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Electrochemical performance of CeO₂ nanoparticle-decorated graphene oxide as an electrode material for supercapacitor

Dongyang Deng¹ · Nan Chen² · Xuechun Xiao¹ · Shangfeng Du³ · Yude Wang²

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Abstract Cerium oxide nanoparticles and cerium oxide nanoparticle-decorated graphene oxide (GO) are synthesized via a facile chemical coprecipitation method in the presence of hexadecyltrimethylammonium bromide (CTAB). Nanostructure studies and electrochemical performances of the as-prepared samples were systematically investigated. The crystalline structure and morphology of the nanocomposites were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), transition electron microscopy (TEM), Raman spectrum, and X-ray photoelectron spectroscopy (XPS). Electrochemical properties of the CeO₂ electrode, the GO electrode, and the nanocomposites electrodes were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements. The CeO₂ nanoparticle-decorated GO (at the mole ratio of CeO₂/GO = 1:4) electrode exhibited excellent supercapacitive behavior with a high specific capacitance of 382.94 F/g at the current density of 3.0 A/g. These superior electrochemical features demonstrate that the CeO₂ nanoparticle-decorated GO is a promising material for next-generation supercapacitor systems.

Keywords Coprecipitation method · CeO₂ nanoparticles · Graphene oxide · Supercapacitors · Electrochemical properties

Introduction 34

Environmental concern over the ever-growing energy demands and curtailed fossil fuel resources has provoked the quest for sustainable energy storage devices with enhanced power and energy densities [1, 2]. Supercapacitors, which are one of the most promising candidates for flexible energy storage devices, have attracted considerable attention due to high power density, long cycle life, and excellent charge–discharge rates compared to common batteries [3–5]. The performances of supercapacitors depend mainly on the properties of their active electrode materials, and they can be usually divided into three types including carbon materials, conducting polymers and metal oxides [6]. Among them, nanostructured metal oxides have attracted much attention due to their favorable redox potential and conductivity to store electrical charge. Therefore, some typical metal oxides, such as RuO₂ [7], MnO₂ [8–10], and Co₃O₄ [11], have been widely investigated as high-capacity electrode materials for supercapacitors. However, several problems such as the high cost, low electrical conductivity, and poor stability limit the practical applications of metal oxides as supercapacitor electrodes. Thus, it is imperative to develop cost-effective, environmentally friendly, and high-performance alternative candidates for supercapacitors.

As one of the most reactive rare earth materials, CeO₂ has attracted a great deal of attention due to its extensive applications [12–15]. CeO₂ in nanometer size can be considered as one of the promising redox supercapacitor materials since CeO₂ is the most abundant, environmental friendly, and least expensive rare earth metal oxide with excellent redox

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64 characteristics. Furthermore, its nanostructure with superior
65 surface area has prominent effect on pseudocapacitance.
66 Nevertheless, because of the intrinsic poor electrical conduc-
67 tivity of metal oxides, only the surface part of electroactive
68 materials can effectively contribute to the total capacitance
69 and the underneath parts could hardly participate in the
70 electrochemical charge storage process, which severely affects
71 the performance of supercapacitors. One approach in solving
72 this problem is to combine carbon materials with high electri-
73 cal conductivity and metal oxides as electrodes for
74 supercapacitors. Recently, Dezfuli and coworkers utilized a
75 sonochemical method to synthesize CeO₂-reduced graphene
76 oxide (RGO), which showed a specific capacitance of 185 F/g
77 at the current density of 2 A/g [16].

78 Graphene oxide (GO), which possesses the characteristics
79 of graphene, shows a great promise for the fabrication of
80 nanoscale structures, and more importantly, contains a range
81 of reactive oxygen functional groups (e.g., carboxylic acids,
82 hydroxy, and carbonyl groups). However, the individual GO
83 sheet exhibits a tendency to aggregate and re-stack owing to
84 the interplanar π - π interactions and van der Waals' forces
85 between the graphene layers [3]. This agglomeration reduces
86 the surface area of the GO films and the diffusion of electro-
87 lyte ions, which results in a decrease in the electrochemical
88 performance. To avoid the re-stacking, composites made of
89 GO and metal oxides seem to be a good solution. This is
90 beneficial to both materials because of their synergistic effect.
91 Metal oxides prevent GO from agglomeration and re-stacking
92 and also increase the available surface area. Besides, GO helps
93 the formation of metal oxide nanostructures with uniformly
94 dispersed controlled morphologies, suppressing the agglom-
95 eration of metal oxides. The oxygen-containing groups within
96 graphene oxide will ensure good electrical contact, interfacial
97 interactions, and bonding between graphene oxide and metal
98 oxide.

99 In the present work, we use a simple facile chemical
100 coprecipitation method to synthesize CeO₂, GO, and CeO₂
101 nanoparticle-decorated GO materials for the application of
102 supercapacitors. The structure, surface morphology, and com-
103 position of the as-prepared samples have been fully investi-
104 gated. The capacitive behaviors of the electrodes were also
105 investigated and compared.

106 Experimental

107 Materials

108 The graphene oxide (GO) was prepared according to modified
109 Hummers' method. And the mass concentration of the as-
110 prepared GO is 10 mg/mL. All the other reagents used in the
111 experiments were purchased from commercial sources of an-
112 alytical grade and used without further purification.

