

Supporting Information

Hierarchical Nickel-Cobalt Sulfide/Niobium Pentoxide Decorated Green Carbon Spheres Toward Efficient Energy Storage

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S1 Experimental Section

S1.1 Chemicals, Equipment, and Materials Characterization

All chemicals were of analytical grade and directly used in the reactions. D(+)-glucose (Merck, Germany), Niobium (V) chloride (Merck, Germany), cobalt (II) chloride hexahydrate (Merck, Germany), nickel (II) chloride hexahydrate (Merck, Germany), ammonia, calcium gluconate, ethanol, sulfuric acid, acetone, thiourea, LiOH (Merck, Germany), and nickel foam (Wuzhou HGP Advanced Materials Technology corp. Ltd., China) were used in this study. Deionized (DI) water (18.2 M Ω , Z-101 Zolalan Water Purification System, Iran) was used in all reactions and measurements.

A tube furnace (Atra Co, Iran) was used for the carbonization process. Field-emission scanning electron microscope (FE-SEM) (TESCAN, MIRA III, Czech Republic) equipped with an energy dispersive spectroscopy (EDS), Fourier-transform infrared spectroscope (FT-IR) (Spectrum 100 Optica FT-IR Spectrometer, PerkinElmer, USA), X-ray diffractometer (XRD) (RIGAKU D/MAX-IIIC diffractometer, D8 Advance using the Cu Ka radiation, Bruker, Germany), Raman spectroscope (XploRA PLUS, HORIBA, France), surface area and pore size analyzer (Bel, Belsorp mini II, Japan) were carried out for investigating surface morphology and structural characterizations. Electrochemical measurements were also carried out using an electrochemical station (Autolab PGSTAT 204, Metrohm, Netherlands).

S1.2. Positive Electrode Preparation

S1.2.1. Preparation of the Nb₂O₅@CSs-NFs

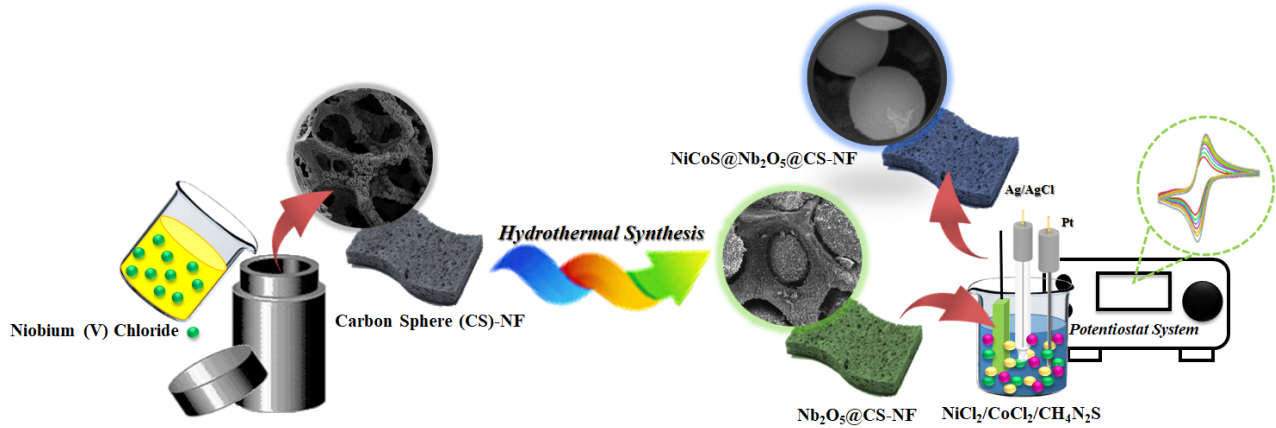
CSs were synthesized directly on a 10 mm × 10 mm × 1.1 mm piece of NF as reported in previous work [1]. In the next step, Nb₂O₅ was incorporated into CSs via a hydrothermal process (Scheme. 1). Initially, 20 mg of NbCl₅ was dispersed in 10 mL of ethylene glycol in an ultrasonic bath. Then, 30 mL of pure ethanol was added to the solution, and the ultrasonic dispersion was continued for 20 min to obtain a homogenous solution. Afterward, the prepared binder-free CS-NF was immersed in the above solution to be soaked with the dissolved Nb₂O₅. Next, the CS-NF and solution were transferred to a 50 mL autoclave, sealed, and maintained at 120 °C for 12 h. The prepared electrode was then rinsed with ethanol and dried at 60 °C. Ultimately, the Nb₂O₅@CS-NF was placed in a tube furnace at 600 °C for 2 h under N₂ atmosphere. The mass of the active material was estimated 1.2 mg cm⁻².

