Supporting Information

In-situ Generated 3D Hierarchical Co₃O₄@MnO₂ Core-Shell Hybrid Materials: Self-assembled Fabrication, Morphological Control and Energy Applications

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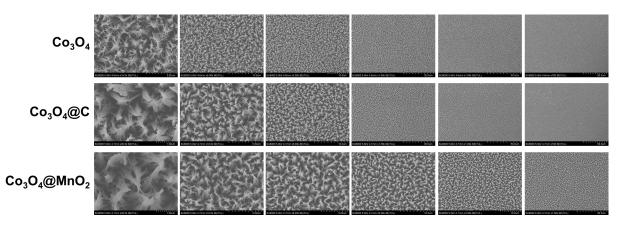


Figure S1. SEM images of the large-scale in-situ 3D hierarchical Co_3O_4 , Co_3O_4 @C and Co_3O_4 @MnO₂ nanoarrays grown on the oblique downward FTO glasses at different magnifications.

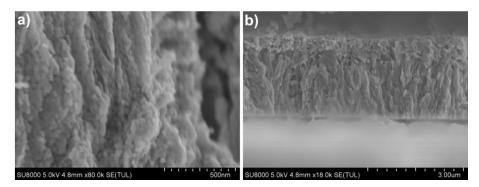


Figure S2. Cross section SEM images of the in-situ 3D hierarchical Co_3O_4 materials grown on the oblique downward FTO glasses at different magnifications.

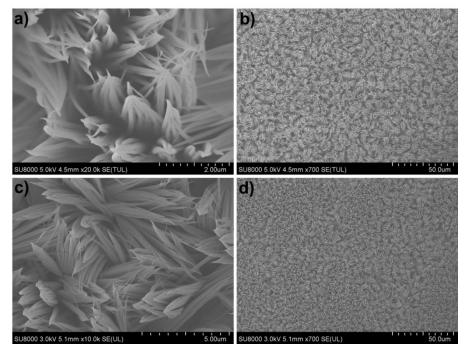


Figure S3. SEM images at different magnifications of the in-situ 3D hierarchical Co_3O_4 nanoarrays on FTO glasses with different orientations. a-b) grown on the oblique upward FTO glass; c-d) grown on the horizontal downward FTO glass.

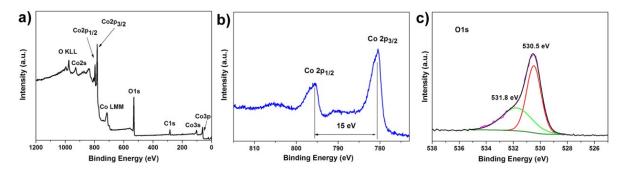


Figure S4. a) XPS spectra of the as-synthesized Co₃O₄ nanoarrays.b-c) XPS survey scan of Co 2p and O 1s, respectively.

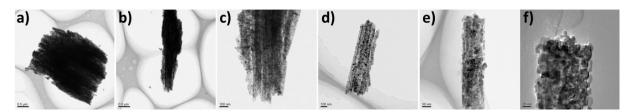


Figure S5. TEM images of the in-situ 3D hierarchical Co₃O₄ nanoarrays at different magnifications.

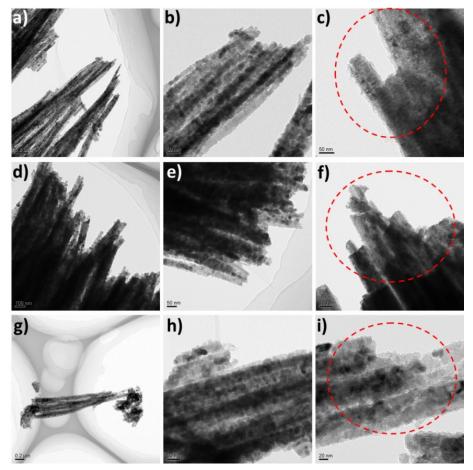


Figure S6. TEM images of the in-situ 3D hierarchical $Co_3O_4@MnO_2$ core-shell hybrid nanoarrays at different magnifications.

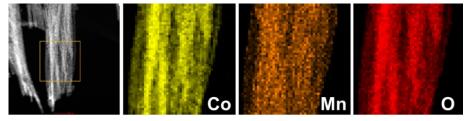


Figure S7. EDS mapping of the in-situ 3D hierarchical Co₃O₄@MnO₂ core-shell hybrid nanoarrays.