Preparation of CeO₂ nanoparticle-decorated GO

113 CeO₂ nanoparticle-decorated GO at different mole ratio was
114 prepared by a facile chemical coprecipitation method. In brief,
115 182 mg hexadecyltrimethylammonium bromide (CTAB) was
116 dissolved into 10 mL distilled water with stirring at the tem-
117 perature of 40 °C until a homogenous solution was obtained.
118 Four hundred thirty-four milligram sample of cerium nitrate
119 hexahydrate was dissolved into 10 mL distilled water with
120 stirring to get transparent solution. Then 10 mL CTAB
121 (0.05 M) was added into the solution dropwise under stirring
122 for 30 min. Next, GO with a certain mole ratio ($n_{\text{CeO}_2}/n_{\text{GO}}$
123 =1:1, 1:2, 1:4, 1:5, respectively) was added into the resulting
124 solution with maintaining stirring for 10 min, and the GO was
125 dispersed in the getted solution by ultrasonic vibration for 1 h.
126 An amount of 10 mL of 25 wt% liquor ammonia was added
127 into the resulting suspension dropwise under stirring. After
128 vigorous stirring for 2 h, the suspension was aged for
129 30 min at room temperature. The resulting products were cen-
130 trifuged, and the precipitates were thoroughly washed with
131 distilled deionized water and ethanol and dried at 60 °C over-
132 night. For comparison, CeO₂ and the GO were also synthe-
133 sized under the same condition as CeO₂ nanoparticle-
134 decorated GO. The resultant products were collected and fur-
135 ther characterized. 136

Structural and morphology characterization

137 The crystallographic structures of the materials were deter-
138 mined by Rigaku D/max-3B diffractometer with a copper tar-
139 get and K $_{\alpha 1}$ radiation ($\lambda = 1.54056 \text{ \AA}$) from 10° to 90° in step
140 of 0.01°. Scanning electron microscopy (SEM) images of the
141 morphology of samples were obtained from FEI
142 QUANTA200 with microscope operating at 30 kV. Detailed
143 studies of the microstructure were also carried out by trans-
144 mission electron microscopy (TEM) (JEOL JEM-2100) at an
145 acceleration voltage of 200 kV. X-ray photoelectron spectro-
146 scopy (XPS) was carried out at room temperature in an
147 ESCALAB 250 system. 148

Electrochemical measurements

149 Nickel foam with the size of 1 cm × 2 cm was first pretreated
150 successively with diluted hydrochloric acid and absolute eth-
151 anol to ensure a clean surface. The electrodes were fabricated
152 as follows: the as-prepared samples, carbon black, and
153 polyvinylidene fluoride (PVDF) were mixed in a mass ratio
154 of 85:10:5. A small amount of ethanol was added to make a
155 homogeneous mixture. Then the resulting mixture was coated
156 onto the nickel foam substrate, which was followed by drying
157 at 60 °C for 24 h in a vacuum oven. The resulting paste was
158 pressed at 10 MPa. Each electrode contained about 3 mg of 159

160 electroactive material and had a geometric surface area of
 161 about 1 cm². A typical three-electrode experimental cell
 162 equipped with a working electrode, a platinum foil counter
 Q1 163 electrode, and a saturated calomel electrode (SCE) was used
 164 for measuring the electrochemical properties of the working
 165 electrode. All electrochemical measurements were carried out
 166 on a CHI 600E electrochemical workstation (ChenHua
 167 Instruments, Shanghai) in 6 M KOH aqueous solution as elec-
 168 trolyte at 25 °C. The electrochemical properties of the prod-
 169 ucts were investigated with cyclic voltammetry (CV), galva-
 170 nostatic charge/discharge (GCD) tests, and electrochemical
 171 impedance spectroscopy (EIS) which were obtained using an
 172 AC voltage of 5 mV in a frequency range from 0.01 Hz to
 173 100 kHz. The specific capacitances (C, (F/g)) as shown in
 174 Table 1 were calculated according to the following equations:

$$C = \frac{I \times t}{\Delta V \times m} \quad (1)$$

175 where *I* (mA) is the constant discharge current, *t* (s) is the
 176 discharging time, *m* (mg) is the total mass of active materials
 177 in both electrodes, and ΔV (V) is the operating voltage win-
 178 drow obtained from the discharge curve excluding the voltage
 179 drop.
 180

181 Results and discussion

182 In order to confirm the structure, phase, and purity of the
 183 materials, X-ray diffraction patterns (XRD) were recorded
 184 for the CeO₂ and CeO₂ nanoparticle-decorated GO (1:4). As
 185 shown in Fig. 1, the curve of CeO₂ and CeO₂ nanoparticle-
 186 decorated GO (1:4) are shown in blue and red, respectively.
 187 The short vertical bars in green represent the positions of the
 188 Bragg reflections. The diffraction peaks of CeO₂ and CeO₂
 189 nanoparticle-decorated GO (1:4) coincide well with the stan-
 190 dard pattern of CeO₂ (JCPDS card no. 81-0792). There is no
 191 diffraction peak originating from the GO species in the XRD
 192 spectrum of CeO₂ nanoparticle-decorated GO (1:4), probably
 193 due to the bad crystallinity of GO in the CeO₂ nanoparticle-
 194 decorated GO (1:4) sample. The characteristics of the XRD
 195 pattern demonstrate that GO does not change the crystal struc-
 196 ture of CeO₂. The width of the diffraction peaks indicates the

