

High-performance Na–CO₂ Batteries with ZnCo₂O₄@CNT as Cathode Catalyst

Subashchandrabose Thoka,^a Zizheng Tong,^b Anirudha Jena,^{b,c} Tai-Feng Hung,^d Ching-Chen Wu,^d Wen-Sheng Chang,^d Fu-Ming Wang,^{e,f,g,h} Xing-Chun Wang,^e Li-Chang Yin,^{*,i} Ho Chang,^{*,c} Shu-Fen Hu,^{*,a} and Ru-Shi Liu^{*,b}

^a*Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan*

^b*Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*

^c*Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan*

^d*Green Energy & Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan*

^e*Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*

^f*Sustainable Energy Center, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*

^g*Department of Chemical Engineering, Chung Yuan Christian University, Taoyuan 32023, Taiwan*

^h*R&D Center for Membrane Technology, Chung Yuan Christian University, Taoyuan 32023, Taiwan*

ⁱ*Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*

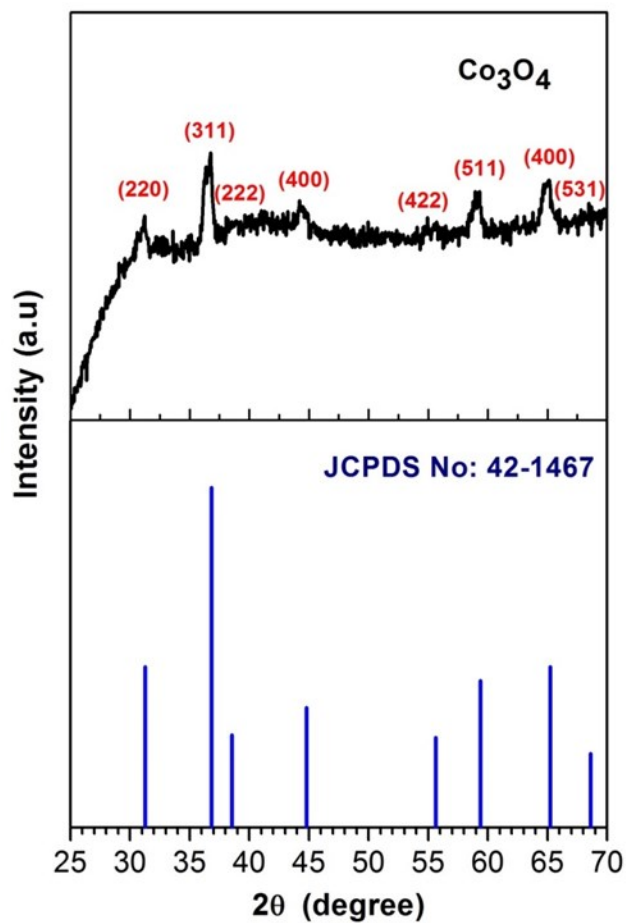


Fig. S1. XRD pattern of the porous Co_3O_4 nanorods.

