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Ni–NiO core–shell inverse opal electrodes for supercapacitors†

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A general template-assisted electrochemical approach was used to synthesize three-dimensional ordered Ni core-NiO shell inverse opals (IOs) as electrodes for supercapacitors. The Ni-NiO IO electrodes displayed pseudo-capacitor behavior, good rate capability and cycling performance.

Electrochemical capacitors (also called supercapacitors and ultracapacitors) are emerging energy storage devices because of their high power density, long cycle life, short charging time, and minimal safety concerns.¹⁻³ Such devices can be used either by themselves as a primary power storage source or as an auxiliary power storage source with rechargeable batteries to meet the energy needs for high power applications such as electric vehicles and industrial mobile equipment. Pseudo-capacitors (or redoxcapacitors) represent one type of supercapacitors that have the potential to achieve high energy densities resulting from the fast and reversible redox reactions at/near the interface of the active storage material and an electrolyte. Among various pseudocapacitor materials, hydrous RuO₂ exhibits the highest performance to date,^{4,5} but its high cost limits its commercial use. Therefore, there has been considerable effort in exploring alternative electrode materials showing pseudo-capacitive behaviors, such as manganese oxide,^{6,7} cobalt oxide,⁸ and nickel oxide.^{9–16}

For high-power applications, adequate power density is only achieved with fast electron and ion transport. Conventional nanostructured electrode materials usually consist of a disordered porous matrix (*e.g.*, sintered nanoparticle film); these electrode materials exhibit poor electrical and mechanical contact and an ill-defined pore network that impedes electronic and ionic conductions during charge/discharge cycling. This study addresses these challenges simultaneously with a structural motif that has not been applied to supercapacitors: a metal core-metal oxide shell inverse opal (IO) electrode. The electrode architecture could potentially improve power density in two ways. The Ni metal core is expected to result in more facile electrical conductivity compared with that of the conventional disordered metal oxide nanoparticle (NP) electrode. Secondly, the periodic pore structure inherent in ordered inverse opals should enable better ionic conduction in the electrolyte filled pores than the tortuous pore structure in disordered metal oxide NP electrodes.

In this study, we describe the synthesis of a Ni–NiO core–shell structure using electrodeposition of Ni metal within a polystyrene bead template and subsequent electrodeposition and thermal annealing to form a NiO shell. The electrochemical characteristics of the resulting Ni–NiO core–shell IO architecture are then examined as a new design for supercapacitor electrodes.

The multilayer polystyrene (PS) opal template was prepared by slow gravimetrical sedimentation of colloidal particles onto a substrate as detailed elsewhere.¹⁷ Polystyrene colloid spheres (Seradyn, carboxylate-modified, medium acid) with an average diameter of 400 nm were deposited onto fluorine-doped tin oxide (FTO) substrates (Hartford Glass, TEC 15). Electrodeposition was carried out using a potentiostat/galvanostat (VMC-4, Princeton Applied Research) in a three-electrode cell using the PS coated substrate as the working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode. To obtain Ni-NiO inverse opals, Ni metal (ca. 460 µg) was first electrodeposited within the pore space of the PS films in a bath prepared by dissolving a mixture of 0.91 M (240 g L^{-1}) NiSO₄·6H₂O, 0.13 M $(30 \text{ g } \text{L}^{-1})$ NiCl₂·6H₂O, and 0.49 M (30 g L⁻¹) H₃BO₃ in distilled water solution at a constant potential of -1.0 V (vs. Ag/ AgCl) for 12 minutes. Samples were then immersed in dimethylformamide for 3 h at 120 °C to dissolve the PS template (thickness: about 2 µm). To prepare the thin NiO active material on the Ni inverse opals, galvanostatic electrodeposition of nickel hydroxide¹¹ was performed in 0.1 M Ni(NO₃)₂ solution at a current density of 1 mA cm⁻² for 5 minutes followed by annealing at 300 °C in air for 1 h; approximately 100 µg NiO was deposited on the surface of the Ni IO structure. Nickel oxide nanoparticles (NP) were purchased from Aldrich (99.8%, <50 nm, specific surface area of $> 50 \text{ m}^2 \text{ g}^{-1}$ by BET). Films of the NiO NPs were prepared by a similar procedure described for preparing TiO₂ NP films.¹⁸ Briefly, a single-layered NiO film was applied from an organic paste (18.2 wt% NiO, 9.1 wt% ethyl cellulose, 72.7 wt% terpineol) via the doctor blade technique, and then it was annealed at a temperature of 300 °C. The average thickness of the NiO NP films was about 2 µm.

