

不同形貌纳米 NiCo_2O_4 的研究进展

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摘要: 纳米 NiCo_2O_4 因其独特的理化性能已广泛应用于能源储存与转换, 尤其是超级电容器领域。鉴于纳米材料的形貌对其性能的重要影响, 本文综述了不同形貌(纳米针、纳米线、纳米管、纳米片、球状、纳米花、珊瑚状及三维复合结构)纳米 NiCo_2O_4 的合成方法及其在相关领域的应用, 叙述了各种制备方法的基本原理、特点以及对纳米 NiCo_2O_4 形貌的调控规律。同时, 简要说明了材料形貌与尺寸对其性能影响的机理及规律。最后, 展望了纳米 NiCo_2O_4 在能源储存与转换领域中未来的发展方向。

关键词: 纳米; NiCo_2O_4 ; 形貌; 制备; 综述

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Preparation of NiCo_2O_4 with Various Morphologies: a Review

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Abstract: NiCo_2O_4 nanomaterials exhibit great potential in the fields of energy storage and conversion especially in supercapacitors for their unique physicochemical properties. Given the important impact of morphology of nano material on its performance, this review focuses on preparation methods and application of NiCo_2O_4 nanostructure with various morphologies including nanoneedle, nanowire, nanotube, nanosheet, sphere, nanoflower, coral-like structure and three-dimensional hybrid structure. Furthermore, the influence of morphology and particle size of NiCo_2O_4 on its properties is also introduced. Finally, the future research direction of NiCo_2O_4 nanomaterials in the fields of energy storage and conversion is prospected.

Key words: nanometer; NiCo_2O_4 ; morphologies; preparation; review

NiCo_2O_4 是一种具有尖晶石结构的二元过渡金属氧化物, 其中, 镍离子占据八面体空隙, 钴离子占据全部四面体及半数的八面体空隙^[1-2], 其导电性及电化学活性远高于单一的镍、钴氧化物, 并且同时存在 $\text{Co}^{3+}/\text{Co}^{2+}$ 和 $\text{Ni}^{3+}/\text{Ni}^{2+}$ 氧化还原电对可进行多电子反应^[3-4]。其晶体结构表面有多种活性中心和官能团, 如表面吸附的—OH 基团、吸附氧等。因

此, NiCo_2O_4 具有独特的光、电、磁及催化性能, 在催化剂^[5-10]、锂离子电池^[11-12]等方向具有一定的研究价值, 且被广泛应用于超级电容器^[13-17]领域。

除了材料的固有性质外, 形貌和尺寸也会极大地影响材料的性能^[18-20]。如当金的尺寸降至几十纳米时, 表面等离子体的共振吸收会使其颜色变成粉色, 金表面的拉曼散射增强^[21], 进一步收缩至 3 nm

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以下时,其催化活性会显著增强^[22];如球形银粉依靠颗粒间的点接触可有效提高其导电性能,被广泛应用于导电浆料^[23];针状或者纤维状磁粉具有各向异性且矩形比大,被广泛应用于高密度垂直磁记录材料^[24]。同样,各种形貌的纳米 NiCo_2O_4 材料的光、电、磁学性能不同,应用的领域也有差异。如 NiCo_2O_4 纳米纤维结构稳定且能加速电子的转移,对氧气析出反应有很高的电催化活性,成为电解水方面的研究热点^[25-26];纳米花、多孔网状结构 NiCo_2O_4 材料的比表面积大,可改善电解质的渗透和离子转移,在锂离子电池、超级电容器领域有着巨大的潜力^[27-29]。选择合适的制备方法是调控材料形貌的有效手段,不同的制备方法可以得到形貌各异的纳米 NiCo_2O_4 材料。因此,本文拟就近年纳米 NiCo_2O_4 形貌控制合成的研究展开论述,并指出今后的发展方向。

1 制备不同形貌的纳米 NiCo_2O_4 材料

1.1 三维形貌

三维结构材料因具有巨大的比表面积和高密度的缺陷而引起科研工作者的广泛关注,尤其在催化、电池、化学传感器和电致变色器件等领域有巨大的应用潜力^[30-31]。常见的三维形貌包括球状、纳米花、珊瑚状和三维复合结构等。合成三维纳米结构的方法主要有水热法、溶胶-凝胶法和微波合成法等。

1.1.1 球状

球状是纳米材料最常见的形貌之一,采用水热法易得到球状纳米粒子。该方法采用水溶液作为反应介质,并通过加热反应容器产生高温高压的环境,从而达到控制材料形貌的目的。制备过程中,水热反应主要控制 NiCo_2O_4 纳米材料前驱体的形貌,热分解后即可得到球状结构的 NiCo_2O_4 ^[32-33]。水热法简单、高效、易控且成本低廉,目前被广泛用于纳米结构的形貌控制合成。

Zou 等^[34]以水、乙醇混合溶液作为溶剂,尿素作为缓释剂和沉淀剂,通过水热法合成了三维结构的 NiCo_2O_4 微球。该微球由高长径比的超细纳米纤维组成,且纳米纤维作为结构单元呈放射状分布于微球表面(图 1)。用这种结构的 NiCo_2O_4 材料制备的电容器,其比容量高(电流密度 2 A/g 时比容量达 1284 F/g)、倍率性能良好、循环稳定性优越(3000 次循环后仅损失 2.5%)。Li 等^[35]以碳球为模板,采用水热法制备了双层空心 NiCo_2O_4 球,碳球的加入显著增加了 NiCo_2O_4 材料的比表面积(单层空心 NiCo_2O_4

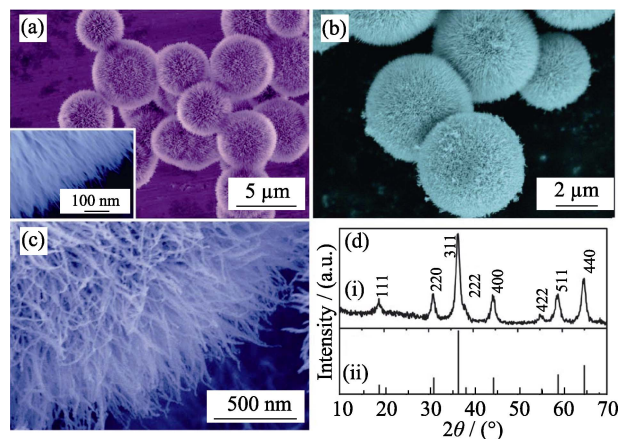


图 1 水热法制备 NiCo_2O_4 微球煅烧(a)前(b)~(c)后的 SEM 照片; (d) NiCo_2O_4 粉末 XRD 图谱^[34]

Fig. 1 SEM images of NiCo_2O_4 microsphere prepared by hydrothermal method: (a) before and (b, c) after calcination with (d) XRD patterns of NiCo_2O_4 powders^[34]

球为 $76.6 \text{ m}^2/\text{g}$, 双层空心 NiCo_2O_4 球为 $115.2 \text{ m}^2/\text{g}$), 提升了比容量(电流密度 1 A/g 下比容量从 445 F/g 上升到 568 F/g)。但碳球模板的使用增加了材料制备的成本,不利于大规模工业化制备。