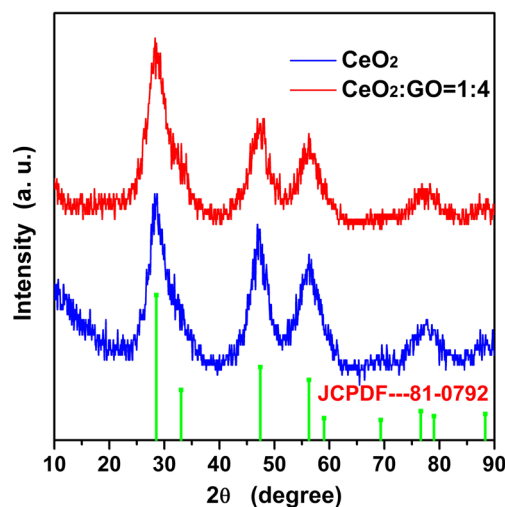


Fig. 1 XRD pattern of the as-prepared CeO₂ and CeO₂/GO (1:4)

small average grain size. The average crystal size of CeO₂ 197
 nanoparticle-decorated GO (1:4) sample is calculated to be 198
 2.31 nm. 199

Raman spectroscopy is a standard technique for determin- 200
 ing the ordered and disordered nature of carbon-based materi- 201
 als. Figure 2 shows the Raman spectra of CeO₂ and CeO₂ 202
 nanoparticle-decorated GO (1:4). One peak at 459.03 cm⁻¹ 203
 could be seen in the Raman spectra of CeO₂ and CeO₂ 204
 nanoparticle-decorated GO (1:4), which is attributed to the 205
 symmetrical stretching mode of the Ce–O₈ vibrational unit 206
 [16]. Peaks were observed at 1345.85 and 1593.16 cm⁻¹ in 207
 the CeO₂ nanoparticle-decorated GO (1:4) spectrum, which 208
 confirmed the D and G bands, respectively. The D band rep- 209
 resents sp³ carbon in the graphitic lattice, which is associated 210
 with the structural defects such as bond length disorder, bond- 211
 angle disorder, and hybridization which can break the symme- 212
 try and selection rules, while the G band is related to the in- 213
 plane vibration of C sp² atoms [17–19]. More intensity of the 214
 D and G bands can be attributed to the high loading of GO in 215
 CeO₂ nanoparticle-decorated GO (1:4). Therefore, the result 216

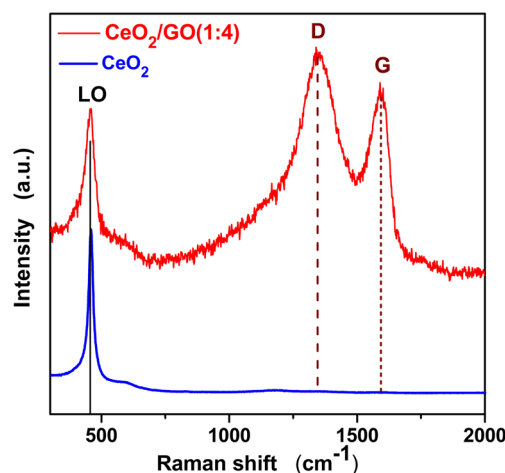


Fig. 2 Raman spectra of the as-prepared CeO₂/GO (1:4)

t1.1 **Table 1** Comparison of
 t1.2 capacitance values for
 CeO₂/GO

Materials	Capacitance (F/g)
CeO ₂	81.18
GO	35.12
CeO ₂ /GO (1:1)	45.29
CeO ₂ /GO (1:2)	82.35
CeO ₂ /GO (1:4)	382.94
CeO ₂ /GO (1:5)	18.37

t1.3 nanocomposites at
 t1.4 different molar ratios at
 t1.5 3 A/g
 t1.6
 t1.7
 t1.8

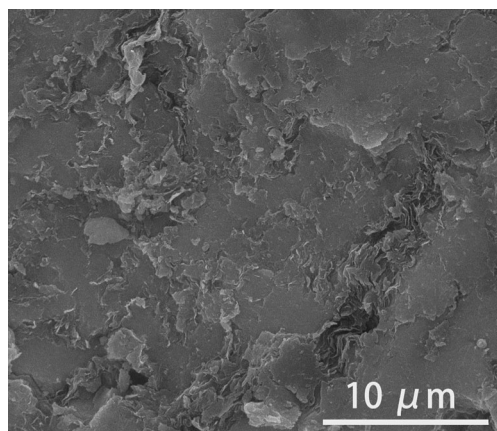


Fig. 3 SEM image of the as-prepared CeO₂/GO (1:4)