The crystallinity of the samples was determined by X-ray diffraction (XRD, SCINTAG DMS-2000 diffractometer with Cu K α radiation). The morphology and microstructure of the samples were examined by field emission scanning electron

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[†] Electronic supplementary information (ESI) available: Current–time profile for Ni deposition, voltage–time profile for Ni(OH)₂ deposition, voltage profiles of the Ni–NiO inverse opal electrode cycled at 1 mA cm⁻² and the cyclic voltammograms of the NiO nanoparticle electrode at scan rates from 5 to 500 mV s⁻¹. See DOI: 10.1039/c0cc05191h



Fig. 1 SEM images of (a) polystyrene beads, (b) Ni metal inverse opal structure, (c) Ni–NiO inverse opal structure, and (d) TEM image of Ni–NiO inverse opal structure showing the (110) plane.

microscopy (FE-SEM, JEOL JSM-7000F) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai F-20UT, operating at 200 kV). Electrochemical measurements were performed with a three-electrode glass cell set-up, consisting of a Ni–NiO IO working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode. Galvanostatic charge/discharge cycling and cyclic voltammetry were carried out using the potentiostat/galvanostat from 0.0 to 0.5 V in 1 M KOH solution at room temperature.

Fig. 1 displays SEM images of the (a) PS opals, (b) Ni metal inverse opals (IOs), (c) Ni–NiO (thin NiO film on a Ni metal core) IOs, and (d) TEM image of Ni-NiO IOs. It can be seen that the PS opals (Fig. 1a) are well-ordered with 400 nm diameter particles in hexagonal symmetry (face-centered cubic lattice: ABCABC). Most samples exhibit some cracks and vacancies which result from film shrinkage during evaporative self-assembly.¹⁹ The electrodeposition of Ni metal with subsequent removal of the PS template produces a well-ordered Ni IO structure (Fig. 1b). Electrodeposition of nickel hydroxide and subsequent annealing leads to a roughening of the IO surface, but otherwise retention of the macroscopic pore ordering (Fig. 1c). Analyses of the SEM images of Ni IO (Fig. 1b) and Ni-NiO IO (Fig. 1c) structures show that the average NiO coating thickness is 12 ± 4 nm. Finally, TEM revealed that the dark Ni metal core network is well connected, suggesting that the core should provide a continuous electrically conductive pathway (Fig. 1d).

Fig. 2 shows the XRD patterns of inverse opals of (a) Ni metal and (b) Ni–NiO structure annealed at 300 °C. The characteristic peaks of rock salt NiO at 37.3° (111), 43.3° (200), 62.9° (220) were observed in the XRD patterns after electrodeposition and subsequent annealing. Annealing transforms the as-deposited nickel hydroxide phase to crystalline NiO.¹¹

Fig. 3a presents the cyclic voltammograms of the Ni–NiO IO electrode annealed at 300 °C in the potential window of 0.0 to 0.5 V. Pairs of well-defined cathodic and anodic peaks are clearly observed over the entire range of scan rates from 5 to 500 mV s⁻¹. Studies^{11–14} of NiO electrodes indicate that these



Fig. 2 XRD of (a) Ni metal inverse opals and (b) Ni–NiO inverse opals annealed at 300 °C. The peaks indicated by asterisks correspond to the FTO substrate.