S1. 2. 2. Preparation of the Ni-Co-S@Nb₂O₅@CSs-NFs

As illustrated in Scheme. S1, a simple electrodeposition process was carried out to synthesize Ni-Co-S onto the Nb₂O₅@CS-NFs. In this regard, a solution of Co (II) chloride hexahydrate (5 mM), Ni (II) chloride hexahydrate (7.5 mM), and CS(NH₂)₂ (0.075 M) was provided, and ammonia solution was added drop by drop until the pH of the solution reached about 6.

Afterward, the prepared solution was transferred to an electrochemical cell as the electrolyte during the electrodeposition. A CV-based electrodeposition was performed while a Nb₂O₅@CS-NF was the working electrode, and a Pt rod and Ag/AgCl (KCl 3.5 M) were auxiliary and reference electrodes, respectively. 15 continuous CV cycles were carried out in a potential range of -1.20 – 0.20 V, in which the potential sweep rate was 5 mV s⁻¹. The Ni-Co-S@Nb₂O₅@CS-NFs were then rinsed with DI water and dried in a 60 °C vacuum oven. The mass loading of the electroactive material was 1 mg cm⁻². The thickness of the prepared electrodes was then

estimated using a digital caliper. The measured thickness of the fabricated positive electrodes was about 1.7 mm.



Scheme. S1. Schematic illustration for the fabrication process of NiCoS@Nb₂O₅@CS-NF electrodes.

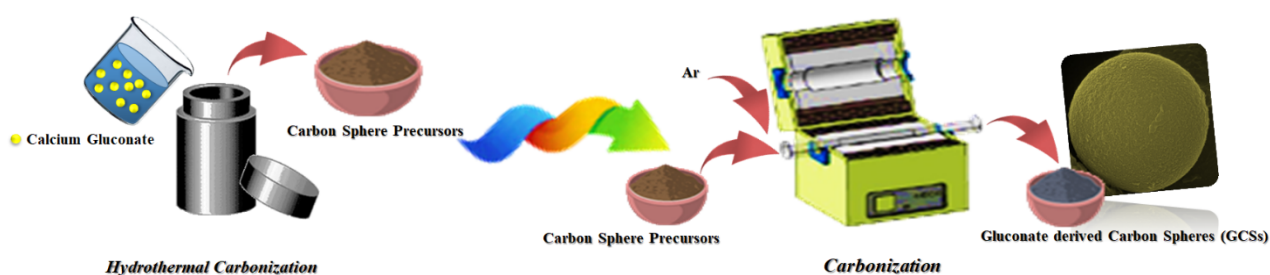
CV and GCD measurements of the positive electrodes were carried out in a 3-electrode cell at ambient temperature. A Hg/HgO electrode was used as the reference and a Pt plate as the counter electrode, where a solution of LiOH 1 M was utilized as the electrolyte. Within a potential range of -0.30 – 0.75 V, CV measurements were performed at different scan rates (1 to 100 mV s⁻¹). Potential thresholds of -0.30 and 0.65 V were chosen for GCD measurements, and current densities were adjusted from 18 up to 180 A L⁻¹. 5000 GCD cycles were carried out at different current densities to evaluate the life stability of the Ni-Co-S@Nb₂O₅@CS-NFs. EIS measurements were done in an OCP setting, and a 5 mV AC potential ranging from 100000 to 0.01 Hz was employed. Volumetric capacity (C L⁻¹) of the Ni-Co-S@Nb₂O₅@CS-NFs was calculated according to Eq. S1 [2,3]:

$$Q_v = \frac{i \int V dt}{v \times V} \quad \text{Eq. S1}$$

In the above equation, i (A) is current, $\int V dt$ (Vs) is the area under the discharge curve, v (L) is the volume of the electrode, and V (V) is the potential range.

S1.3. Negative Electrode Preparation

The negative electrodes' active material was prepared through a one-pot hydrothermal synthesis. Initially, a 50 mL solution of calcium gluconate (12 mM) was provided and added into a Teflon-lined stainless-steel autoclave. The reaction was carried out at 180 °C for 12 h. As the autoclave cooled down, a brown solid product was centrifuged and washed with DI water and ethanol. Then, the precipitate was placed in an oven at 60 °C for 24 h. Afterward, the g-CSs were carbonized in a tube furnace at 800 °C for 3 h in an Ar atmosphere (Scheme. S2). Ultimately, a paste of the g-CSs, PVDF (5% in NMP), and carbon black with a mass ratio of 16:1:3 was prepared, and a piece of NF (1 cm × 1 cm) was covered with the paste. . A 1.86 mm thickness was then achieved for the negative electrodes.



