Electronic Supplementary Information

Hierarchical porous CeO_2 micro rice supported Ni foam binder free electrode and its enhanced pseudocapacitor performance by redox additive electrolyte

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1. Structural and morphological studies of CeO_2 micro rice after 5000 charge-discharge cycles:

The XRD patterns of the CeO_2 micro rice supported Ni-foam substrate before and after 5000 charge-discharge cycles in KH and RAE were depicted in Fig. S1. The appearance of (111), (200), (220), (311), (222), (400), (331), and (420) planes confirms the formation of CeO_2 structure on Ni foam substrate. Along with these planes, some extra peaks were appeared due to the surface oxidation of Ni foam substrate on hydrothermal reaction. There were no phase changes detected after 5000 cycles of charge-discharge. Compared to the as-prepared binder-free electrode, the peak intensities of the substrates were changed after 5000 charge-discharge cycles in KH and RAE. The peak intensity in RAE was slightly reduced. In KH, there was a large change in peak intensities of CeO_2 peaks and it was in coherence with the experimental results of 5000 GCD cycles, the capacitance drop in KH (85.3%) was high compared to the RAE (92.7%).

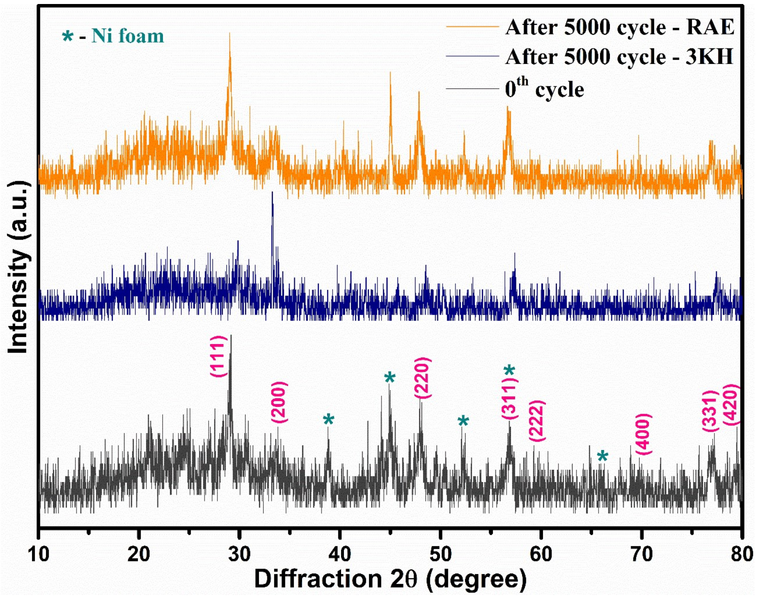

Fig. S1 XRD patterns of CeO_2 micro rice supported Ni-foam substrate before and after 5000 charge-discharge cycles