Fig. 3 (a) Cyclic voltammograms of the Ni–NiO inverse opal electrode annealed at 300 $^{\circ}$ C at various scan rates (5–500 mV s⁻¹) and (b) capacitance of the Ni–NiO inverse opal and nanoparticle electrodes as a function of the scan rate.

peaks are associated with the pseudo-capacitive behavior resulting from reversible faradic redox reactions:

$$NiO + OH^{-} \leftrightarrow NiOOH + e^{-}$$
(1)

The CV curves in Fig. 3a are quite symmetric, implying good reversibility of the redox reactions (eqn (1)) on the NiO surface. The shape of the current responses are essentially the same over the entire range of scan rates, indicative of rapid faradic reactions at high scan rates. The current response increases approximately proportionally with increasing scan rates, suggesting that the rates of electronic and ionic transport are not limiting at scan rates as high as 500 mV s⁻¹. Notably,

a Ni metal IO annealed without the electrochemically-deposited Ni(OH)₂ film showed 3-fold less capacitance than that of the NiO deposited film, suggesting that the electrochemicallyprepared NiO has stronger capacitive behavior than that from oxidized Ni metal. Fig. 3b shows the scan-rate dependence of the capacitance of the Ni-NiO IO electrode. The rate capability of a NiO NP film with a similar film thickness is also plotted in Fig. 3b for comparison. The IO electrode exhibits a higher rate capability than the NP electrode. At the highest scan rate (500 mV s^{-1}), the capacitance of the IO electrode is maintained up to 80% of that at 5 mV s⁻¹, versus only 50% for the NP electrode. The faster charge/discharge kinetics of the IO electrode is presumably resulting from the higher electrical conductivity provided by the Ni metal core and the greater ionic conductivity afforded by the ordered pore network in the IO structure. This rapid charge/discharge rate is an attractive feature for high-power supercapacitor applications, which are essential for fast energy output applications such as hybrid electric vehicles.

Fig. 4a shows several cycles of representative voltage profiles of the Ni–NiO core–shell IO electrodes from galvanostatic charge/discharge measurements performed at a constant current density (0.2 mA cm⁻²). The shapes of the charge/ discharge curves appeared unchanged during the entire cycling, suggesting that the NiO microstructure is stable during the repeated charge/discharge cycles. It is noteworthy that the shapes of voltage profiles cycled at 1 mA cm⁻² (Fig. S3, ESI†) are essentially the same as the ones shown in Fig. 4a. There is no significant current–resistance drop, suggesting that the Ni–NiO IO electrode is suitable for supercapacitor applications. Cycle performance of the Ni–NiO IO electrode for the first 1000 cycles, evaluated by plotting the



Fig. 4 (a) Typical voltage profiles and (b) cycle performance of the Ni–NiO inverse opal electrode. The current density was 0.2 mA cm^{-2} .

capacitance *versus* cycle number, is presented in Fig. 4b. The capacitance of the Ni–NiO IO electrode increases slightly with cycling, which could be ascribed to a slow infiltration of electrolyte into the nanopores within the NiO layer during the cycling process. The weight of the NiO active material was estimated from the structural parameters of the IO films. From the FCC lattice, pore size (*ca.* 300 nm), and NiO shell layer thickness (*ca.* 12 ± 4 nm), we estimate that the specific capacitance of the Ni–NiO IO electrode was about 96 ± 32 F g⁻¹, in agreement with those reported for other NiO electrodes.^{10,11,13–15} It is expected that the specific capacitance of the IO electrodes could be further enhanced by optimizing Ni–NiO IO morphological properties (*e.g.* pore size, NiO shell layer thickness, and annealing temperature).¹¹

In summary, Ni–NiO core–shell IO electrodes were fabricated using electrodeposition within a polystyrene bead template. The XRD and SEM images confirmed that the periodic IO structure consisted of a Ni metal core and a NiO shell film in well-ordered hexagonal symmetry. The specific capacitance of the NiO component of the Ni–NiO IO electrode was about 96 ± 32 F g⁻¹. The IO electrode showed better rate capability than the randomly-mixed NiO NP electrode, which is attributed to the Ni metal core and the ordered pore network in the IO structure. These results suggest that the Ni–NiO IO architecture appears to be a promising electrode architecture for supercapacitors.

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