Hierarchical Nanowires via Oriented Attachment for Energy Storage Devices

Liang He¹, Mengyu Yan¹, Yunlong Zhao¹, Liqiang Mai¹
1. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, WUT-Harvard Joint Nano Key Laboratory, Wuhan University of Technology, Wuhan 430070, China.
Email: mlq518@whut.edu.cn

Hierarchical structures with high surface/body ratios, large surface areas, better permeability and more surface active sites can significantly increase energy density, power density and cycle performance, decrease self-aggregation of electrode material, and have great potential for energy storage devices. In the present work, through the crystal growth mechanism of 'oriented attachment', a series of hierarchical structures nanowires have been obtained, including hierarchical heterostructured nanowires, hierarchical mesoporous nanowires, and hierarchical scrolled nanowires which exhibit outstanding electrochemical performances and show potential applications in energy storage¹⁻⁴.

To increase faster ion diffusion and electron transport and lead to the improvement of energy density of supercapacitor, our group has synthesized the 3D hierarchical MnMoO₄/CoMoO₄ heterostructured nanowires¹. The ‘substrate’, MnMoO₄, has similar lattice parameters and can guide CoMoO₄ nanoparticle self-assembly and oriented crystallization to form this hierarchical heterostructured nanowires (Fig. 1a). We fabricated asymmetric supercapacitors. Compare with pure 1D nanowires, hierarchical heterostructured nanowires increase specific capacitance and energy density up to an order of magnitude. Recently, based on the ‘oriented attachment’, we also synthesized of hierarchical nanostructured material by growing Co(OH)₂ nanoflakes uprightly onto MoO₂ thin film with the enhanced capacitance of 800 F/g at 20 A/g.

To provide continuous free oxygen diffusion channels, we synthesized hierarchical ‘rods in wire’ mesoporous La₀.₅Sr₀.₅CoO₂.₉₁ (LSCO) nanowires. Those LSCO nanorods self-assemble at a low stirring rate and a bigger water pool in microemulsion, and then templated itself for the oriented growth of attached nanorods, which results in the formation of hierarchical mesoporous LSCO nanowires (Fig. 1b). We fabricated Li-air battery based on hierarchical mesoporous LSCO nanowires, which exhibits ultrahigh capacity, c.a., over 11000 mAh/g, with the improvement of one order of magnitude than LSCO nanoparticles.

Besides, to enhance stability of nanowire electrodes, V₂O₅ nanowire templated semi-hollow bicontinuous graphene scrolls architecture is designed and constructed through “oriented assembly” and “self-scroll” strategy (Fig. 1c). The VGS with interior cavities provide continuous electron and lithium ion transfer channel and space for free volume expansion of V₂O₅ nanowires during cycling, thus representing a unique architecture for excellent lithium ion storage capacity and cycling performance.

References
(2) Zhao, Y., et al. (2012). "Hierarchical mesoporous perovskite La₀.₅Sr₀.₅CoO₂.₉₁ nanowires with ultrahigh capacity for Li-air batteries." PNAS 109(48): 19569-19574.
(3) Yan, M. Y., et al. (2013). "Nanowire templated semi-hollow bicontinuous graphene scrolls: designed construction, mechanism and enhanced energy storage performances." JACS. Accepted.