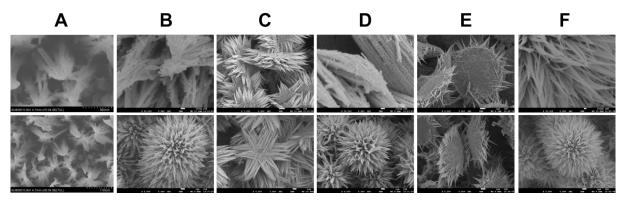


Figure S8. SEM images of the in-situ 3D hierarchical Co₃O₄@C A-F materials with different morphologies.

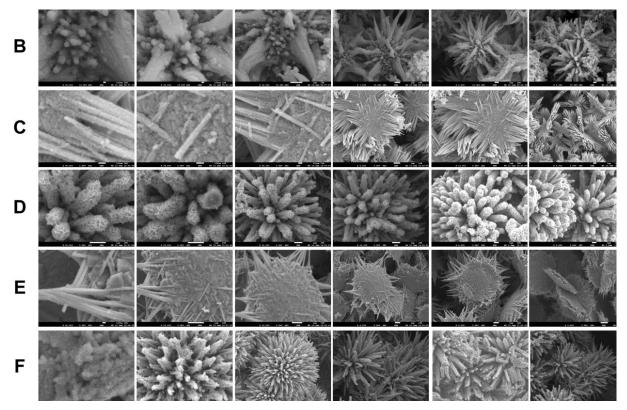


Figure S9. SEM images of the in-situ 3D hierarchical Co_3O_4 @MnO₂ core-shell hybrid A-F materials with different morphologies.

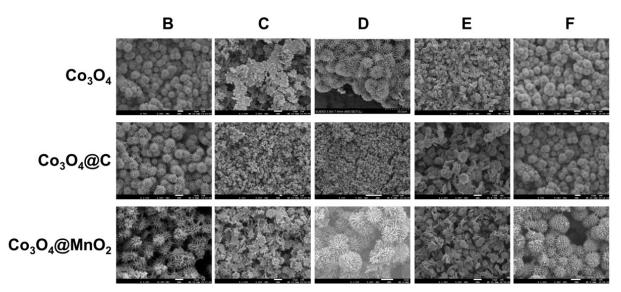


Figure S10. SEM images of the large-scale in-situ 3D hierarchical Co_3O_4 , Co_3O_4 , Co_3O_4 , Co_3O_4 , MnO_2 B-F materials.

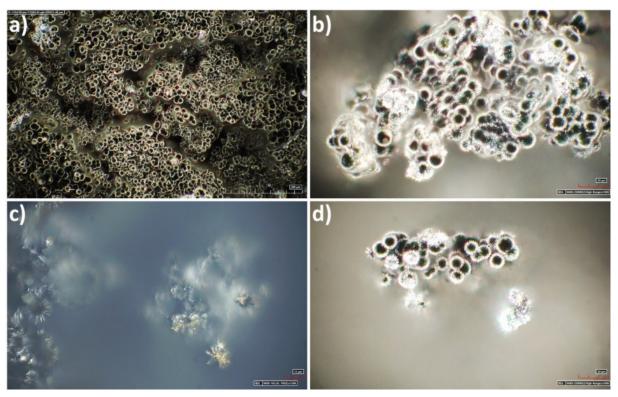


Figure S11. 3D Digital Microscope images of the in-situ synthesized 3D hierarchical a) Co₃O₄ B and b-d) Co₃O₄@MnO₂ B.

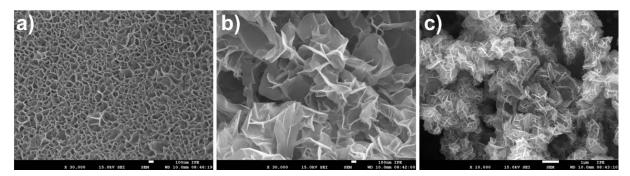


Figure S12. SEM images of the in-situ ultrathin 3D hierarchical a) MnO₂ layer and b-c) the corresponding 3D hierarchical MnO₂ nanoparticales in the in-situ process.