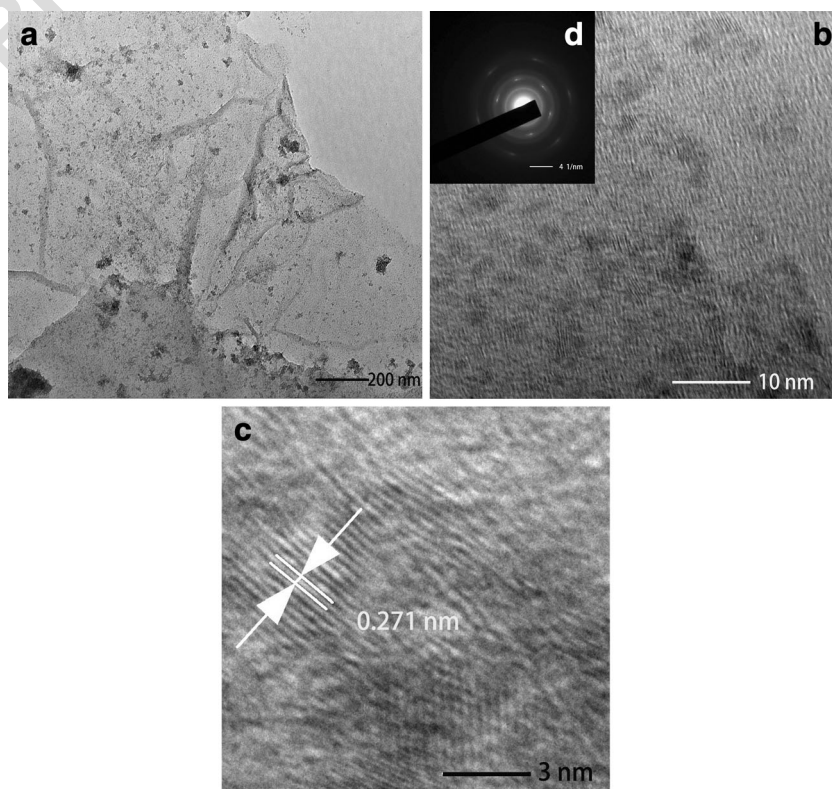
217 of the Raman measurement confirms that the CeO₂
 218 nanoparticle-decorated GO (1:4) has been formed during the
 219 facile chemical coprecipitation treatment.

220 The morphology of the CeO₂ nanoparticle-decorated GO
 221 (1:4) sample was characterized using SEM. As shown in
 222 Fig. 3, crumpled sheets observed were GO, whereas none
 223 CeO₂ nanoparticles were observed in CeO₂ nanoparticle-
 224 decorated GO (1:4) sample. It is probably due to the crystal
 225 size of CeO₂ that is so small. In order to find CeO₂ nanopar-
 226 ticles, the sample was further investigated by TEM and HR-
 227 TEM. From Fig. 4a, one can find that the distribution of CeO₂
 228 nanoparticles across the surface of the GO sheets is clearly
 229 visible, suggesting that the chemical coprecipitation method

230 is a simple and efficient way of synthesizing CeO₂
 231 nanoparticle-decorated GO. In Fig. 4b, CeO₂ nanoparticles
 232 were uniformly spread throughout the GO sheets. The size
 233 of CeO₂ is about 2–3 nm, which is in satisfactory agreement
 234 with the results from the XRD studies. Furthermore, in Fig. 4d
 235 (inset of Fig. 4b), the SAED pattern of the nanocomposite also
 236 displayed bright diffraction rings, conforming the growth of
 237 polycrystalline CeO₂ on the graphene sheets [19]. As shown
 238 in Fig. 4c, the HR-TEM image of the CeO₂ nanoparticle-
 239 decorated GO (1:4) sample shows the orientation of grains
 240 in different directions, and the lattice fringes are clearly visible
 241 with space of 0.271 nm corresponding to the (200) planes of
 242 CeO₂.

243 XPS was employed to characterize the surface chemical
 244 compositions and the valence states of the as-synthesized
 245 CeO₂ nanoparticle-decorated GO (1:4), as shown in Fig. 5.
 246 As is shown in Fig. 5a, one finds that the C1s consists of three
 247 components: C–C (284.67 eV), C–O (286.25 eV), and C=O
 248 (287.98 eV). This spectrum was fully consistent with those
 249 reported previously [20]. The high-resolution XPS spectrum
 250 of O1s is shown in Fig. 5b. Especially, the state of O1s indi-
 251 cates that there are two sorts of oxygen on the surface. One is
 252 the lattice oxygen (O_{lattice}) and the other is adsorbed oxygen
 253 (O_x⁻). The peaks of adsorbed oxygen and lattice oxygen are
 254 shown at binding energies of 531.24 and 529.08 eV, respec-
 255 tively [21]. O_{lattice} is attributed to the oxygen ions in the crystal
 256 lattice which are thought to be pretty stable and have no con-
 257 tribution to the reactions on the electrode. Meanwhile, O_x⁻ is

Fig. 4 TEM images of the as-prepared CeO₂/GO (1:4)