Scheme. S2. Schematic illustration for the fabrication process of the negative electrode active materials.

CV measurements of the g-CS-NF were performed in a 3-electrode system in which Hg/HgO and Pt plate were the reference and auxiliary electrodes, respectively. The potential

range for CV measurements was from -1.0 to 0.1 V, and the measurements were done at 10 mV s⁻¹ up to 100 mV s⁻¹. GCD measurements were carried out between -1.0 to +0.1 V at different current densities. Moreover, 4750 GCD cycles were conducted to investigate the stability of the negative electrode. EIS measurements condition was same as mentioned earlier. The volumetric capacitance of the g-CS-NFs was obtained from GCDs according to Eq. S2 [4,5]:

$$C_v = \frac{i \times \Delta t}{v \times \Delta V} \quad \text{Eq. S2}$$

where Δt (s) is the discharge time, i (A) is the current, ΔV (V) is the potential range, and v (L) is the volume of the electrode.

S1. 4. Ni-Co-S@Nb₂O₅@CS-NF//g-CS-NF Asymmetric Devices

Using Eq. S3, two balanced pieces of Ni-Co-S@Nb₂O₅@CS-NFs and g-CS-NFs were used as positive and negative electrodes, respectively [6]:

$$\frac{v^+}{v^-} = \frac{C_v^- \times \Delta V^-}{C_v^+ \times \Delta V^+} \quad \text{Eq. S3}$$

where v^+ and v^- (L) are the volumes of positive and negative electrodes, C_v is the volumetric capacitance of the electrodes, and ΔV is the potential window of electrodes. The positive and negative superscripts denote the positive and negative electrodes. The device was soaked in LiOH 1M, and a piece of cellulose acetate paper was used as the separator.

CV measurements were conducted from 0.00 to 1.75 V at different scan rates from 1 up to 100 mV s⁻¹. In addition, GCD measurements were performed between 0.0 to 1.7 V from 2 to 20 A L⁻¹. The cycle durability of the device was investigated through 5000 GCD cycles. Volumetric capacity (C L⁻¹) of the ASCs was estimated based on Eq. S4 [3,6]:

$$Q_{cell} = \frac{i \int V dt}{v_t \times \Delta V} \quad Eq. S4$$

, where i (A) is current, $\int V dt$ (Vs) is the area under the discharge curve, v_t (L) is the total volume of positive and negative electrodes, and ΔV (V) is the potential window of the ASC.

Energy (Wh L⁻¹) and power (kW L⁻¹) densities were estimated according to Eq. S5 and 6 [4]:

$$E = \frac{Q_{cell} \times \Delta V^2}{2 \times 3.6} \quad Eq. S5$$

$$P = \frac{E \times 3.6}{\Delta t} \quad Eq. S6$$

, where Q_{cell} (C L⁻¹), ΔV (V), and Δt (s) are volumetric capacity, potential range, and discharge time, respectively.

S2. SEM Characterization of CS-NFs and Nb₂O₅@CS-NFs

As seen in Fig. S1(a) and S1(b), CSs appeared in a complete and uniform spherical shape. The EDS mapping analysis was also conducted to shine more light on the elemental composition of the CS-NFs and the outcomes are provided in Fig. S1(e) and S1(f). The EDS elemental maps provide clear evidence on successful coverage of NFs by CSs.