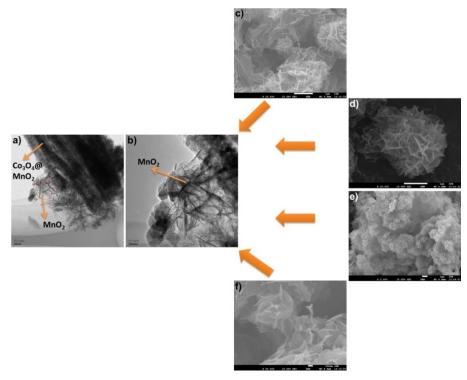


Figure S13. a-b) HRTEM of the MnO_2 layer in the $Co_3O_4@MnO_2$ hybrid architecture. c-f) HRSEM images of the MnO_2 nanoparticales.

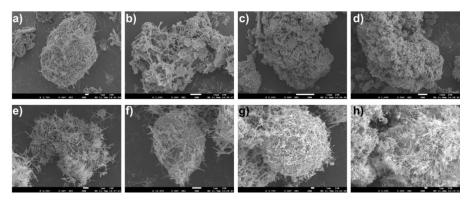


Figure S14. SEM images of a-d) the obtained Co_3O_4 materials and e-f) $Co_3O_4@MnO_2$ materials synthesized by the traditional method without any substrate.

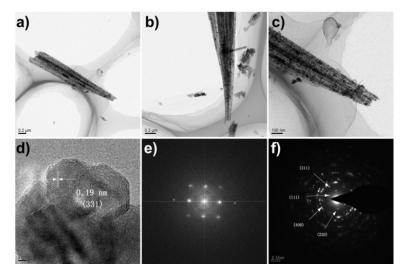


Figure S15. TEM images of the in-situ 3D hierarchical Co_3O_4 material C.

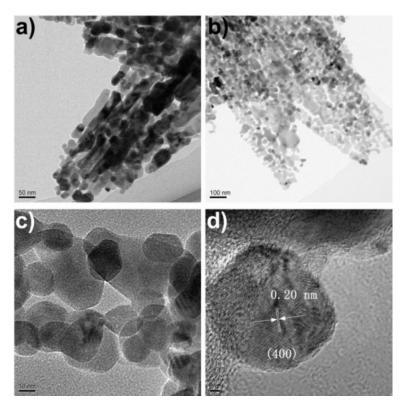


Figure S16. TEM images of the in-situ 3D hierarchical Co₃O₄ material D.

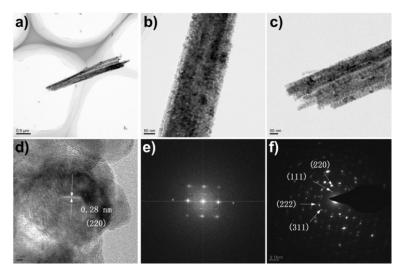


Figure S17. TEM images of the in-situ 3D hierarchical Co₃O₄ material E.

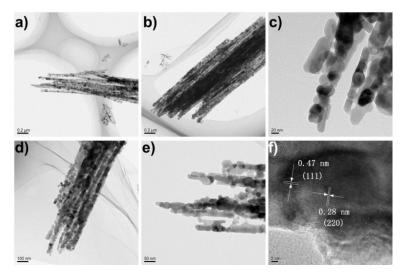


Figure S18. TEM images of the in-situ 3D hierarchical Co₃O₄ material F.

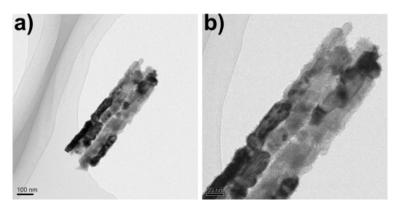


Figure S19. TEM images of the in-situ 3D hierarchical Co₃O₄@MnO₂ hybrid material D.

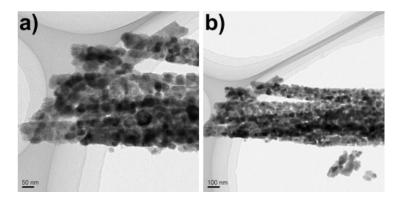


Figure S20. TEM images of the in-situ 3D hierarchical Co₃O₄@MnO₂ hybrid material F.

