-DMB3, CB@CMP-BQ3, CB, and CB–O.

and micropore volume ($V_{\rm mic}$) of 0.16 cm³ g⁻¹, the SA and $V_{\rm mic}$ of CMP-BQ were reduced to 313 m² g⁻¹ and 0.091 cm³ g⁻¹, respectively (Fig. 4a), matching with the conventional observations in the PSM of CMPs in the literature.13 Whilst the SA and $V_{\rm mic}$ of CB@CMP-DMB3 were measured to 524 m² g⁻¹ and 0.15 cm³ g⁻¹, respectively, those of CB@CMP-BQ3 were reduced to 301 $m^2\ g^{-1}$ and 0.073 $cm^3\ g^{-1}\text{,}$ respectively (Fig. 4b). As the relative amounts of CB increased, the SAs of CB@CMP-DMB2 and CB@CMP-DMB1 were reduced to 452 and 363 m² g⁻¹, respectively, with $V_{\rm mic}$ values of 0.13 and 0.072 cm³ g⁻¹ (Fig. S4 in the ESI[†]). In addition, the SAs of CB@CMP-BQ2 and CB@CMP-BQ1 were reduced to 229 and 173 m² g⁻¹, respectively, with $V_{\rm mic}$ values of 0.020 and 0.018 cm³ g⁻¹ (Fig. S4 in the ESI[†]). These trends indicate that the CMP-DMB and CMP-BQ have much higher surface areas and microporosity than the CB and CB-O. As expected, the CB and CB-O showed low surface areas of 68 and 78 m² g⁻¹, respectively, and nonmicroporosity (Fig. 4c).

The chemical structures of CMP and CB materials were characterized by infrared (IR) and solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy (Fig. 4d and e, S5 and S6 in the ESI[†]). In the IR spectrum of CMP-DMB, the unique C-O vibrations of methoxy groups were observed at 1035 and 1216 cm⁻¹, in addition to the aromatic C=C vibrations at 1493 and 1586 cm^{-1} (Fig. 4d). In comparison, the CMP-BQ showed a new vibration peak at $\sim 1710 \text{ cm}^{-1}$, indicating the formation of benzoquinone moieties. In the IR spectrum of CB@CMP-BQ3, the C-O vibrations significantly disappeared with the appearance of a new C=C peak at 1538 cm^{-1} , indicating that the PSM of CB@CMP-DMB3 was more efficient than that of CMP-DMB, due to the reduced thickness of the CMP-DMB materials. The IR spectra of CB and CB-O did not show specific vibration peaks, indicating that the observed IR peaks of CB@CMP-DMBs and CB@CMP-BQs originated from CMP materials (Fig. 4d).

In the solid state ¹³C NMR spectrum of CMP-DMB, aromatic ¹³C peaks were observed at 113, 124, 132, and 154 ppm (Fig. 4e). Particularly, the ¹³C peak at 154 ppm corresponds to the aromatic carbons adjacent to methoxy groups. The ¹³C peaks of methoxy groups and internal alkynes appeared at 55 and 87–93 ppm, respectively, indicating that the CMP-DMB was formed through the coupling of two building blocks. The ¹³C spectrum of CMP-BQ showed significant changes of the aromatic ¹³C peaks. In addition, the ¹³C peaks of methoxy groups (55 ppm) and the aromatic carbons adjacent to methoxy groups (154 ppm) significantly reduced. Instead, a new ¹³C peak of carbonyl groups appeared at 185 ppm, indicating the successful generation of benzoquinone moieties in CMP-BQ.

Whilst the observed changes in the ¹³C NMR spectra of CB@CMP-DMB3 and CB@CMP-BQ3 were the same as those of CMP-DMB and CMP-BQ, the ¹³C peak of methoxy groups (55 ppm) completely disappeared in the ¹³C NMR spectrum of CB@CMP-BQ3, indicating the more efficient PSM process of CB@CMP-DMBs than CMP-DMB. CB@CMP-DMB1 and CB@CMP-DMB2 showed the same ¹³C NMR spectra as CB@CMP-DMB3 (Fig. S6† in the ESI). In addition, the ¹³C NMR spectra of CB@CMP-BQ1 and CB@CMP-BQ2 were the same as those of CB@CMP-BQ3. It is noteworthy that the CB and CB-O did not show specific ¹³C peaks.