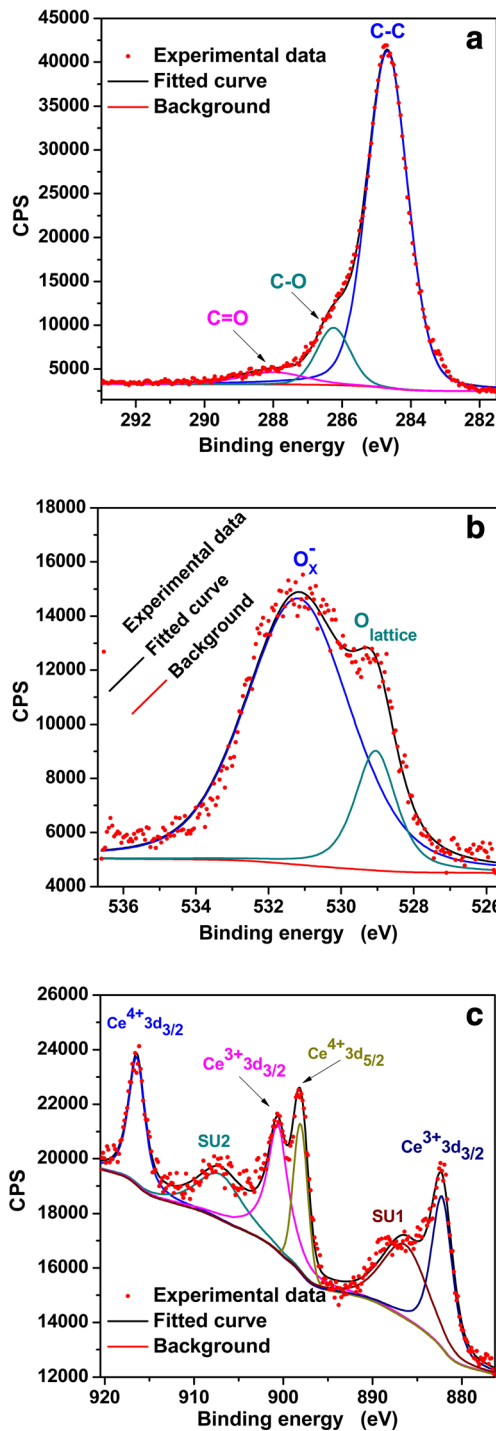


Fig. 5 The high-resolution XPS survey spectra of C 1s (a), O 1s (b), and Ce (c) of the as-prepared CeO₂/GO (1:4)

258 attributed to the absorbed oxygen ions, which is active in
 259 reactions on the electrode. Through calculating the areas of
 260 O_x^- and $O_{lattice}$ emission lines, the concentrations of O_x^- and
 261 $O_{lattice}$ to OIs are estimated to be 83.44 and 16.56 %, respec-
 262 tively. As one can see, the percentage of O_x^- is so large, which
 263 may be a key issue in reactions on the electrode. Therefore, the

264 as-prepared CeO₂ nanoparticle-decorated GO (1:4) exhibited
 265 amazing electrochemical properties. The Ce3d core level peak
 266 can be confirmed by XPS analysis, as shown in Fig.5c. Due to
 267 its highly non-stoichiometric nature, Ce atoms with both 3+
 268 and 4+ valences are presented in CeO₂ nanoparticle-decorated
 269 GO (1:4). The main peaks of Ce⁴⁺ 3d_{3/2} and Ce⁴⁺ 3d_{5/2} are
 270 shown at binding energies of 917.49 and 898.18 eV, respec-
 271 tively. Those of Ce³⁺ 3d_{3/2} and Ce³⁺ 3d_{5/2} are located at
 272 900.62 and 882.40 eV, respectively. Two additional satellite
 273 lines SU1 and SU2, which means “shake-up,” are shown at
 274 886.63 and 916.49 eV, respectively. To rationalize XPS find-
 275 ings, one can state that the presence of Ce³⁺ is a result of
 276 oxygen vacancies and this effect is enhanced in nanoparticles
 277 because a larger fraction of the atoms is on the surface as the
 278 particle size is reduced and the surface atoms have reduced
 279 coordination [22]. The oxygen vacancies that lead to the trans-
 280 formation between Ce⁴⁺ and Ce³⁺ may be a key issue in reac-
 281 tions on the electrode. Through calculating the ratio of peak
 282 areas, one can find that the mole ratio of Ce³⁺/Ce⁴⁺ is 1.59 for
 283 CeO₂ nanoparticle-decorated GO (1:4). It is obvious that
 284 CeO₂ nanoparticle-decorated GO (1:4) sample has a strong
 285 oxygen storage and release capacity via the redox shift be-
 286 tween Ce⁴⁺ and Ce³⁺ under oxidizing and reducing condi-
 287 tions, respectively.

288 To test the supercapacitive performance of pure CeO₂, GO,
 289 and CeO₂ nanoparticle-decorated GO (1:4) electrodes, CV
 290 was firstly recorded in a three-electrode system using saturat-
 291 ed calomel electrode (SCE) as the reference and platinum foil
 292 as the counter electrode. The capacitive behavior of pure
 293 CeO₂, GO, and CeO₂ nanoparticle-decorated GO (1:4) elec-
 294 trodes was systematically examined in this work and typical
 295 CV curves of pure CeO₂, GO, and CeO₂ nanoparticle-decorat-
 296 ed GO (1:4) measured at 10 mV/s in 6 M KOH which
 297 are shown in Fig. 6a. The CV curves show that CeO₂
 298 nanoparticle-decorated GO (1:4) nanocomposite electrode
 299 has the largest enclosed area, compared with CeO₂ and GO
 300 electrodes, exhibiting the highest specific capacitance. We just
 301 qualitatively describe the electrochemical performance of the
 302 CeO₂ nanoparticle-decorated GO (1:4) electrode, CeO₂ nano-
 303 particle electrode, and GO electrode by the CV curve. And
 304 then we use GCD tests to quantitatively describe the spec-
 305 ific capacitance of electrodes. In the CeO₂ nanoparticle-decorat-
 306 ed GO (1:4) sample, the synergistic effect is found by
 307 combining CeO₂ and GO, which reasonably resulted from the
 308 uniform dispersion of CeO₂ nanocrystals onto the surface of
 309 GO sheets and better electronic conductivity of the GO.
 310 Hence, a high electrochemical performance can be achieved.
 311 Figure 6b shows the CV curves of CeO₂ nanoparticle-decorat-
 312 ed GO (1:4) electrode at different scan rates of 5, 10,
 313 20, 50, and 100 mV/s in a potential range of 0 to 0.51 V. One
 314 pair of redox peaks is observed in every CV curve, which
 315 reveals that the capacitance characteristic of CeO₂
 316 nanoparticle-decorated GO (1:4) sample is typical