与水热法不同,溶剂热法采用有机溶剂为反应环境,有机溶剂的性质往往对产物的形貌有重要影响。Liu 等^[36]以乙二醇作溶剂,采用简单的溶剂热法合成三维球状 NiCo_2O_4 ,并探究了在微波场的作用下,不同形貌 NiCo_2O_4 对有机底物的催化降解性能。与 NiCo_2O_4 纳米片、纳米棒、纳米颗粒相比,三维球状 NiCo_2O_4 催化降解效率最高:仅 10 min 内,该材料对刚果红的降解率就可达到 90.1%,其原因在于三维球状结构能有效利用微波场,展示出比表面积大的特性。

1.1.2 纳米花

纳米花的合成主要是采用基于液相反应的“软化学”路线,并通过自下而上的方法将纳米片或纳米纤维等初级结构单元组装成类似花状的多级结构。 NiCo_2O_4 纳米花的制备多采用水热法,其中表面活性剂发挥了重要作用,相关研究表明溴化十六烷三甲基铵(CTAB)、聚乙烯吡咯烷酮(PVP)、柠檬酸等表面活性剂有助于构建材料形貌与改善性能^[2,37-39]。An 等^[38]使用 PVP 作为表面活性剂,通过水热法制备了三维花状 NiCo_2O_4 ,其比表面积可达 $212.6 \text{ m}^2/\text{g}$,当电流密度为 1 A/g 时比容量高达 1191.2 F/g。然而该条件制备的三维花状 NiCo_2O_4 在充放电过程中易发生结构坍塌,循环稳定性不佳。Zhang 等^[40]同样在水热法中添加 PVP 并于 $180 \text{ }^\circ\text{C}$ 条件下合成了花状 NiCo_2O_4 ,PVP 作为结构导向剂通过配位效应可以有效地控制 NiCo_2O_4 的形貌^[41]。在反应过程中,PVP 通

过吡咯烷酮环上的官能团与金属离子配位, 有利于晶粒的各向异性生长, 并将粒子组装成花状结构^[42]。此外, NiCo_2O_4 表面上吸附的 PVP 在热分解过程中发生脱附并放出气体, 有助于分级介孔结构的形成。Cheng 等^[43]通过水热法制备了三维花状镍钴氧化物(图 2), 并研究了前驱体成分与热分解温度对产物形貌的影响。结果表明前驱体中镍含量越高, 相同热分解温度下产物的比表面积越大, 其原因在于 NiO 晶体尺寸更小且镍氢氧化物热分解温度更高。另外, 热分解温度也是影响产物多孔结构与颗粒大小的重要因素, 当热分解温度从 300 °C 升高到 500 °C 时, 比表面积缩小 1/4。

水热法虽易于控制产物形貌, 但要求严格控制反应条件, 多数情况下还需要结构导向剂。而微波法作为一种常用的辅助手段也可用于花状结构的合成。微波辅助可以快速加热到设定温度, 促进结晶过程迅速进行, 同时促使 NiCo_2O_4 前驱体发生相转变^[44-45]。Lei 等^[46]通过微波辅助法控制合成了花状 NiCo_2O_4 , 该花状结构由厚度约 15 nm 的花瓣状纳米片构筑而成(图 3)。他们通过改变反应时间探究花状结构的形成机制。当反应时间非常短时(2 min), 产物由大量的纳米颗粒聚集而成; 反应时间达到 5 min 时, 样品开始呈现花状结构, 该结构由花瓣状纳米片组成, 纳米片上附着的纳米颗粒是下一阶段纳米片生长的位点; 反应时间达到 15 min 时形成完整的花状结构。

1.1.3 珊瑚状

珊瑚状 NiCo_2O_4 的制备方法主要为溶胶-凝胶法。溶胶-凝胶法过程简单、成本低且产物纯度高、

均匀性好而被科研工作者广泛用于材料的制备。该方法将包含无机金属盐或者金属有机物的前驱体溶液转化为无机固态, 再通过热分解制备产物粉末^[47-49]。制备过程中, 表面活性剂、溶剂、反应时间与温度是决定产物结构与形貌的主要因素^[50]。Wu 等^[51]使用柠檬酸作为螯合配位体, H_2O -DMF(*N,N*-二甲基甲酰胺)作为混合溶剂, 通过溶胶-凝胶法合成了珊瑚状 NiCo_2O_4 。产物作为超级电容器电极在质量负荷为 5.6 mg/cm^2 下最大比容量可达 217 F/g, 且 600 次充放电循环后容量保持率为 96.3%。溶胶-凝胶法制得的纳米材料均匀性好, 化学计量比也可精确控制, 但也受到成本高、易团聚等因素的制约。

1.1.4 三维复合结构

三维复合结构因形貌多样、比表面积大而成为当今的研究热点, 其合成多采用模板法。该法易于调控材料的尺寸及形状, 是制备特殊形貌纳米材料最重要的方法之一。纳米碳材料比表面积大、导电性好、化学稳定性高, 目前被广泛用于模板法合成三维复合结构材料^[52-56]。Wu 等^[57]首先以泡沫镍为模板, 通过化学气相沉积制备掺氮碳纳米管, 并形成三维交织网状结构。接着在掺氮碳纳米管上电沉积生长超细 NiCo_2O_4 纳米片(图 4), 掺氮碳纳米管作为模板为离子和电子转移提供了优良的导电通道。该三维复合材料作为超级电容器电极表现出高比容量(电流密度 1 A/g 时比容量达 1472 F/g)、良好的倍率性能以及杰出的循环稳定性(3000 次循环后仅损失 1%)。Nguyen 等^[58]在泡沫镍支持的石墨烯上电沉积尺寸为 3~5 nm 的 NiCo_2O_4 纳米颗粒。该复合结构具有巨大的比表面积和出色的结构稳定性, 在高电

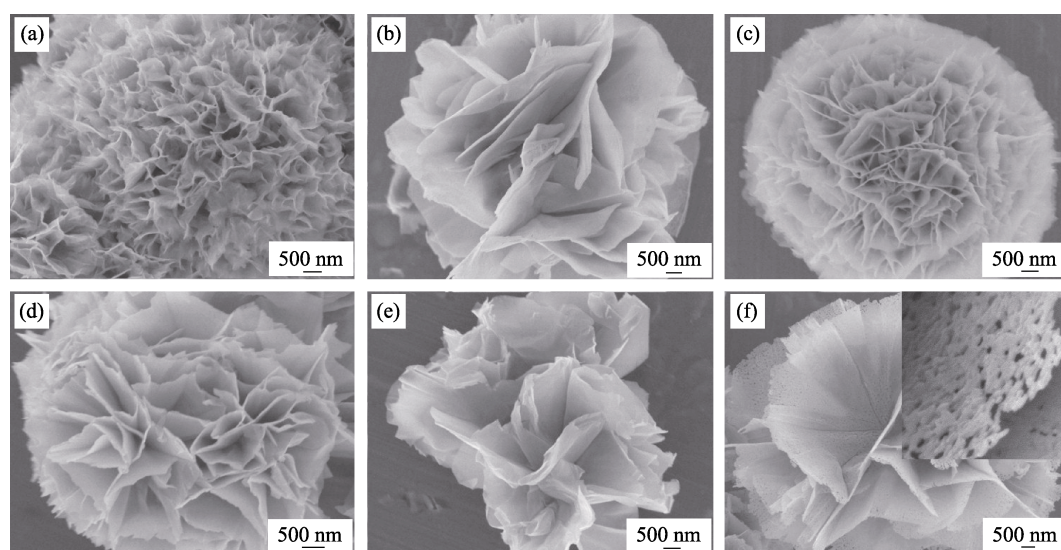


图 2 Ni/Co 摩尔比为 (a) 1:0、(b) 7:3、(c) 5:5、(d) 3:7 和(e)-(f) 0:1 的花状结构镍钴氧化物的 SEM 照片^[43]