According to the powder X-ray diffraction (PXRD) studies (Fig. S7 in the ESI[†]), whilst the CB and CB–O showed broad peaks at 2θ of 25 and 44° , the CMP-DMB and CMP-BQ were completely amorphous, matching with the conventional observations of CMP materials in the literature.^{1–5} As the amount of CMP-DMB and CMP-BQ increased in the CB@CMP-DMBs and CB@CMP-BQs, the PXRD peaks of CB nanoparticles became broader, due to the reduced amount of CB in the materials. Thermogravimetric analysis (TGA) showed that the CMP-BQ and CB@CMP-BQ3 are thermally stable up to 245 and 250 °C, respectively (Fig. S8 in the ESI[†]).

Considering the entrapped conductive CB nanoparticles, the high surface areas of CB@CMP-BQs, and the existence of the redox-active benzoquinone moieties, the electrochemical performance of CB@CMP-BQs as electrode materials for coin cell-type pseudocapacitors were investigated. Fig. 5 and S9–S13 in the ESI† summarize the results.

According to cyclic voltammetry, while CB–O did not show a specific electrochemical response, CMP-BQ displayed relatively weak pseudocapacitive behavior (Fig. 5a). In comparison, the pseudocapacitive behavior of CB@CMP-BQ3 was dramatically enhanced with reversible redox peaks. In addition, the pseudocapacitive responses increased from CB@CMP-BQ1 to CB@CMP-BQ2 and CB@CMP-BQ3 (Fig. S9–S11 in the ESI†). Charge–discharge (CD) profiles also showed the same trend (Fig. 5b). While CB–O showed a poor electrochemical feature, CMP-BQ showed pseudocapacitive behavior.^{5c,d,i,6e} In comparison, the CD profile of CB@CMP-BQ3 showed the enhanced pseudocapacitive behavior (Fig. 5b). The enhanced electrochemical performance of CB@CMP-BQ3 is attributed to the redox contribution of benzoquinone moieties and the enhanced conductivities by the entrapped CB particles.



Fig. 5 (a) Cyclic voltammograms and (b) charge–discharge profiles of CB–O, CMP-BQ, and CB@CMP-BQ3. (c) Scan rate-dependent cyclic voltammograms of CB@CMP-BQ3. (d) Cyclic voltammograms of CB@CMP-DMB3 and CB@CMP-BQ3. (e) Rate performance and (f) Nyquist plots of CB@CMP-BQ1, CB@CMP-BQ2, CB@CMP-BQ3, CMP-BQ, and CB–O. For the electrochemical behaviors of CB@CMP-BQ1 and CB@CMP-BQ2, refer to Fig. S9–S13 in the ESI†.

As the scan rate increased gradually from 10 mV s⁻¹ to 500 mV s⁻¹, the pseudocapacitive response of CB@CMP-BQ3 gradually increased (Fig. 5c). To investigate the redox contribution of the benzoquinone moieties of CB@CMP-BQ3, the electrochemical behavior of CB@CMP-DMB3 with *p*-dimethoxybenzene moieties was studied. As shown in Fig. 5d, while CB@CMP-DMB3 revealed a moderate capacitive feature, CB@CMP-BQ3 displayed clear redox behavior with enhanced electrochemical performance, indicating the redox contribution of benzoquinone moieties and enhanced conductivity.

The rate performance of CB@CMP-BQs was investigated (Fig. 5e). CB@CMP-BQ3 showed capacitances of 424, 373, 350, and 324 F g^{-1} at current densities of 0.5, 1, 2, and 4 A g^{-1} , respectively. Even at high current densities of 10 and 20 A g^{-1} , CB@CMP-BQ3 maintained significant capacitances of 280 and 250 F g^{-1} , respectively. The capacitances of CB@CMP-BQ3 are superior or comparable to those of recent CMP-based electrode materials in two-electrode supercapacitors in the literature (Table S2 in the ESI[†]).^{5,6} For example, Tang et al. reported CMPgraphene composites bearing redox-active ferrocenes, which showed a capacitance of 231 F g^{-1} (@0.5 A g^{-1}) in two-electrode devices.6b Liao et al. synthesized CMPs bearing redox-active anthraquinones, showing a capacitance of 168 F g^{-1} ((a) 1 A g⁻¹) in two-electrode devices.^{5f} Very recently, Gu *et al.* showed redox-active dihydrophenazine-containing porous organic polymers, showing capacitances up to 324 F g⁻¹ $(\textcircled{0}0.5 \text{ A g}^{-1})$.^{5a} In addition, our research group reported CMPs bearing redox-active 1,4-di(3-phenylpropynoyl)benzenes, displaying a capacitance of 220 F g^{-1} (@ 0.5 A g^{-1}) in coin cell-type supercapacitors.^{5e} The excellent electrochemical performance of CB@CMP-BQ3 with the capacitances of 423 ($@0.5 \text{ A g}^{-1}$) and 373 F g^{-1} (@1 A g^{-1}) indicates the effective CB trapping strategy to realize high performance CMP-based electrode materials.