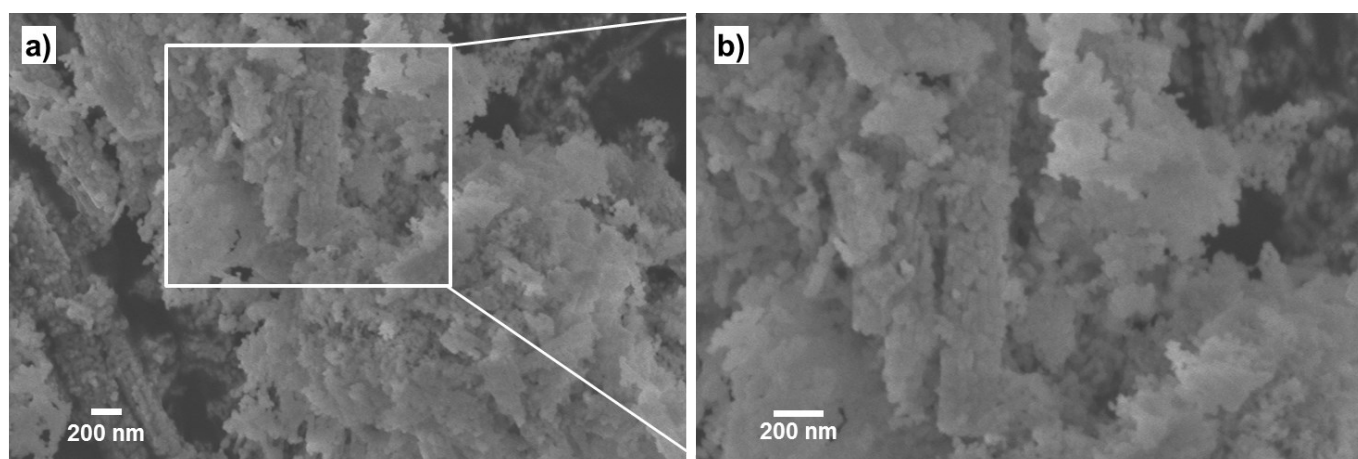


Fig. S2. SEM images of the porous Co_3O_4 nanorods at (a) low and (b) high magnifications.

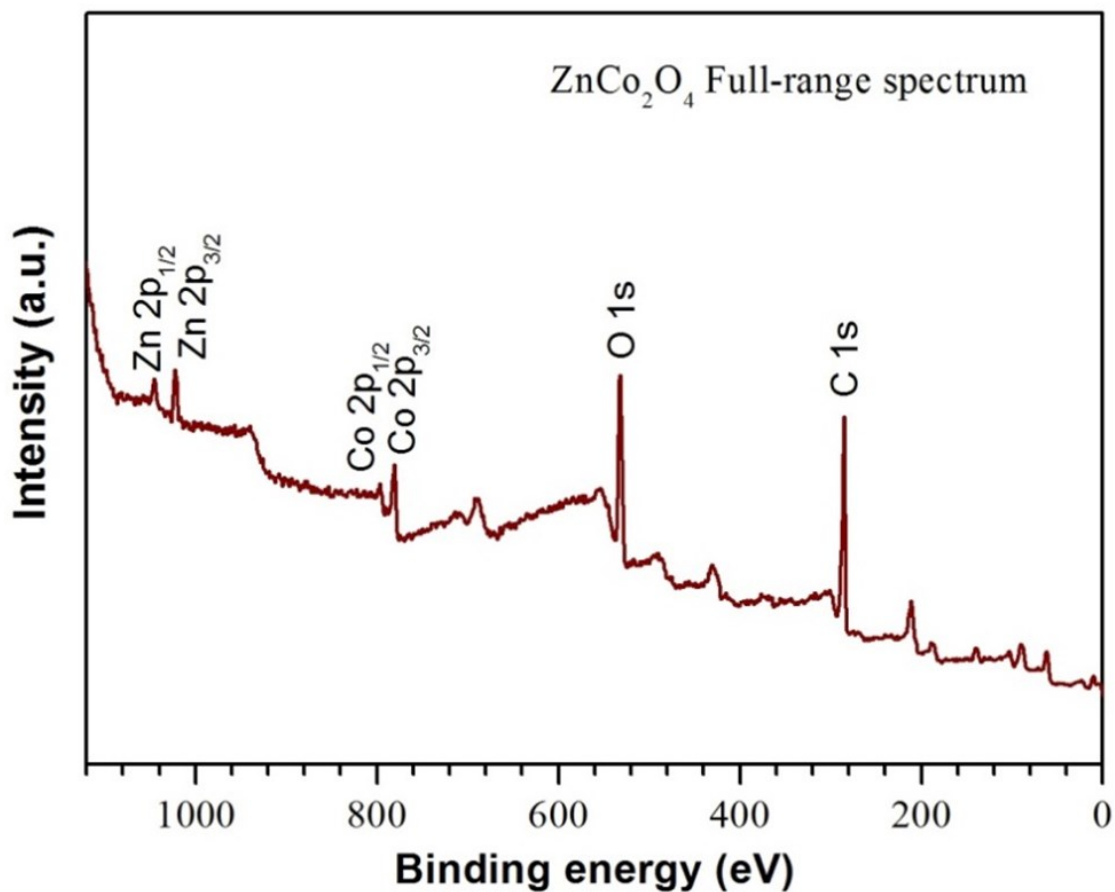


Fig. S3. Survey XPS spectrum of the as-synthesized ZnCo_2O_4 porous nanorods.