Fig. 2 SEM images of flower-like nickel-cobalt oxides prepared with initial Ni/Co molar ratio of (a) 1:0, (b) 7:3, (c) 5:5, (d) 3:7 and (e, f) 0:1^[43]

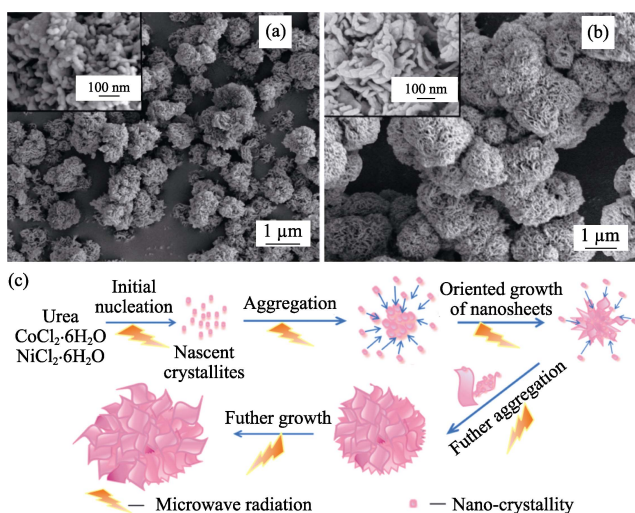


图 3 (a)~(b) 微波辅助法获得的花状 NiCo_2O_4 的 SEM 照片, (c) 花状形貌形成过程示意图^[46]

Fig. 3 (a, b) SEM images of flower-shaped NiCo_2O_4 prepared by microwave-assisted approach, (c) schematic illustration of the morphological evolution of flower-shaped microsphere precursors^[46]

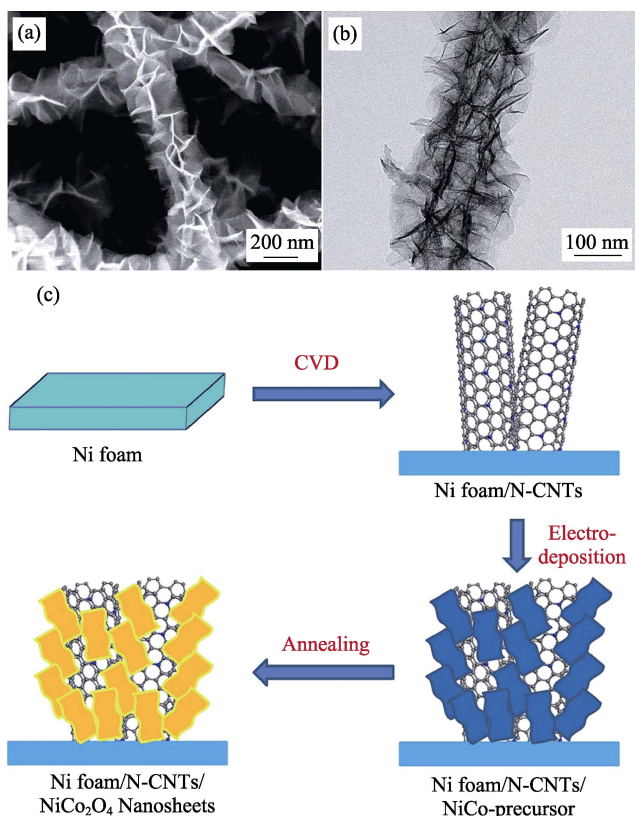


图 4 (a)~(b) N-CNT/ NiCo_2O_4 纳米片的 TEM 照片和 (c) N-CNT/ NiCo_2O_4 的制备过程示意图^[57]

Fig. 4 (a, b) TEM images of the N-CNT/ NiCo_2O_4 nanosheets, (c) schematic diagram of the fabrication process of N-CNT/ NiCo_2O_4 ^[57]

流密度 7.5 A/g 下比电容仍高达 1950 F/g 。

除碳纳米材料外,金属氧化物也常用作 NiCo_2O_4 三维复合结构合成的模板。金属氧化物(如 Co_3O_4 、

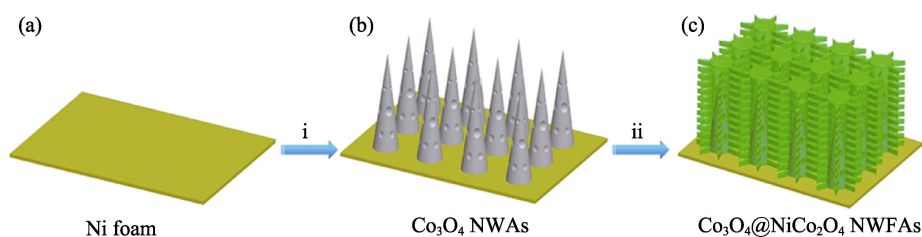
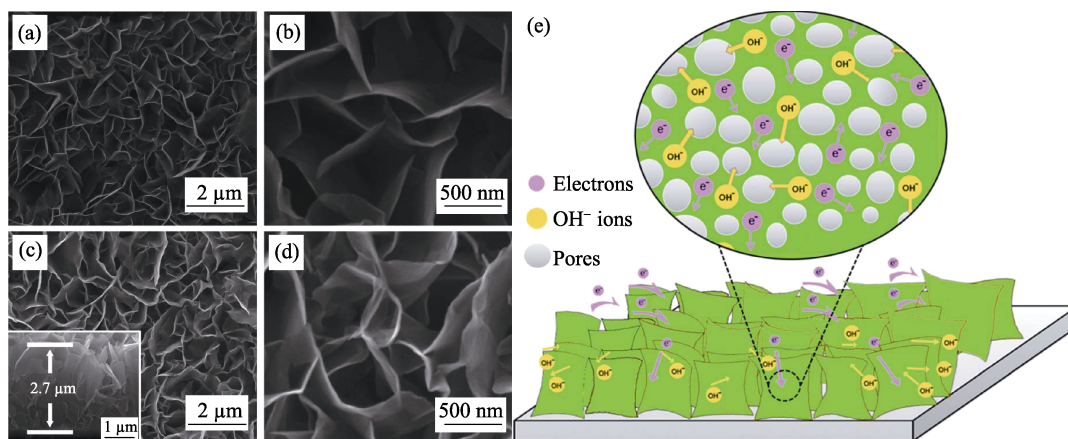
NiO)与 NiCo_2O_4 复合而成的三维材料具有丰富的活性位点、优良的电子收集率以及显著的协同效应^[59]。Zhang 等^[60]以 Co_3O_4 纳米线阵列为模板,电沉积合成尺寸小于 10 nm 的超细 NiCo_2O_4 纳米片(图 5)。 Co_3O_4 与 NiCo_2O_4 纳米结构的复合展现出了优秀的协同效应。 Co_3O_4 纳米阵列为 NiCo_2O_4 的生长提供了模板,避免了颗粒团聚,并确保了离子的有效扩散;而 NiCo_2O_4 的引入则降低了 Co_3O_4 的电荷转移电阻,促进了活性材料中电子的快速传递。该复合材料作为超级电容器电极具有良好的电化学性能:高电流密度 20 A/g 下比容量高达 526.7 F/g (几乎是原 Co_3O_4 比容量的 2.5 倍)。