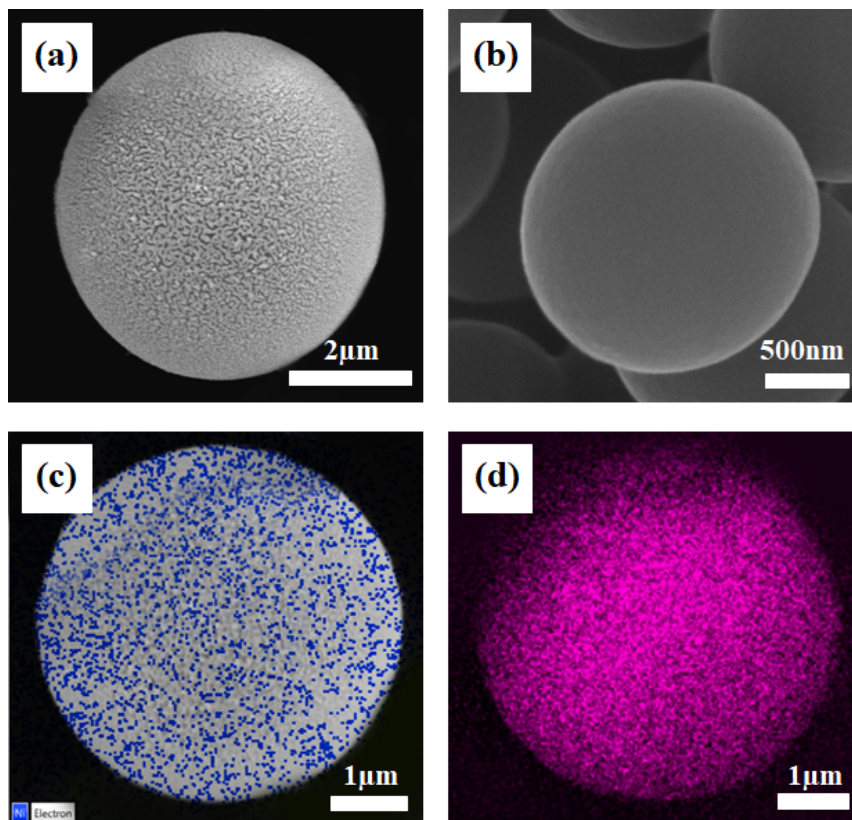


Fig. S1. (a, b) Surface morphology of CSs, and (c, d) the corresponding EDS maps of the elements C and Ni.

FE-SEM images of $\text{Nb}_2\text{O}_5@\text{CSs-NF}$ are displayed in Fig. S2(a)-(d). Fig. S2(a) demonstrates the direct formation of $\text{Nb}_2\text{O}_5@\text{CSs}$ onto the NF skeleton. As seen in Fig. S2(b)-(d), nanoarrays of Nb_2O_5 nanostructures were directly decorated onto the CSs. Furthermore, the mapping results presented in Fig. S2(e) and S2(f) testify the existence of Nb, Ni, and O on the surface of CSs.

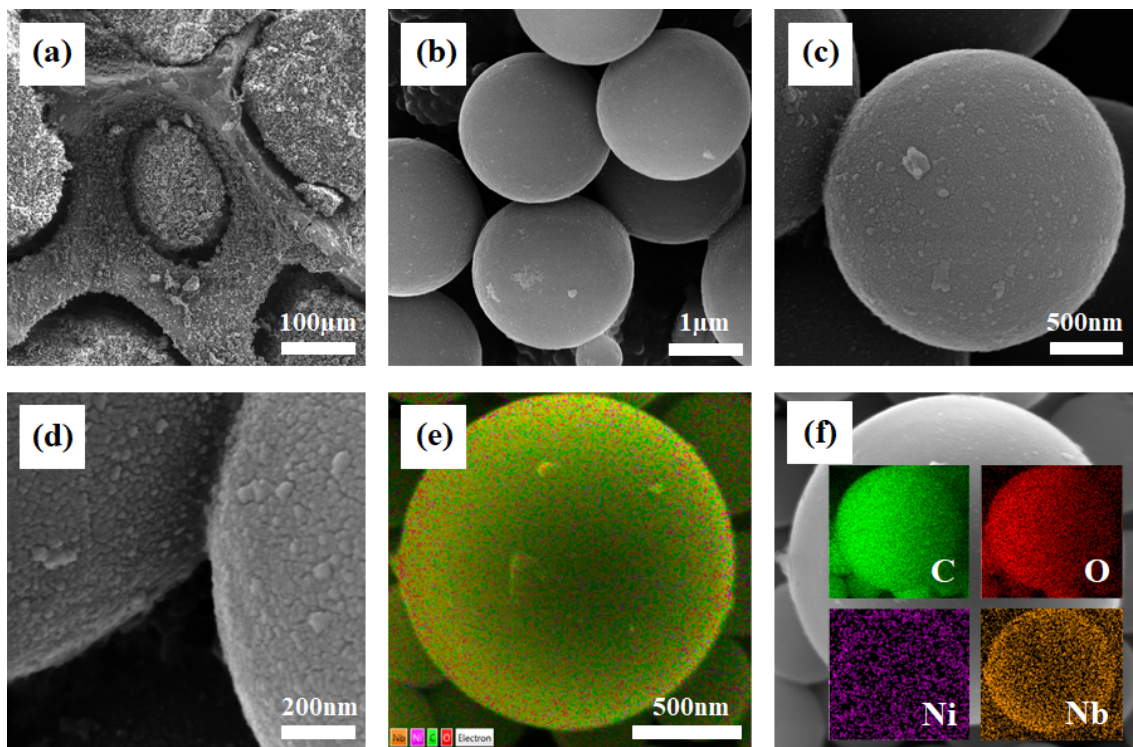


Figure S2. Surface morphology of (a–d) Nb₂O₅-decorated CS integrally decorated onto the NFs at different magnifications and (e, f) the corresponding EDS maps of the elements C, O, Ni, and Nb.