Samples	Absorption edge	Path	R (Å)	CN	σ^2 (Å ²)	R factor
Co	Co K-edge	Co–O	1.92(2)	3.3(2)	0.000(0)	0.01749
		Co–Co	2.87(8)	6.7(6)	0.008(2)	
Zn	Zn K-edge	Zn–O	1.95(0)	2.9(5)	0.004(4)	0.00526
		Zn–Co	3.35(5)	10.2(4)	0.009(8)	

Table S1. Fitting results of Co and Zn K-edge EXAFS signals for the ZnCo_2O_4 @CNT pristine electrode.

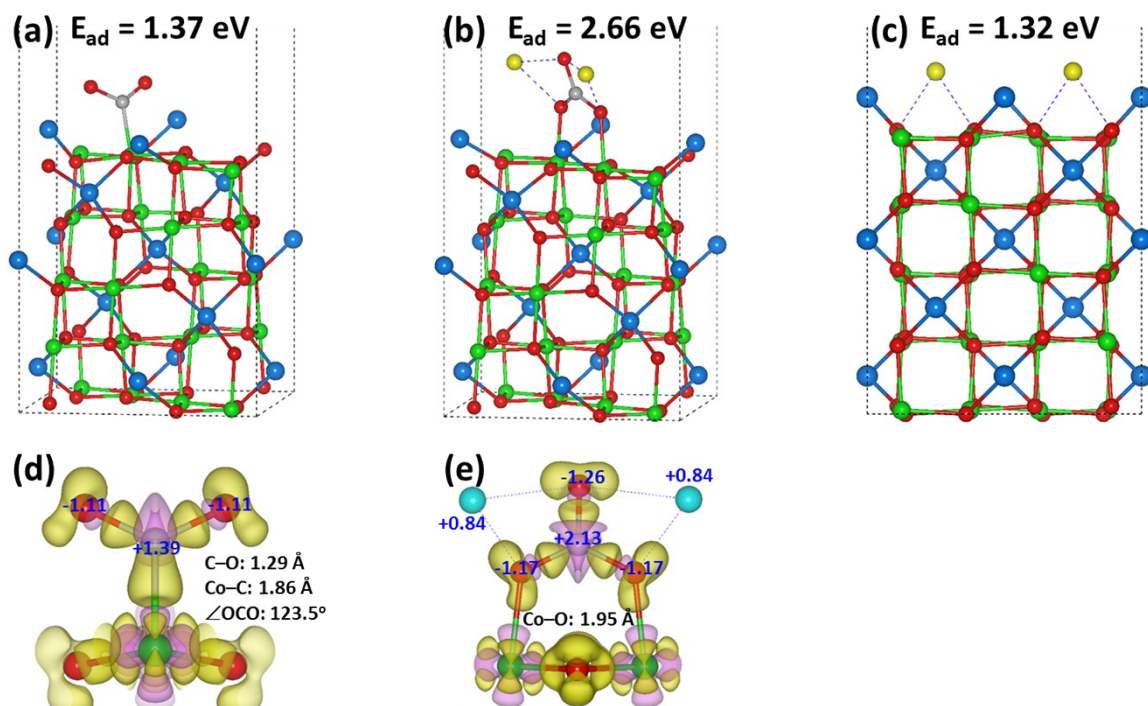


Fig. S4. Schematic structures of (a) CO₂, (b) Na₂CO₃ cluster, and (c) Na atom adsorption on the ZnCo₂O₄ (001) surface with exposed Co and Zn atoms. The Zn, Co, O, C, and Na atoms are denoted by the blue, green, red, grey, and yellow balls, respectively. (d and e) Charge density plots of CO₂ and Na₂CO₃ on the ZnCo₂O₄ (001) surface with adsorption configurations shown in (a) and (b), respectively. The iso-surface level is set to be 0.02 e/Å³. The yellow and purple regions represent the charge accumulation and depletion, respectively. In (e), the Na atoms are denoted by light blue balls for clarity. The relevant bond length (in Å), bond angle, and charge population (in blue text) of the CO₂ molecule and Na₂CO₃ cluster after adsorption are presented.