As the amount of CMP-BQ decreased, the capacitances of CB@CMP-BQ2 and CB@CMP-BQ1 decreased to 236 and 157 F g^{-1} at a current density of 0.5 A g^{-1} (Fig. 5e). The control CB–O showed capacitances of only 0.79, 0.21, and 0.078 F g^{-1} at current densities of 0.5, 10, and 20 A g^{-1} , respectively, confirming that the main electrochemical contribution of CB@CMP-BQ originated from CMP-BQ. The CMP-BQ without CB showed poor capacitances of 36, 30, 27, 15, and 7 F g^{-1} at current densities of 0.5, 1, 2, 10, and 20 A g^{-1} , respectively, indicating the role of the entrapped CB particles.

The enhanced conductivities of CB@CMP-BQs were investigated by electrochemical impedance spectroscopy (EIS) (Fig. 5f and S12 in the ESI[†]).¹⁴ Whilst CB–O was fully conductive, CMP-BQ showed poor conductivity with a charge transfer resistance ($R_{\rm ct}$) of 12 Ω . As the amount of CB in CB@CMP-BQs increased, $R_{\rm ct}$ decreased from 3.2 Ω (CB@CMP-BQ3) to 1.3 (CB@CMP-BQ2) and 0.91 Ω (CB@CMP-BQ1), indicating the conductivity-enhancing role of CB particles. Whilst the conductivity of CB–O could not be measured, due to a too low value, those of CB–O, CB@CMP-BQ1, CB@CMP-BQ2, and CB@CMP-BQ3 were 7.8 × 10², 5.4 × 10², 3.0 × 10², and 1.9 × 10² S m⁻¹ respectively (Fig. S13 in the ESI[†]), matching with the trend of EIS studies.

The charge/discharge cycling performance of CB@CMP-BQ3 was studied (Fig. 6a). While CB@CMP-BQ3 showed



Fig. 6 (a) Charge/discharge cycling performance of CB@CMP-BQ3 in coin cell-type pseudocapacitors. (b) Nyquist plots and (c) TEM images of CB@CMP-BQ3 before and after 10 000 charge/discharge cycles.

a capacitance of 373 F g⁻¹ (@1 A g⁻¹) at the first cycle, it maintained the 95.7% of the original capacitance at the 10 000th cycle. Even at a high current density of 10 A g⁻¹, CB@CMP-BQ3 retained 95.7% of the original capacitance (280 F g⁻¹) at the 10 000th cycle, indicating excellent cycling stability. After 10 000 cycles, the R_{ct} values increased slightly from 3.2 Ω to 3.9 Ω (Fig. 6b). CB@CMP-BQ3, recovered after 10 000 cycles, was investigated by TEM and IR studies. As shown in Fig. 6c and S14 in the ESI,† the original core–shell and chemical structure of CB@CMP-BQ3 were completely retained.

Conclusions

This work suggests a new chemical strategy for the realization of the true electrochemical performance of CMP-based electrode materials. During the synthesis of CMP materials, conductive CB particles could be entrapped to form CB@CMP. In addition, redox-active benzoquinone moieties could be generated in CB@CMP-BQ through post-synthetic modification. Due to the enhanced conductivities and the existence of redox-active benzoquinone moieties, CB@CMP-BQ3 showed excellent electrochemical performance as an electrode material for pseudocapacitors. We believe that the chemical engineering strategy of this work can be easily applied to the development of various CMP-based energy storage materials.

Author contributions

S. U. Son: conceptualization, supervision, writing original draft, and review & editing. J. Choi: supervision, investigation, and

formal synthesis. C. Kang, Y. -J. Ko, and S. M. Lee: investigation and formal analysis. H. J. Kim: formal analysis and supervision.

Conflicts of interest

There are no conflicts to declare.

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