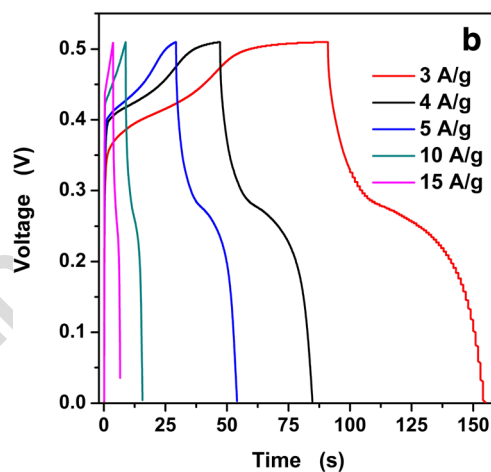
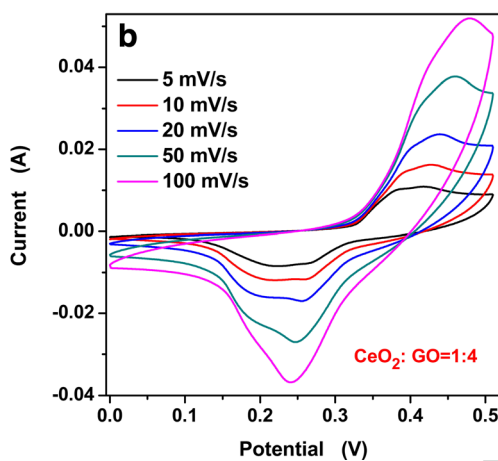
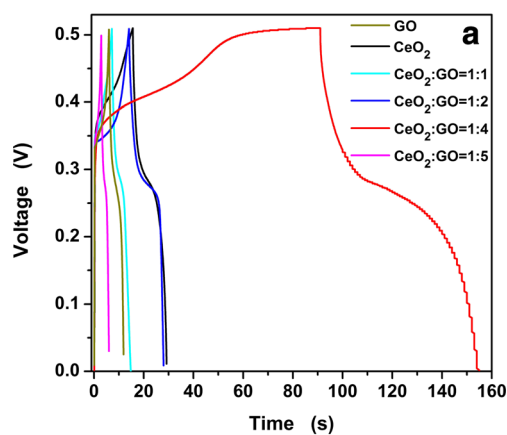
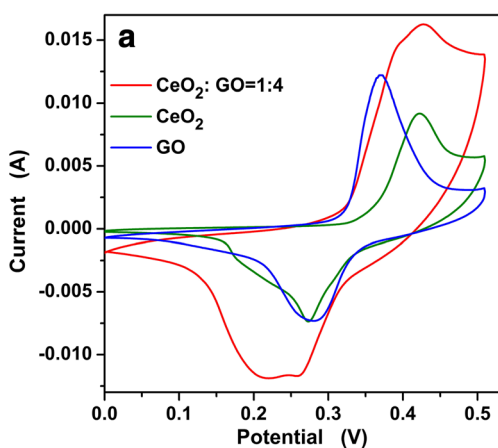


Fig. 6 a CV curves of pure CeO₂, GO, and CeO₂/GO (1:4) nanoparticle electrodes at 10 mV/s; b CV curves of CeO₂/GO (1:4) nanoparticle electrode at different scan rates

Fig. 7 a Charge-discharge curves of pure CeO₂, GO, and CeO₂/GO nanoparticle electrodes at 3 A/g; b charge-discharge curves of CeO₂/GO (1:4) nanoparticle electrode at 3–15 A/g

317 pseudocapacitance. At low scan rates (5–20 mV/s), no curve
 318 shows significant changes in the shape with increasing scan
 319 rate, indicating highly reversible redox reactions. This shows
 320 stability of electrolytes in the supercapacitor. However, the
 321 shape of the CV curves is slightly distorted as the scan rate
 322 increase, especially at a high scan rate of 100 mV/s.

323 The charge–discharge curves of the as-synthesized materials
 324 are shown in Fig. 7. Charge–discharge curves of CeO₂,
 325 GO, and CeO₂ nanoparticle-decorated GO at 3.0 A/g are
 326 shown in Fig. 7a. The discharge-specific capacitance values
 327 of CeO₂, GO, and CeO₂ nanoparticle-decorated GO (1:4)
 328 calculated from the discharge curves are 81.18, 35.12, and
 329 382.94 F/g at the current density of 3.0 A/g, respectively.
 330 One can see that the specific capacitance of the as-prepared
 331 CeO₂ nanoparticle-decorated GO (1:4) nanocomposite sample
 332 was 990.37 % higher than that of GO electrode and 371.72 %
 333 higher than that of CeO₂ electrode, respectively. The result
 334 quantitatively expresses the meaning of compositing
 335 CeO₂ and GO. The specific capacitance values of CeO₂
 336 nanoparticle-decorated GO nanocomposites at different mole
 337 ratio at the current density of 3.0 A/g are shown in Table 1.
 338 Among the obtained samples, the CeO₂ nanoparticle-