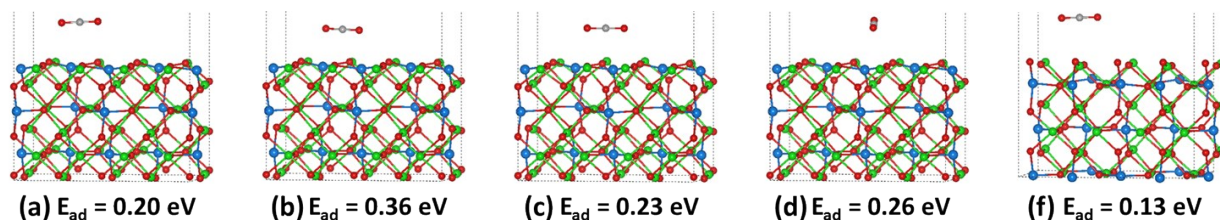


Fig. S5. (a–d) Fully relaxed structures of CO₂ on ZnCo₂O₄ with different adsorption configurations for the (110) surface with exposed Co and Zn atoms. (e) Fully relaxed structures of CO₂ on the ZnCo₂O₄ (110) surface with only exposed Co atoms. The Zn, Co, O, and C atoms are denoted by the blue, green, red, and grey balls, respectively.

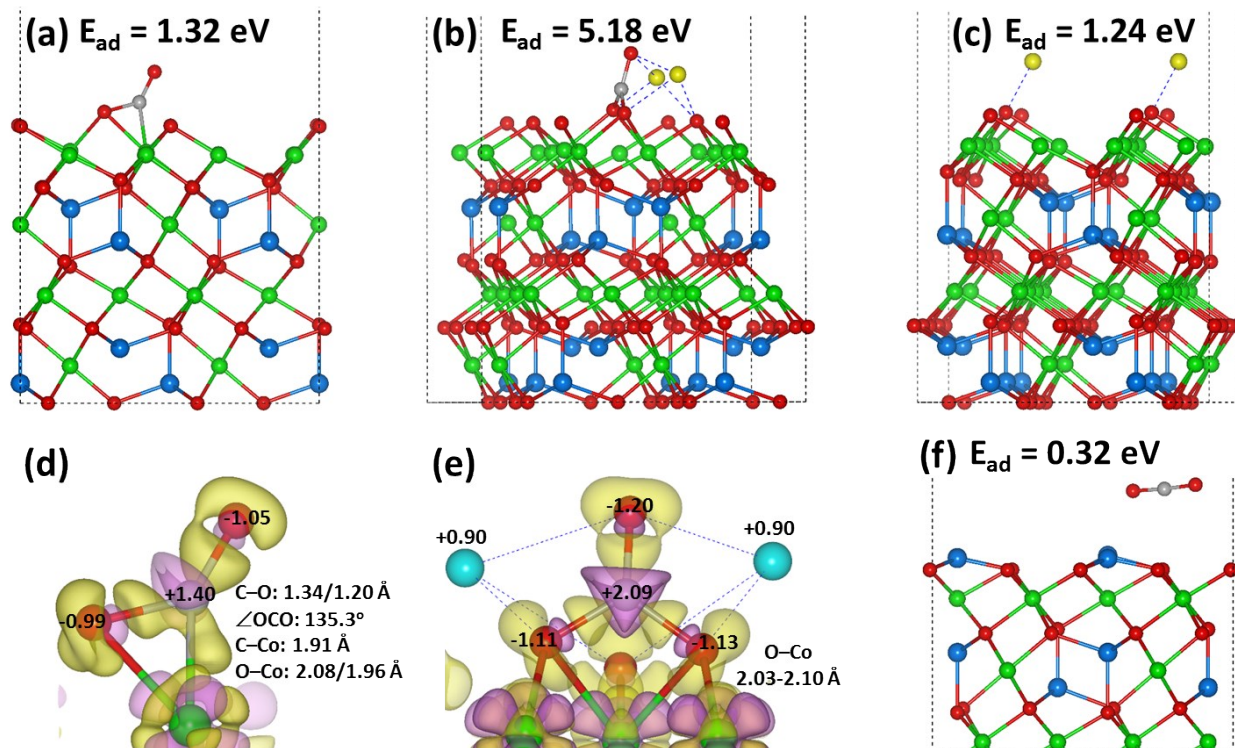


Fig. S6. Schematic structures of (a) CO₂, (b) Na₂CO₃ cluster, and (c) Na atom adsorption on the ZnCo₂O₄ (111) surface with only exposed Co atoms. The Zn, Co, O, C, and Na atoms are denoted by the blue, green, red, grey, and yellow balls, respectively. (d and e) Charge density plots of