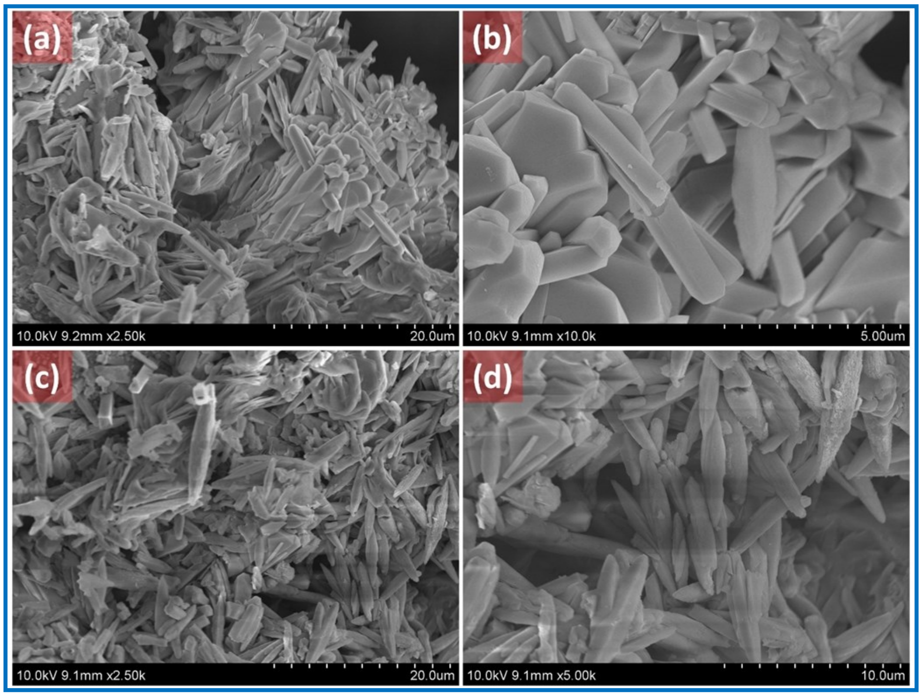

Fig. S2 SEM images of CeO_2 micro rice supported Ni-foam substrate after 5000 charge-discharge cycles in (a,b) KH and (c,d) RAE

The morphological studies of CeO_2 micro rice supported Ni-foam substrate after 5000 charge-discharge cycles in both KH and RAE have been depicted in Fig. S2. The SEM images of CeO_2/NF in RAE were depicted in Fig. S2 (a,b). This indicates that the surface of the CeO_2 micro rice was looking smooth even after 5000 cycles. Similarly, the SEM images of the CeO_2/NF in the KH has been depicted in Fig. S2 (c,d) indicates that the surface was slightly rough, due to a large number of cycles and corrosion and workload of the electrode in KH. The SEM report also supports the GCD cycling test results.

2. Effect of precursor concentration on CeO_2 morphology:

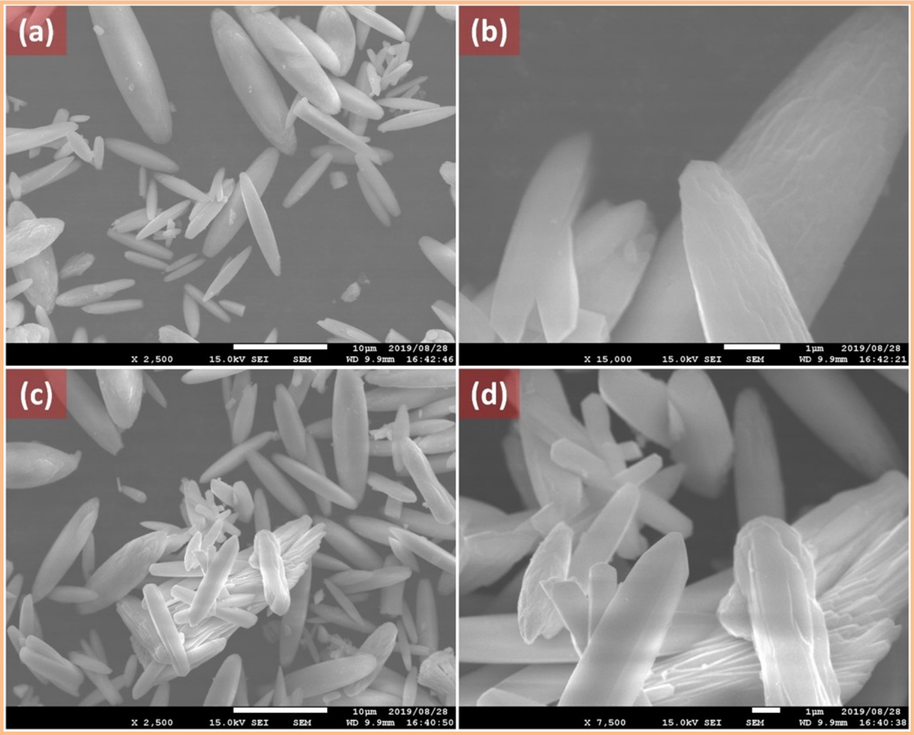

Fig. S3 (a-d) SEM images of CeO_2 micro rice synthesized with 30 mM $Ce(NO_3)_2.6H_2O$ under different magnifications