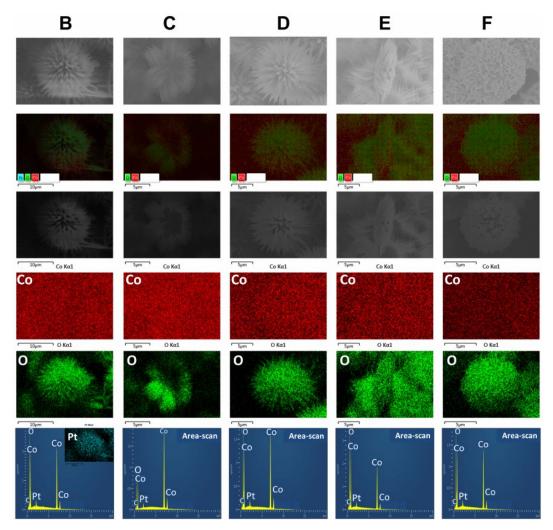


Figure S21. EDS mapping and Area-scan EDS spectra from a whole single $Co_3O_4@C$ 3D hierarchical structure B-F.

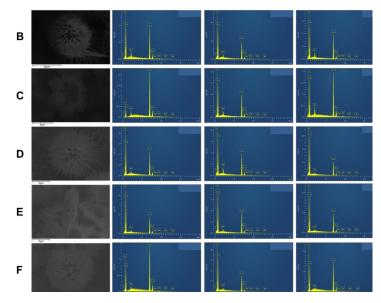


Figure S22. EDS spectra by the spot-scan method from a whole single 3D hierarchical Co₃O₄@C structure (B-F).

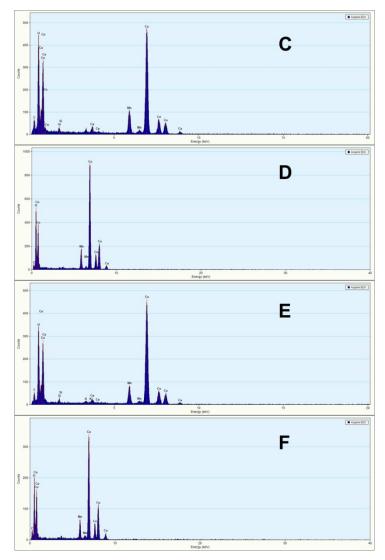


Figure S23. EDS spectra by the spot-scan method from a whole single 3D hierarchical Co_3O_4 @MnO₂ structure (C-F).

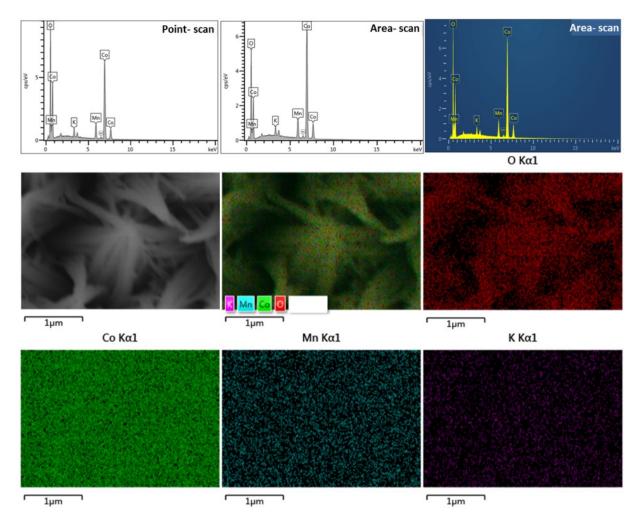


Figure S24. EDS mapping and EDS spectra by both the area-scan and spot-scan methods from a whole single 3D hierarchical $Co_3O_4@MnO_2$ structure (A).

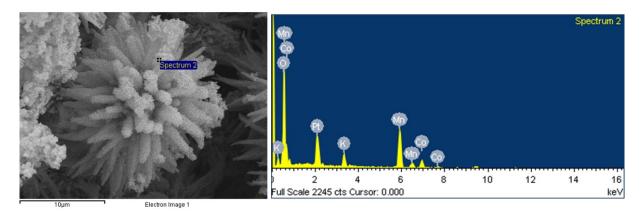


Figure S25. EDS spectra by the spot-scan method from a whole single 3D hierarchical Co_3O_4 @MnO₂ structure (B).