339 decorated GO (1:4) exhibits the best electrochemical perfor-
 340 mance and the specific capacitance value can be reached to
 341 382.94 F/g at the current density of 3.0 A/g. According to the
 342 results in Table 1, the composition of CeO₂/GO composites
 343 plays a significant role in specific capacitance. In Fig. 4, one
 344 can see that the size of CeO₂ is about 2–3 nm, so the number
 345 of the particles is large. When the content of GO is less, there
 346 is not enough GO to provide support for CeO₂; small CeO₂
 347 particles cannot be evenly dispersed on the GO. So the spec-
 348 ific capacitance is lower. When the molar ratios of CeO₂/GO
 349 reaches 1:4, there is enough GO to provide support for CeO₂.
 350 The synergistic effect is found by combining CeO₂ and GO,
 351 which reasonably resulted from the uniform dispersion of
 352 CeO₂ nanocrystals onto the surface of GO sheets and better
 353 electronic conductivity of the GO. Hence, a high electrochem-
 354 ical performance can be achieved. Continuing increasing the
 355 amount of the GO, the individual GO sheet exhibits a tenden-
 356 cy to aggregate and re-stack owing to the interplanar π - π
 357 interactions and van der Waals forces between the GO layers.
 358 The agglomeration reduces the surface area of the GO films
 359 and the diffusion of electrolyte ions, which results in a de-
 360 crease in the electrochemical performance. Moreover, the

361 agglomeration of GO sheets cut off the contact between elec-
 362 trolyte and cerium oxide on the surface of the folding covers,
 363 resulting in a loss of the specific capacitance. Figure 7b shows
 364 the galvanostatic charge/discharge (GCD) curves of the CeO₂
 365 nanoparticle-decorated GO (1:4) electrode in the 0–0.51 V
 366 potential window. The value of specific capacitance calculated
 367 by the GCD method for CeO₂ nanoparticle-decorated GO
 368 (1:4), at current densities of 3.0, 4.0, 5.0, 10.0, and 15.0 A/g,
 369 was found to be 382.94, 295.69, 244.12, 137.06, and 85.68 F/
 370 g, respectively. Besides, the specific capacitance values of
 371 CeO₂ nanoparticle-decorated GO (1:4) are much higher than
 372 the other CeO₂-based electrode materials, as shown in Table 2
 373 [16, 23–34].

374 The calculated specific capacitance values as a function of
 375 current density for CeO₂, GO, and CeO₂ nanoparticle-
 376 decorated GO (1:4) sample are shown in Fig. 8. For the red
 377 curve, it can be observed that the specific capacitance de-
 378 creases with the increasing current density from 3.0 to
 379 15.0 A/g. Generally, the rate capability is heavily dependent

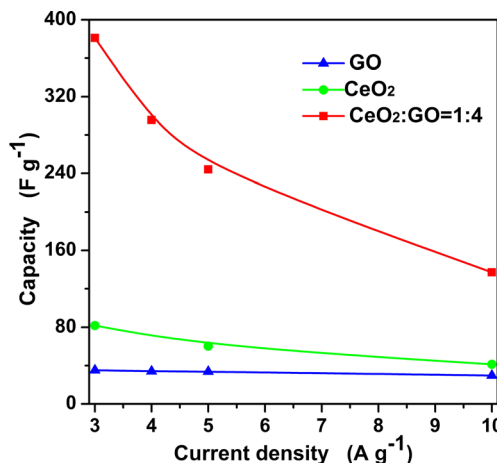


Fig. 8 Specific capacitance of CeO₂, GO, and CeO₂/GO (1:4) nanoparticle electrodes as a function of current density

on three processes: the ion diffusion in the electrolyte, the 380
 surface adsorption of ions on the electrode materials, and the 381
 charge transfer in the electrode. The specific capacitance 382

Q2 t2.1 **Table 2** Comparison of
 t2.2 capacitance values for various
 structural morphologies of CeO₂-
 based electrodes

Materials	Capacitance (F/g)	Current density (A/g) or scan rates (mV/s)	electrolyte	References
Graphene-ceria	110	10 mV/s	1 M H ₂ SO ₄	[23]
Pure CeO ₂	75			
CeO ₂	57	5 mV/s	3 M KOH	[24]
CeO ₂ -deposited 3D graphene	208	1 A/g		
Graphene/CeO ₂	89.0	1 A/g	2 M KOH	[25]
CeO ₂ -RGO	185	2 A/g	0.5 M Na ₂ SO ₄	[16]
Fe/CeO ₂ -decorated carbon nanofibers	56	Not given	1 M KOH	[26]
CeO ₂ /activated carbon	243	1 A/g	1 M H ₂ SO ₄	[27]
Ag/CeO ₂ /rGO	432.82	1 A/g	3 M KOH	[28]
CeO ₂ octahedron @MnO ₂	178.5	0.25 A/g	1 M Na ₂ SO ₄	[29]
CeO ₂ nanowire @MnO ₂	255.2			
CeO ₂ /Fe ₂ O ₃ composite nanospindles	142.6	5 mV/s	6 M KOH	[30]
Carbon-coated CeO ₂ nanorods	644	0.5 A/g	3 M KOH	[31]
Porous carbon/cerium oxide nanoparticle	150	0.25 A/g	1 M TEABF ₄ in acetonitrile	[32]
Hexagonal CeO ₂ nanoparticles (CTAB)	320 ± 3	2 A/g	K ₂ SO ₄	[33]
NiO-CeO ₂	314	1 A/g	3 M KOH	[34]
CeO ₂	81.18	3 A/g	6 M KOH	<i>This work</i>
	60.37	5 A/g		
	41.39	10 A/g		
GO	35.12	3 A/g		
	33.73	5 A/g		
	29.63	10 A/g		
CeO ₂ /GO (1:4)	382.94	3 A/g		
	295.69	4 A/g		
	244.12	5 A/g		

383 decreases with increasing current density owing to reduced
 384 penetration of electrolyte into the pores of electrode materials
 385 [35].