1.2 二维形貌

与三维纳米材料不同,二维纳米材料是由纳米晶构成的单层或多层薄层结构材料,其在两个维度上具有延伸性。该结构表面积大,离子迁移路径短,具有广阔的应用前景^[61-65]。二维钴酸镍纳米材料的主要形貌为纳米片,其合成方法包括电沉积、化学沉积等。

电沉积主要通过电解过程将电镀液中悬浮的微米或亚微米尺寸的颗粒沉积在电化学合成的固相基底上^[66-68],包括前驱体溶液的形成、纳米颗粒的共电沉积和热分解等过程^[69]。Lou 等^[70]在泡沫镍的基底上利用电沉积合成了超细多孔 NiCo_2O_4 纳米片。该介孔结构有利于电极间电解质的迁移,同时促进双电层间的充放电,并使氧化还原反应快速发生。产物作为超级电容器电极在高电流密度(20 A/g)下依然展现出极高的比容量(1450 F/g)。Lu 等^[71]通过无模板电沉积法控制合成了厚度为 $20\sim 40 \text{ nm}$ 且具有微孔结构的 NiCo_2O_4 纳米片(图 6)。该纳米片在空气气氛、 $200 \text{ }^\circ\text{C}$ 下煅烧 3 h 后形貌与结构均未发生改变,表明其层状的纳米结构具有较好的热稳定性。 NiCo_2O_4 纳米片独特的相连介孔结构可以加速电子和离子的渗透与扩散,从而显著提升其电化学性能。电沉积法虽然工艺简单且产物纯度高,但需要消耗大量电能,在工业应用中受到限制。

化学沉积法作为一种常见的纳米薄膜材料制备方法,通过控制水浴温度、pH、溶液浓度和反应时间等条件,可以在基底表面合成不同形貌的纳米材料^[72]。Zhang 等^[64]通过化学浴沉积法在不同的导电基底(泡沫镍、钛箔、不锈钢箔、柔性石墨纸)上合成了 NiCo_2O_4 纳米片。该结构比表面积可达 $112.6 \text{ m}^2/\text{g}$,孔径为 $2\sim 5 \text{ nm}$ 。将该材料循环 3000 次后,在低电流密度(8.5 mA/cm^2)下损失量仅为 6.7% ,而高电流密度(25 mA/cm^2)下损失量为 17.1% 。Pu 等^[73]通过水热法和热处理制备了平均直径约为 100 nm 、

图 5 $\text{Co}_3\text{O}_4@/\text{NiCo}_2\text{O}_4$ 纳米复合物的制备过程示意图^[60]Fig. 5 Illustration of the fabrication process of $\text{Co}_3\text{O}_4@/\text{NiCo}_2\text{O}_4$ ^[60]图 6 电沉积法制备的 NiCo_2O_4 纳米片在煅烧(a)~(b)前、(c)~(d)后的 SEM 照片; (e) NiCo_2O_4 纳米片上电子与离子传递示意图^[71]Fig. 6 SEM images of NiCo_2O_4 nanosheets prepared by electrodeposition: (a, b) before and (c, d) after calcination, and (e) schematic illustration of the transportation of species on porous NiCo_2O_4 nanosheets^[71]

厚度为 25 nm 的 NiCo_2O_4 六方纳米片, 并研究了热处理温度对形貌及电化学性能的影响。相较 350 °C 而言, 热处理温度为 300 °C 时所得产物的比表面积更大(67.08 m^2/g)、孔径更小(8.32 nm), 因而其表现出更加优越的电化学性能。

1.3 一维形貌

一维纳米材料具有单分散性、多孔性、结构稳定性的特点而在近年吸引了广泛注意^[74-76]。一维纳米材料通常指具有高长径比的形貌^[77], 具体表现为纳米针、纳米线、纳米管等。目前制备一维纳米材料的方法包括液相法、水热法及静电纺丝法等。

1.3.1 纳米针

纳米针是最常见的一维纳米形貌之一, 采用液相法易得到纳米针形貌的材料。Zhang 等^[78]以泡沫镍为基底, 采用液相沉淀热分解法控制形貌, 合成了 NiCo_2O_4 纳米针。制备过程中, 反应条件对前驱体的形貌影响比较大: 沉淀剂尿素的加入量增加, 长径比也随之增大; 延长反应时间使 NiCo_2O_4 短纳米棒转变为纳米针, 通过热分解即可原位得到底部直径约 100 nm、尖端直径 3~5 nm 的 NiCo_2O_4 纳米针。将这种结构的 NiCo_2O_4 应用于超级电容器, 电容器的容量和循环稳定性均显著提高, 可能是由于其比表面积大且一维结构有利于增大电极/电解液

间的接触面积。

1.3.2 纳米线

纳米线的合成常采用液相沉积法。该方法通过成核、聚集、合并和颗粒长大等过程, 从过饱和溶液中析出固体沉淀, 以达到制备纳米材料的目的。固相析出过程中, 成核中心是颗粒聚集的基础, 而聚集颗粒的合并则为纳米结构的形成提供了保障^[79-80]。Jiang 等^[81]以乙醇和聚乙二醇为混合溶剂, 草酸为沉淀剂, 通过持续搅拌液相获得前驱体。将前驱体在 250 °C、空气条件下煅烧 3 h 即可得到多孔 NiCo_2O_4 纳米线, 该纳米线由尺寸为 3~6 nm 的超细纳米颗粒组成, 比表面积为 202.2 m^2/g 。多孔 NiCo_2O_4 纳米线应用于超级电容器时具有较高的比容量(电流密度为 1 A/g 时比电容高达 743 F/g)、优秀的倍率性能(电流密度为 40 A/g 时容量保持率为 78.6%)、良好的循环稳定性(3000 次循环后仅下降 6.2%)。