S3. Ni-Co-S@Nb₂O₅@CS-NF//g-CS-NF Asymmetric Device Capacitive Behavior Compared with the Reported Literature

Table S1. Capacitive performance of the fabricated ASCs compared to the reported literature.

Electrode		Electrolyte	C_{sp} or Q	E_{max}	P_{max}	Cycle Stability	Ref.
Positive	Negative						
T-Nb ₂ O ₅ @Ni ₂ P	AC	KOH (2M)	28.8 mAh g ⁻¹	30.2 Wh kg ⁻¹	453 W kg ⁻¹	90% (after 5k cycles)	[7]
S-Nb ₂ O ₅ @NS-PCNF	AC	NaClO ₄ (1M) in EC/PC/FEC	-	112 Wh kg ⁻¹	7949 W kg ⁻¹	81% (after 10k cycles)	[8]
T-Nb ₂ O ₅ /NG	AC	NaClO ₄ (1M) in EC/PC/FEC	46 mAh g ⁻¹	40.5 Wh kg ⁻¹	100 W kg ⁻¹	63% (after 5k cycles)	[9]
T-Nb ₂ O ₅ @G@m-T-Nb ₂ O ₅	AC	NaClO ₄ (1M) in EC/PC/FEC	28 F g ⁻¹	56.1 Wh kg ⁻¹	7200 W kg ⁻¹	89% (after 0.8k cycles)	[10]
m-Nb ₂ O ₅ /C	AC	NaClO ₄ (1M) in EC/PC/FEC	-	73 Wh kg ⁻¹	20000 W kg ⁻¹	90% (after 2k cycles)	[11]
T-Nb ₂ O ₅ @C/rGO	AC	NaPF ₆ (1M) in EC/DMC/FEC	-	76 Wh kg ⁻¹	80 W kg ⁻¹	>90% (after 3k cycles)	[12]
T-Nb ₂ O/CNFs	GF/m-CNFs	NaClO ₄ (1M) in PC/FEC	62 mAh g ⁻¹	11.2 mWh cm ⁻³	5.4 W cm ⁻³	80% (after 5k cycles)	[13]
NiCoS@Nb ₂ O ₅ @CS-NF	g-CS@NF	LiOH (1M)	1022 mC cm ⁻³	410.4 mWh cm ⁻³	29.770 W cm ⁻³	89% (after 5k cycles)	This work

T-Nb₂O₅=orthorhombic niobium pentoxide nanowires, Ni₂P=ultrathin porous nickel phosphide nanoflakes, AC=activated carbon, S-Nb₂O₅@NS-PCNF=sulfur-doped Nb₂O₅ quantum dots uniformly embedded with nitrogen and sulfur co-doped micro porous carbon nanofibers, T-Nb₂O₅/NG=T-Nb₂O₅ nanoparticke/N-doped graphene hybriide anode, NaClO₄/EC/PC/FEC=sodium perchlorate (1M) in a matrix of ethylene carbonate and propylene carbonate 1:1 vol ratio and 0.5 wt% fluoroethylene carbonate, m-Nb₂O₅/C=Nb₂O₅ nanoparticles embedded in a carbon matrix, T-Nb₂O₅@G@m-T-Nb₂O₅=sandwich-like mesoporous T-Nb₂O₅@graphene@mesoporous T-Nb₂O₅ nanosheets, NaPF₆ (EC/DMC/FEC)= 1.0 M NaPF₆ in ethylene carbonate/dimethyl carbonate containing 5 wt% fluoroethylene carbonate (EC/DMC + 5 wt% FEC, volume ratio of EC/DMC = 1:1), T-Nb₂O₅@C/rGO=T-Nb₂O₅/carbon core-shell nanoparticles/reduced graphene oxide, CNFs=Carbon nanofiber films, GF/mCNFs=graphene framework/mesoporous carbon nanofibers.

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