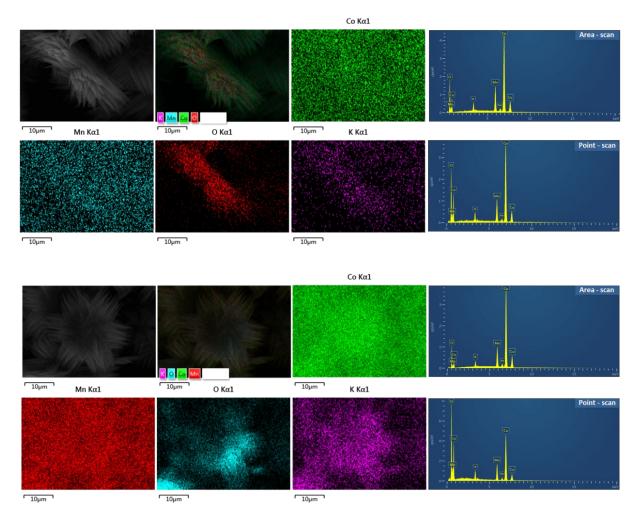


Figure S26. EDS mapping and EDS spectra by both the area-scan and spot-scan methods from a whole single 3D hierarchical $Co_3O_4@MnO_2$ structure (C).

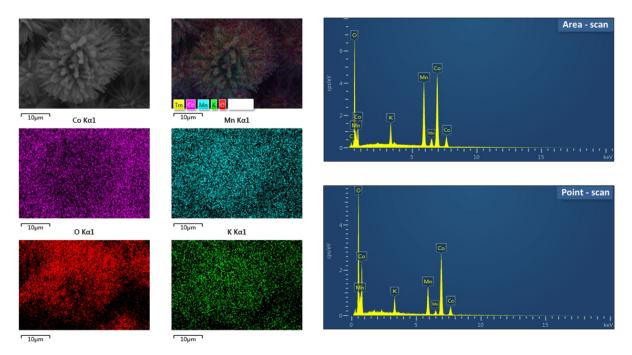
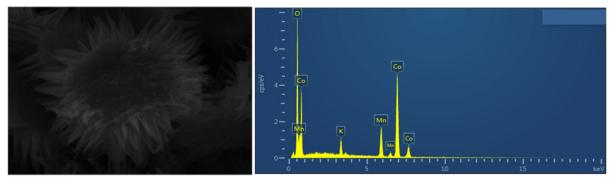


Figure S27. EDS mapping and EDS spectra by both the area-scan and spot-scan methods from a whole single 3D hierarchical $Co_3O_4@MnO_2$ structure (D).



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Figure S28. EDS spectra by the spot-scan method from a whole single 3D hierarchical Co_3O_4 @MnO₂ structure (E).

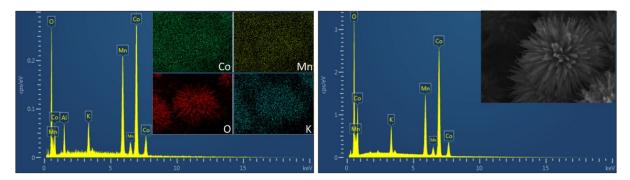


Figure S29. EDS mapping and EDS spectra by both the area-scan and spot-scan methods from a whole single 3D hierarchical $Co_3O_4@MnO_2$ structure (F).

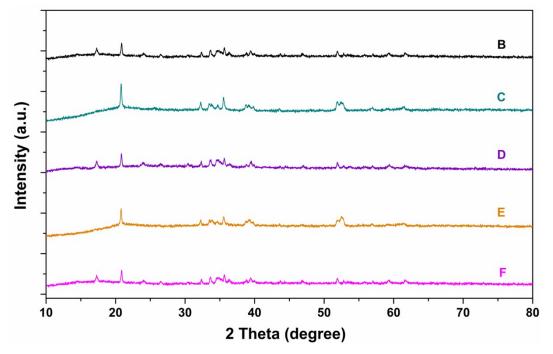


Figure S30. XRD patterns of the Co(OH)F precursors for the in-situ synthesized 3D hierarchical Co_3O_4 B-F materials.

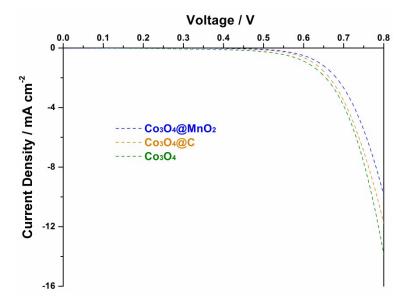


Figure S31. Dark I-V curves of the DSSCs based on Co_3O_4 , Co_3O_4 @C and Co_3O_4 @MnO₂ counter electrodes.

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