CO₂ and Na₂CO₃ on the ZnCo₂O₄ (111) surface with adsorption configurations shown in (a) and (b), respectively. The iso-surface level is set to be 0.02 e/Å³. The yellow and purple regions represent the charge accumulation and depletion, respectively. In (e), the Na atoms are denoted by the light blue balls for clarity. (f) Schematic structures of CO₂ adsorption on the ZnCo₂O₄ (111) surface with only exposed Zn atoms. The relevant bond length (in Å), bond angle, and charge population (in blue text) of the CO₂ molecule and Na₂CO₃ cluster after adsorption are presented.

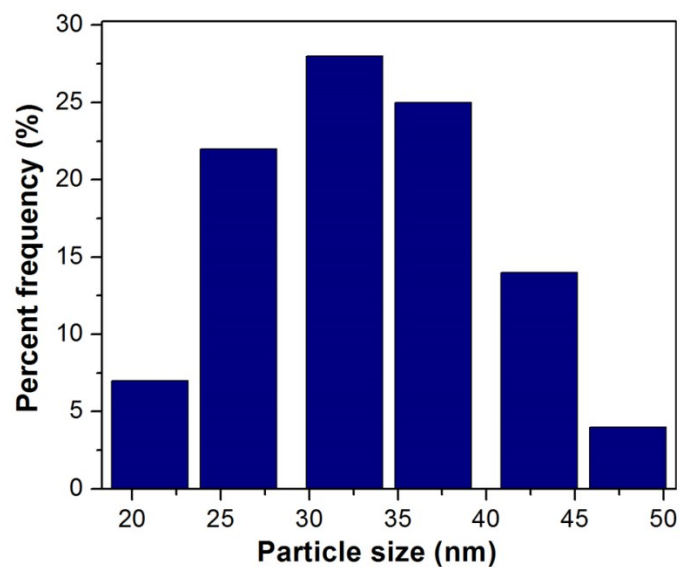


Figure S7. Particle size distribution histogram of nanoparticles composed in ZnCo_2O_4 nanorods.