Shen 等^[82]采用表面活性剂辅助水热法并结合短时间热处理在碳布上合成了 NiCo_2O_4 纳米线阵列。该纳米线直径约 150 nm, 长度可达几个微米, 由许多直径 10~20 nm 的纳米粒组成(图 7)。Chen 等^[83]结合水热法和电化学沉积法制备了核壳结构的 NiCo_2O_4 纳米线。该纳米线对氧析出反应具有良好的电催化性, 在电流密度 10 mA/cm^2 下展现出高阳极电流、低起始电位, 且过电势仅为 320 mV。

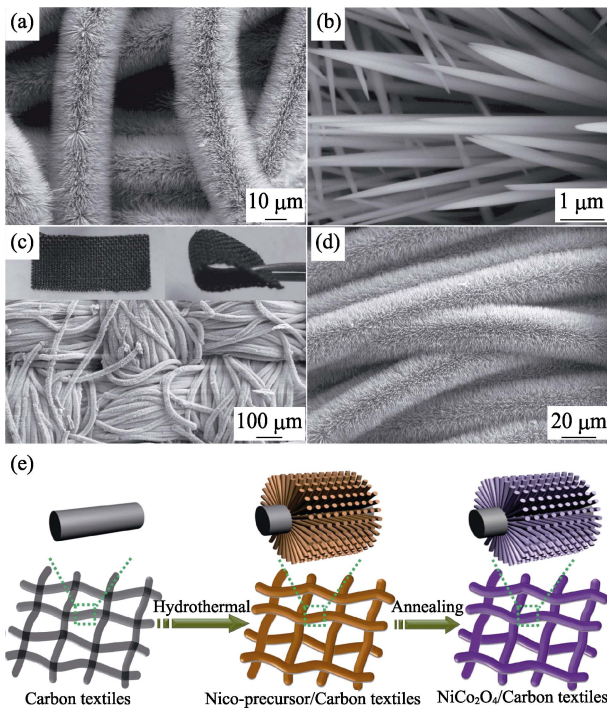


图 7 碳基 NiCo_2O_4 纳米线阵列前驱体的(a)低倍和(b)高倍 SEM 照片; 碳基 NiCo_2O_4 纳米线阵列的(c)低倍和(d)高倍 SEM 照片; (e)碳基 NiCo_2O_4 纳米线阵列的合成示意图^[81]

Fig. 7 SEM images of the NiCo_2O_4 precursor NWAs/carbon textiles composite: (a) low and (b) high magnification, SEM images of the NiCo_2O_4 NWAs/carbon textiles composite: (c) low and (d) high magnification, and (e) schematic illustration of the formation of NiCo_2O_4 NWAs/carbon textiles composite^[81]

1.3.3 纳米管

相比于其他制备方法, 静电纺丝是一种简单、多功能且经济有效的制备纳米材料的方法^[84-85]。在纳米材料的制备过程中, 前驱体浓度、溶液黏度、聚合物类型以及静电纺丝参数(外加电压、工作距离、进给速度)等因素会对纳米材料的形貌和尺寸分布产生影响^[30]。Srinivasan 等^[86]使用静电纺丝法制备了多孔 NiCo_2O_4 纳米管。在制备过程中发现, 前驱体浓度与产物形貌的关系密切: 当前驱体与 PVP 浓度比分别为 0.61:1, 0.44:1 和 0.87:1 时, 可分别得到直径约 100 nm、壁厚约 33 nm 的纳米管、纳米线和纳米带(图 8)。其中 NiCo_2O_4 多孔纳米管具有较大的比表面积和空心一维纳米结构, 作为超级电容器, 在电流密度 1 A/g 时比容量可达 1647 F/g。

静电纺丝法虽然操作简单、可连续生产, 但其对溶液浓度、电场强度、给料速度等要求也较高, 而水热法成本较低且反应条件易控制。Lou 等^[87]通过一步水热法制备了 NiCo_2O_4 分层四方微管, 并研究了反应时间对产物形貌的影响。反应初始阶段合成顶部为塔尖状的光滑四方棱柱(图 9(a)); 反应时间

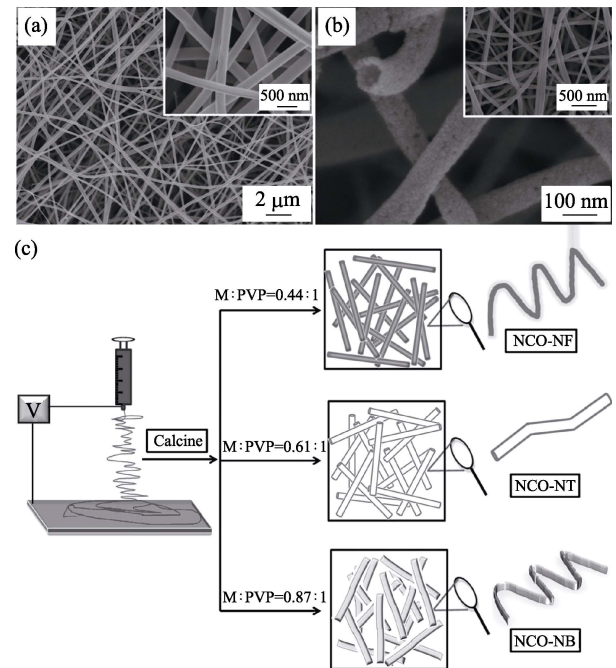


图 8 (a)~(b) NiCo_2O_4 纳米管 SEM 照片, (c) NiCo_2O_4 纳米管、纳米线、纳米环的制备过程示意图^[86]

Fig. 8 (a, b) SEM images of the NiCo_2O_4 nanotubes and (c) schematic illustration of preparation of NiCo_2O_4 nanofibers, nanotubes and nanobelts^[86]

延长到 6 h, 棱柱表面开始形成一些小而细的纳米片(图 9(b)); 随着水热反应过程的推进, 纳米片开始长大并固定层状外壳, 同时内层核开始从两端收缩(图 9(c)); 反应结束时, 初始的固体棱柱完全转化为由纳米片构成的空心微管(图 9(d))。

2 结论与展望

形貌对材料的性能有着重要的影响, 目前可采用不同的制备方法得到多种形貌的纳米 NiCo_2O_4 。一维纳米 NiCo_2O_4 主要通过液相法和静电纺丝法获得, 二维纳米 NiCo_2O_4 主要通过电沉积法与化学沉积法等方法获得, 而采用水热法、溶胶-凝胶法和模板法等通常可以制备出三维纳米 NiCo_2O_4 。三维结构的纳米 NiCo_2O_4 通常具有较大的比表面积与高密度缺陷, 在能源储存与转换领域有较大优势。另外, 将特殊结构的 NiCo_2O_4 纳米材料与碳纳米材料复合, 可极大地扩大材料的比表面积, 提高孔隙率, 增加电化学活性位点, 缩短电子与离子的传递路径, 显著提高材料的电化学性能。因此碳基 NiCo_2O_4 三维复合材料在未来具有重要的研究价值。总之, 采用合适的制备体系, 使之易于实现纳米粒子尺寸、形貌、有序排列等方面的调控是未来纳米 NiCo_2O_4 制备研究的重点。