386 The EIS analysis is an important technique for investiga-
 387 tion of the supercapacitive performance and typical resistance
 388 of electrode materials for supercapacitors. The Nyquist imped-
 389 ance plots for CeO₂, GO, and CeO₂ nanoparticle-decorated
 390 GO (1:4) electrodes in 6 M KOH solutions over the frequency
 391 range from 0.01 to 100 kHz are shown in Fig. 9. The plots are
 392 composed of a line in the lower frequency region. However,
 393 there is no small semicircle at high frequency region. The
 394 straight line of the Nyquist plot at high frequency is related
 395 to the Warburg resistance resulting from the frequency depen-
 396 dence of ion diffusion/transport in the electrolyte [20, 36]. The
 397 large Warburg region of these electrodes shows the greater
 398 variations in ion diffusion path lengths and increased obstruc-
 399 tion of ion movement. The more vertical shape, indicating fast
 400 diffusion of ions in electrolyte during charge/discharge pro-
 401 cess, is an ideally capacitive behavior [37]. The presence of
 402 GO with high electrical conductivity resulted in a lower resis-
 403 tance of charge transfer. The EIS result is in good agreement
 404 with the CV and GCD results.

405 The advantages of composite electrode CeO₂ nanoparticle-
 406 decorated GO (1:4) over the pure CeO₂ and GO were clearly
 407 demonstrated. Additionally, the cycling stability of the CeO₂
 408 nanoparticle-decorated GO (1:4) electrode in 6 M KOH solu-
 409 tion between 0 to 0.51 V was investigated at a current density
 410 of 5.0 A/g. As shown in Fig. 10, the capacitive retention was
 411 about 86.05 % after 500 cycles, indicating a good cycling
 412 ability of the composite materials. Before 100 cycles, the sup-
 413 port GO allowed the deposition of the CeO₂ nanoparticle on
 414 the surfaces of GO sheets, which would enhance the mechan-
 415 ical strength of composite materials, resulting in the long
 416 charge/discharge cycling ability. After 250 cycles, the specific
 417 capacitance suffers a decline. The electrode materials were
 418 synthesized by a simple facile chemical coprecipitation

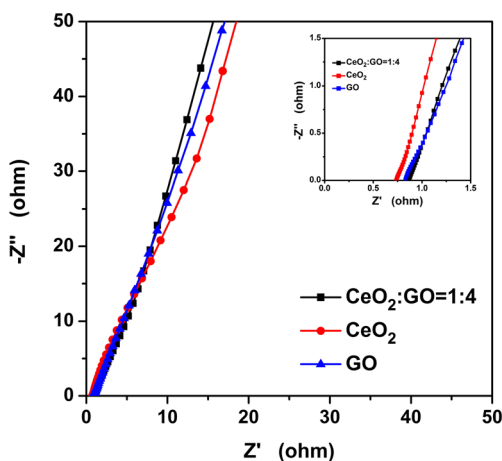


Fig. 9 Nyquist plots of CeO₂, GO, and CeO₂/GO (1:4) nanocomposite electrodes

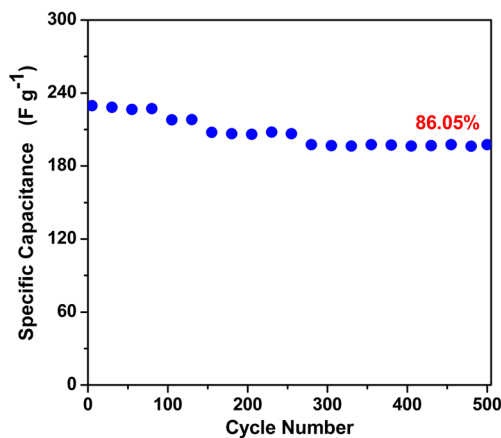


Fig. 10 Cycling performance of CeO₂/GO (1:4) nanocomposite electrode at the current density of 5 A/g

419 method at room temperature. Due to the relatively low reac-
 420 tion temperature and the short aging time (just 30 min), the
 421 size of CeO₂ particles is very small that helps to get a higher
 422 specific capacitance compared with other methods in the lit-
 423 erature as shown in Table 2. At the same time, the small size of
 424 CeO₂ particles could not guarantee long-term stability and
 425 superior cycling performance. The goodish cyclic stability
 426 exhibited by the CeO₂ nanoparticle-decorated GO (1:4) sam-
 427 ple reveals that it is possible to use the nanocomposite in
 428 practical energy storage systems.

Conclusions

429 The nanostructured CeO₂ nanoparticle-decorated GO (at dif-
 430 ferent molar ratio) materials have been synthesized by a sim-
 431 ple and inexpensive chemical coprecipitation method. The
 432 samples were systematically characterized by XRD, SEM,
 433 TEM, XPS, and Raman spectrum. The size of CeO₂ nanopar-
 434 ticle in CeO₂ nanoparticle-decorated GO (1:4) sample was
 435 about 2–3 nm. Electrochemical investigations reveal that
 436 CeO₂ nanoparticle-decorated GO (1:4) electrode can offer
 437 high specific capacitance (382.94 F/g at the current density
 438 of 3.0 A/g), attributing to the contributions of the good elec-
 439 trical conductivity of GO and the pseudocapacitance of the
 440 CeO₂ nanoparticles. Additionally, over 86 % of the original
 441 capacitance was retained after 500 cycles, indicating a good
 442 cycle stability of composite materials. These results show that
 443 a new class of material with high electrochemical performance
 444 has been identified.

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