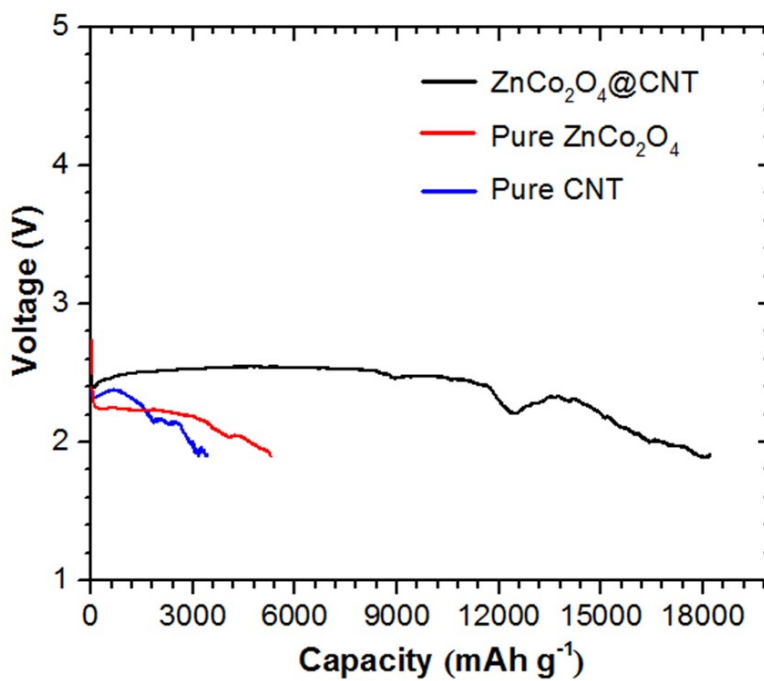


Figure S8. Full discharge curves of $\text{ZnCo}_2\text{O}_4\text{@CNT}$, pure ZnCo_2O_4 , and pure CNT cathode materials in Na- CO_2 batteries under the cut-off voltage of 1.9 V and the current density of 100 mA g^{-1} .

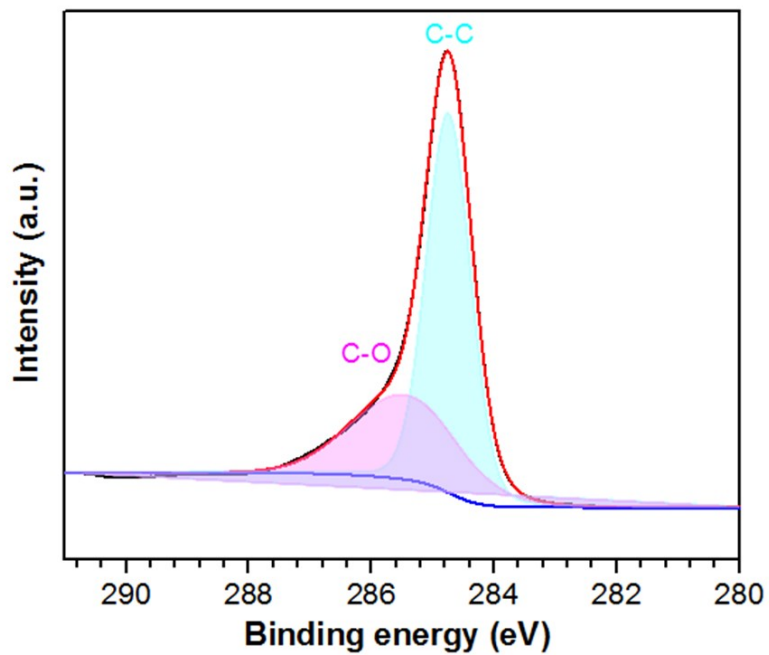


Figure S9. C 1s high-resolution X-ray photoelectron spectra of the pristine ZnCo₂O₄@CNT cathode.