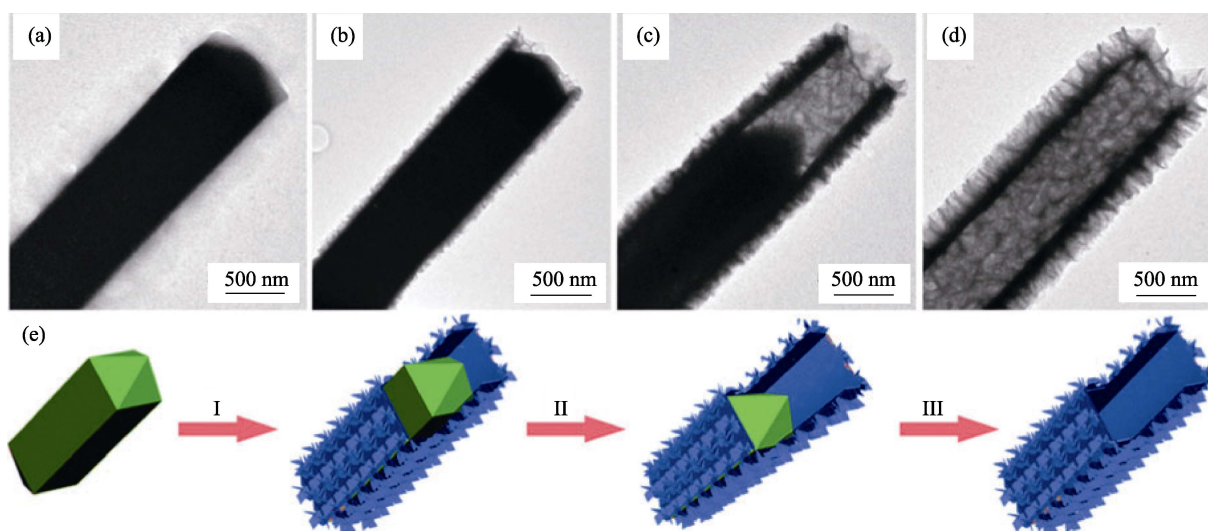


图 9 不同反应时间得到 NiCo₂O₄ 样品的 TEM 照片: (a) 4 h, (b) 6 h, (c) 10 h, (d) 12 h; (e) NiCo₂O₄ 分层四方微管制备过程示意图^[87]
 Fig. 9 Representative TEM images of the samples obtained after reaction for (a) 4 h, (b) 6 h, (c) 10 h, (d) 12 h and (e) their corresponding schematic illustration of the formation process for hierarchical NiCo₂O₄ tetragonal microtubes^[87]

参考文献:

- [1] WANG Q, LIU B, WANG X, *et al.* Morphology evolution of urchin-like NiCo₂O₄ nanostructures and their applications as pseudocapacitors and photoelectrochemical cells. *Journal of Materials Chemistry*, 2012, **22(40)**: 21647–21653.
- [2] YUAN C, LI J, HOU L, *et al.* Polymer-assisted synthesis of a 3D hierarchical porous network-like spinel NiCo₂O₄ framework towards high-performance electrochemical capacitors. *Journal of Materials Chemistry A*, 2013, **1(37)**: 11145–11151.
- [3] HU L, WU L, LIAO M, *et al.* Electrical transport properties of large, individual NiCo₂O₄ nanoplates. *Advanced Functional Materials*, 2012, **22(5)**: 998–1004.
- [4] WU Z, ZHU Y, JI X. NiCo₂O₄-based materials for electrochemical supercapacitors. *Journal of Materials Chemistry A*, 2014, **2(36)**: 14759–14772.
- [5] QIAN L, GU L, YANG L, *et al.* Direct growth of NiCo₂O₄ nanostructures on conductive substrates with enhanced electrocatalytic activity and stability for methanol oxidation. *Nanoscale*, 2013, **5(16)**: 7388–7396.
- [6] ZHAN J, LU E, CAI M, *et al.* Controlled synthesis and electrocatalytic performance of porous nickel cobaltite rods. *Journal of Inorganic Materials*, 2017, **32(1)**: 11–17.
- [7] DING R, QI L, JIA M, *et al.* Facile synthesis of mesoporous spinel NiCo₂O₄ nanostructures as highly efficient electrocatalysts for urea electro-oxidation. *Nanoscale*, 2014, **6(3)**: 1369–1376.
- [8] HAN L, YU X Y, LOU X W. Formation of prussian-blue-analog nanocages via a direct etching method and their conversion into Ni-Co-mixed oxide for enhanced oxygen evolution. *Advanced Materials*, 2016, **28(23)**: 4601–4605.
- [9] GAO X, ZHANG H, LI Q, *et al.* Hierarchical NiCo₂O₄ hollow microcuboids as bifunctional electrocatalysts for overall water-splitting. *Angewandte Chemie International Edition*, 2016, **55(21)**: 6290–6294.
- [10] WANG J, FU Y, XU Y, *et al.* Hierarchical NiCo₂O₄ hollow nanospheres as high efficient bi-functional catalysts for oxygen reduction and evolution reactions. *International Journal of Hydrogen Energy*, 2016, **41(21)**: 8847–8854.
- [11] LI L, CHEAH Y, KO Y, *et al.* The facile synthesis of hierarchical porous flower-like NiCo₂O₄ with superior lithium storage properties. *Journal of Materials Chemistry A*, 2013, **1(36)**: 10935–10941.
- [12] LI J, XIONG S, LIU Y, *et al.* High electrochemical performance of monodisperse NiCo₂O₄ mesoporous microspheres as an anode material for Li-ion batteries. *ACS Appl. Mater. Interfaces*, 2013, **5(3)**: 981–988.
- [13] MA L, SHEN X, HU Z, *et al.* High performance supercapacitor electrode materials based on porous NiCo₂O₄ hexagonal nanoplates/reduced graphene oxide composites. *Chemical Engineering Journal*, 2015, **262(15)**: 980–988.
- [14] GAO Z, YANG W, WANG J, *et al.* Flexible all-solid-state hierarchical NiCo₂O₄/porous graphene paper asymmetric supercapacitors with an exceptional combination of electrochemical properties. *Nano Energy*, 2015, **13**: 306–317.
- [15] YU L, GUAN B, XIAO W, *et al.* Formation of yolk-shelled Ni-Co mixed oxide nanoprisms with enhanced electrochemical performance for hybrid supercapacitors and lithium ion batteries. *Advanced Energy Materials*, 2015, **5(21)**: 1500981–1–7.
- [16] WANG N, ZHAO P, ZHANG Q, *et al.* Monodisperse nickel/cobalt oxide composite hollow spheres with mesoporous shell for hybrid supercapacitor: a facile fabrication and excellent electrochemical performance. *Composites Part B Engineering*, 2017, **113(15)**: 144–151.
- [17] GUAN C, LIU X, REN W, *et al.* Rational design of metal-organic framework derived hollow NiCo₂O₄ arrays for flexible supercapacitor and electrocatalysis. *Advanced Energy Materials*, 2017, **7(8)**: 1602391–1–8.
- [18] WEN R J, YANG Z H, FAN X, *et al.* Electrochemical performances of ZnO with different morphology as anodic materials for Ni/Zn secondary batteries. *Electrochimica Acta*, 2012, **83(12)**: 376–382.
- [19] TONG T, SHEREEF A, WU J, *et al.* Effects of material morphology on the phototoxicity of nano-TiO₂ to bacteria. *Environmental Science & Technology*, 2013, **47(21)**: 12486–12495.
- [20] ZHANG Q, UCHAKER E, CANDELARIA S L, *et al.* Nanomaterials for energy conversion and storage. *Chemical Society Reviews*, 2013, **42(7)**: 3127–3171.