To study the effect of precursor concentration on the surface morphology of the CeO_2 micro rices, the CeO_2 synthesis procedures were repeated under different precursor concentration (30 mM and 70 mM $Ce(NO_3)_2.6H_2O$). The SEM images of the CeO_2 micro rice synthesized by the 30 mM and 70 mM $Ce(NO_3)_2.6H_2O$ concentrations were depicted in Fig. S3, S4. The Fig. S3 illustrates the SEM images of CeO_2 micro rices synthesized with 30 mM $Ce(NO_3)_2.6H_2O$ concentration, which confirmed the formation of CeO_2 micro rices with inhomogeneous size distribution. At same time, the SEM images of CeO_2 miro rices prepared with the 70 mM $Ce(NO_3)_2.6H_2O$ concentration (Fig. S4), confirmed the formation of almost even sized micro rices with excessive CeO_2 nanoparticles over it, due to high precursor concentration. But, in both the cases, the surface morphology of the prepared CeO_2 miro rices were almost same. Altogether elucidates that the 50 mM $Ce(NO_3)_2.6H_2O$ concentration was the optimal concentration for the ideal CeO_2 micro rice structure formation with uniform size distribution to attain the high electrochemical performances.

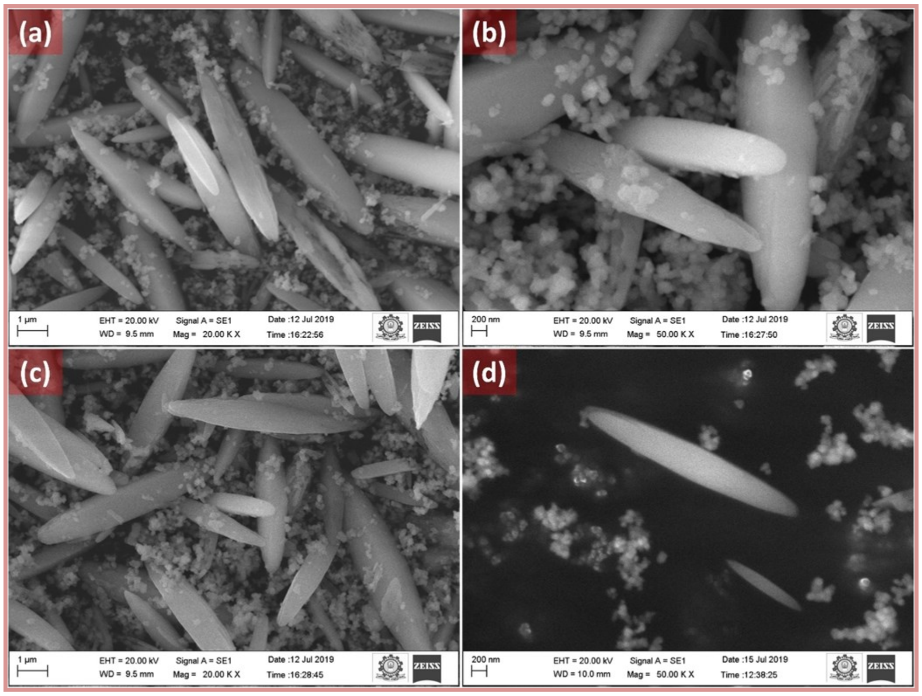

Fig. S4 (a-d)SEM images of CeO_2 micro rice synthesized with 70 mM $Ce(NO_3)_2.6H_2O$

3. Chargeing-discharging mechanism of RAE/CeO_2:

The charging and discharging mechanism of RAE and CeO_2 based binder free electrode was illustrated in equations (S1-S4),

Charging,

$$Ce^{3+} - e^{-} \rightarrow Ce^{4+} \qquad (S1)$$

$$[Fe(CN)_6]^{3-} + e^{-} \rightarrow [Fe(CN)_6]^{4-} \qquad (S2)$$

Discharging,

$$[Fe(CN)_6]^{4-} - e^- \rightarrow [Fe(CN)_6]^{3-} \qquad (S3)$$

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad (S4)$$