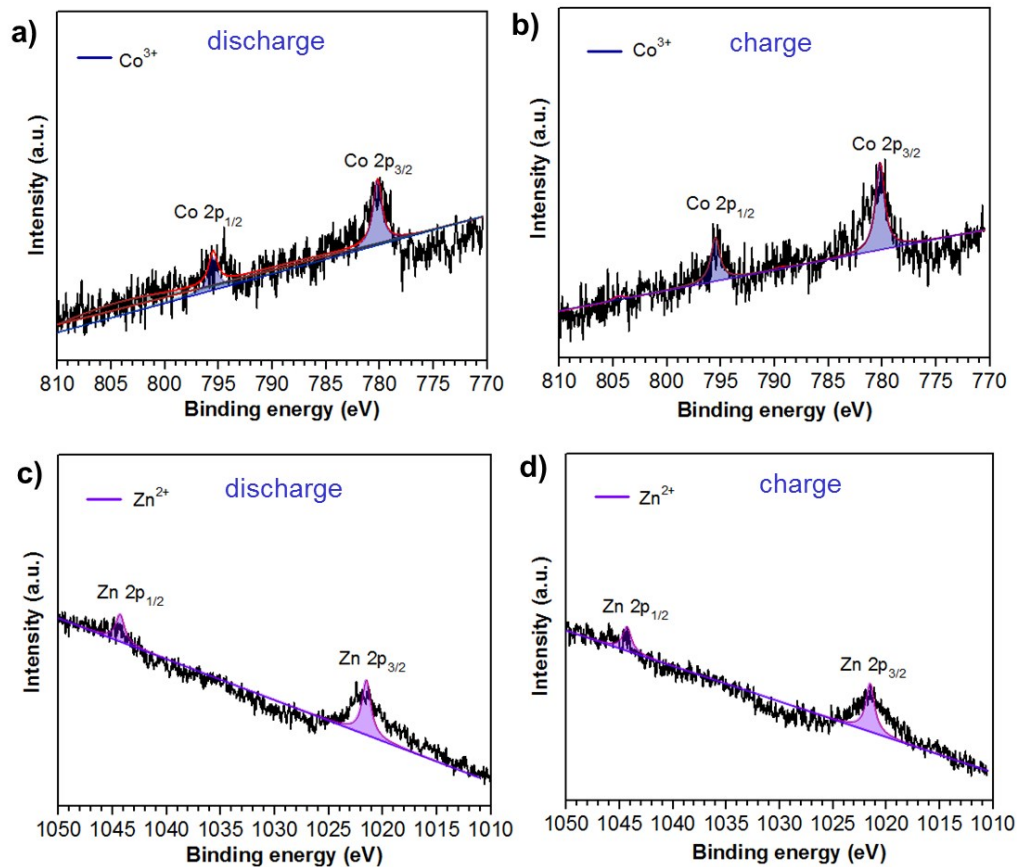


Figure S10. High-resolution X-ray photoelectron spectra of Co 2p and Zn 2p of the porous ZnCo₂O₄ nanorods at different stages. (a, c) discharged state, and (b, d) charged state in the Na-CO₂ batteries at 100 mA g⁻¹ under the limited capacity of 500 mAh g⁻¹.

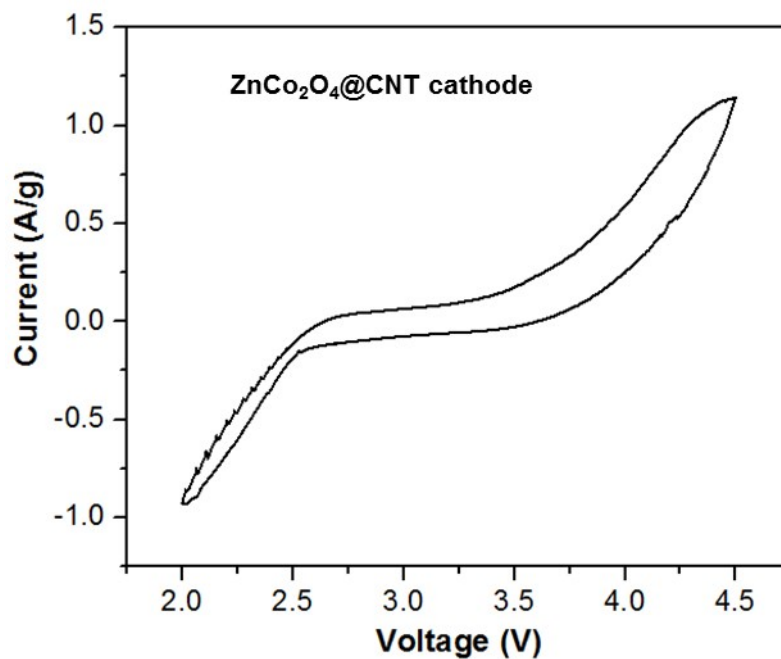


Figure S11. Cyclic voltammety curves of Na–CO₂ battery with ZnCo₂O₄@CNT cathode operating between 2–4.5V at a scan rate of 0.1 mVs⁻¹.