- [21] GHOSH S K, PAL T. Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications. *Chemical Reviews*, 2007, **107**(11): 4797–4862.
- [22] SARDAR R, FUNSTON A M, MULVANEY P, *et al.* Gold nanoparticles: past, present, and future. *Langmuir*, 2009, **25**(24): 13840–13851.
- [23] YUAN L, WAN C, YE X, *et al.* Facial synthesis of silver-incorporated conductive polypyrrole submicron spheres for supercapacitors. *Electrochimica Acta*, 2016, **213**(20): 115–123.
- [24] KIM J, LEE S B, LEE S K, *et al.* Magnetic thermal dissipations of FeCo hollow fibers filled in composite sheets under alternating magnetic field. *Applied Surface Science*, 2017, **415**(1): 114–118.
- [25] JIN C, LU F, CAO X, *et al.* Facile synthesis and excellent electrochemical properties of NiCo₂O₄ spinel nanowire arrays as a bifunctional catalyst for the oxygen reduction and evolution reaction. *Journal of Materials Chemistry A*, 2013, **1**(39): 12170–12177.
- [26] PENG Z, JIA D, AL-ENIZI A M, *et al.* From water oxidation to reduction: homologous Ni-Co based nanowires as complementary water splitting electrocatalysts. *Advanced Energy Materials*, 2015, **5**(9): 1402031–1–7.
- [27] CHEN H, JIANG J, ZHANG L, *et al.* Facile synthesized porous NiCo₂O₄ flowerlike nanostructure for high-rate supercapacitors. *Journal of Power Sources*, 2014, **248**(4): 28–36.
- [28] WANG Q, WANG X, XU J, *et al.* Flexible coaxial-type fiber supercapacitor based on NiCo₂O₄ nanosheets electrodes. *Nano Energy*, 2014, **8**(9): 44–51.
- [29] ZHOU J, HUANG Y, CAO X, *et al.* Two-dimensional NiCo₂O₄ nanosheet-coated three-dimensional graphene networks for high-rate, long-cycle-life supercapacitors. *Nanoscale*, 2015, **7**(16): 7035–7039.
- [30] CHEN D, WANG Q, WANG R, *et al.* Ternary oxide nanostructured materials for supercapacitors: a review. *Journal of Materials Chemistry A*, 2015, **3**(19): 10158–10173.
- [31] ZHANG L, WU H B, LOU X W. Iron-oxide-based advanced anode materials for lithium-ion batteries. *Advanced Energy Materials*, 2014, **4**(4): 1300958–1–11.
- [32] ZHAO Q, MA L, ZHANG Q, *et al.* SnO₂-based nanomaterials: synthesis and application in lithium-ion batteries and supercapacitors. *Journal of Nanomaterials*, 2015, **2015**(6): 6–21.
- [33] WANG C, ZHOU E, DENG X, *et al.* Three-dimensionally porous NiCo₂O₄ nanoneedle arrays for high performance supercapacitor. *Science of Advanced Materials*, 2016, **8**(6): 1298–1304.
- [34] ZOU R, XU K, WANG T, *et al.* Chain-like NiCo₂O₄ nanowires with different exposed reactive planes for high-performance supercapacitors. *Journal of Materials Chemistry A*, 2013, **1**(30): 8560–8566.
- [35] LI X, JIANG L, ZHOU C, *et al.* Integrating large specific surface area and high conductivity in hydrogenated NiCo₂O₄ double-shell hollow spheres to improve supercapacitors. *NPG Asia Materials*, 2015, **7**(3): 165–173.
- [36] LIU X, DAN X, ZHANG D, *et al.* Superior performance of 3D Co-Ni bimetallic oxides for catalytic degradation of organic dye: investigation on the effect of catalyst morphology and catalytic mechanism. *Applied Catalysis B: Environmental*, 2016, **186**: 193–203.
- [37] HSU C T, HU C C. Synthesis and characterization of mesoporous spinel NiCo₂O₄ using surfactant-assembled dispersion for asymmetric supercapacitors. *Journal of Power Sources*, 2013, **242**(22): 662–671.
- [38] AN C, WANG Y, HUANG Y, *et al.* Novel three-dimensional NiCo₂O₄ architectures: solvothermal synthesis and electrochemical properties. *CrystEngComm*, 2013, **16**(3): 385–392.
- [39] KONG L B, LU C, LIU M C, *et al.* Effect of surfactant on the morphology and capacitive performance of porous NiCo₂O₄. *Journal of Solid State Electrochemistry*, 2013, **17**(5): 1463–1471.
- [40] ZHANG Y, MA M, YANG J, *et al.* Selective synthesis of hierarchical mesoporous spinel NiCo₂O₄ for high-performance supercapacitors. *Nanoscale*, 2014, **6**(8): 4303–4308.
- [41] WANG X, WU X L, GUO Y G, *et al.* Synthesis and lithium storage properties of Co₃O₄ nanosheet-assembled multishelled hollow spheres. *Advanced Functional Materials*, 2010, **20**(10): 1680–1686.
- [42] LEE D, KIM B, CHEN Z. One-pot synthesis of a mesoporous NiCo₂O₄ nanoplatelet and graphene hybrid and its oxygen reduction and evolution activities as an efficient bi-functional electrocatalyst. *Journal of Materials Chemistry A*, 2013, **1**(15): 4754–4762.
- [43] ZHANG J, LIU F, CHENG J P, *et al.* Binary nickel-cobalt oxides electrode materials for high-performance supercapacitors: influence of its composition and porous nature. *ACS Applied Materials & Interfaces*, 2015, **7**(32): 17630–17640.
- [44] TSENG C C, LEE J L, LIU Y M, *et al.* Microwave-assisted hydrothermal synthesis of spinel nickel cobaltite and application for supercapacitors. *Journal of the Taiwan Institute of Chemical Engineers*, 2013, **44**(3): 415–419.
- [45] HU C C, HSU C T, CHANG K H, *et al.* Microwave-assisted hydrothermal annealing of binary Ni-Co oxy-hydroxides for asymmetric supercapacitors. *Journal of Power Sources*, 2013, **238**(28): 180–189.
- [46] LEI Y, LI J, WANG Y, *et al.* Rapid microwave-assisted green synthesis of 3D hierarchical flower-shaped NiCo₂O₄ microsphere for high-performance supercapacitor. *ACS Applied Materials & Interfaces*, 2014, **6**(3): 1773–1780.
- [47] HENCH L L, WEST J K. The Sol-Gel process. *Chemical Reviews*, 1990, **90**(1): 33–72.
- [48] NIEDERBERGER M. Nonaqueous Sol-Gel routes to metal oxide nanoparticles. *Accounts of Chemical Research*, 2007, **38**(49): 793–800.
- [49] LIVAGE J, HENRY M, SANCHEZ C. Sol-Gel chemistry of transition metal oxides. *Progress in Solid State Chemistry*, 1988, **18**(4): 259–341.
- [50] SUI R, YOUNG J L, BERLINGUETTE C P. Sol-Gel synthesis of linear Sn-doped TiO₂ nanostructures. *Journal of Materials Chemistry*, 2009, **20**(3): 498–503.
- [51] YE Q W, XIANG Y C, PING T J, *et al.* Sol-Gel approach for controllable synthesis and electrochemical properties of NiCo₂O₄ crystals as electrode materials for application in supercapacitors. *Electrochimica Acta*, 2011, **56**(22): 7517–7522.
- [52] LIU W, LU C, LIANG K, *et al.* A three dimensional vertically aligned multiwall carbon nanotube/NiCo₂O₄ core/shell structure for novel high-performance supercapacitors. *Journal of Materials Chemistry A*, 2014, **2**(14): 5100–5107.
- [53] CAI F, KANG Y, CHEN H, *et al.* Hierarchical CNT@NiCo₂O₄ core-shell hybrid nanostructure for high-performance supercapacitors. *Journal of Materials Chemistry A*, 2014, **2**(29): 11509–11515.
- [54] WEI Y, CHEN S, SU D, *et al.* 3D mesoporous hybrid NiCo₂O₄@graphene nanoarchitectures as electrode materials for supercapacitors with enhanced performances. *Journal of Materials Chemistry A*, 2014, **2**(21): 8103–8109.

- [55] WANG L, WANG X, XIAO X, *et al.* Reduced graphene oxide/nickel cobaltite nanoflake composites for high specific capacitance supercapacitors. *Electrochimica Acta*, 2013, **111(6)**: 937–945.
- [56] SUN S, WANG S, LI S, *et al.* Asymmetric supercapacitors based on NiCo₂O₄/three dimensional graphene composite and three dimensional graphene with high energy density. *Journal of Materials Chemistry A*, 2016, **4(47)**: 1–8.
- [57] WU J, GUO P, MI R, *et al.* Ultrathin NiCo₂O₄ nanosheets grown on three-dimensional interwoven nitrogen-doped carbon nanotubes as binder-free electrodes for high-performance supercapacitors. *Journal of Materials Chemistry A*, 2015, **3(29)**: 15331–15338.
- [58] NGUYEN V H, SHIM J J. Three-dimensional nickel foam/graphene/NiCo₂O₄ as high-performance electrodes for supercapacitors. *Journal of Power Sources*, 2015, **273(1)**: 110–117.
- [59] YU L, ZHANG G, YUAN C, *et al.* Hierarchical NiCo₂O₄@MnO₂ core-shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes. *Chemical Communications*, 2013, **49(2)**: 137–139.
- [60] ZHANG G, WANG T, YU X, *et al.* Nanoforest of hierarchical Co₃O₄@NiCo₂O₄ nanowire arrays for high-performance supercapacitors. *Nano Energy*, 2013, **2(5)**: 586–594.
- [61] RAN L, DUAY J, SANG B L. Heterogeneous nanostructured electrode materials for electrochemical energy storage. *Chemical Communications*, 2011, **47(5)**: 1384–1404.
- [62] DENG F, YU L, CHENG G, *et al.* Synthesis of ultrathin mesoporous NiCo₂O₄ nanosheets on carbon fiber paper as integrated high-performance electrodes for supercapacitors. *Journal of Power Sources*, 2014, **251(2)**: 202–207.
- [63] DU J, ZHOU G, ZHANG H, *et al.* Ultrathin porous NiCo₂O₄ nanosheet arrays on flexible carbon fabric for high-performance supercapacitors. *ACS Applied Materials & Interfaces*, 2013, **5(15)**: 7405–7409.
- [64] ZHANG G, LOU X W. General solution growth of mesoporous NiCo₂O₄ nanosheets on various conductive substrates as high-performance electrodes for supercapacitors. *Advanced Materials*, 2013, **25(7)**: 976–979.
- [65] ZHANG G, WEN D L X. Controlled growth of NiCo₂O₄ nanorods and ultrathin nanosheets on carbon nanofibers for high-performance supercapacitors. *Scientific Reports*, 2013, **3(3)**: 1470–1–6.
- [66] MUSIANI M. Electrodeposition of composites: an expanding subject in electrochemical materials science. *Electrochimica Acta*, 2000, **45(20)**: 3397–3402.
- [67] PEI A, ZHENG G, SHI F, *et al.* Nanoscale nucleation and growth of electrodeposited lithium metal. *Nano Letters*, 2017, **17(2)**: 1132–1139.
- [68] TU Z, ZACHMAN M J, CHOUDHURY S, *et al.* Nanoporous hybrid electrolytes for high-energy batteries based on reactive metal anodes. *Advanced Energy Materials*, 2017, **7(8)**: 1602367–1–9.
- [69] TORABINEJAD V, ALIOFKHAZRAEI M, ASSAREH S, *et al.* Electrodeposition of Ni-Fe alloys, composites, and nano coatings—a review. *Journal of Alloys & Compounds*, 2016, **691**: 841–859.
- [70] YUAN C, LI J, HOU L, *et al.* Ultrathin mesoporous NiCo₂O₄ nanosheets supported on Ni foam as advanced electrodes for supercapacitors. *Advanced Functional Materials*, 2012, **22(21)**: 4592–4597.
- [71] LU X, HUANG X, XIE S, *et al.* Controllable synthesis of porous nickel-cobalt oxide nanosheets for supercapacitors. *Journal of Materials Chemistry*, 2012, **22(26)**: 13357–13364.
- [72] PAWAR S M, PAWAR B S, KIM J H, *et al.* Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. *Current Applied Physics*, 2011, **11(2)**: 117–161.
- [73] PU J, WANG J, JIN X, *et al.* Porous hexagonal NiCo₂O₄ nanoplates as electrode materials for supercapacitors. *Electrochimica Acta*, 2013, **106(9)**: 226–234.
- [74] WEI Q, XIONG F, TAN S, *et al.* Porous one-dimensional nanomaterials: design, fabrication and applications in electrochemical energy storage. *Advanced Materials*, 2017, **29(20)**: 1602300–1–39.
- [75] XIAO F X, MIAO J, TAO H B, *et al.* One-dimensional hybrid nanostructures for heterogeneous photocatalysis and photoelectrocatalysis. *Small*, 2015, **11(18)**: 2115–2131.
- [76] ZHAN J, CAI M, ZHANG C, *et al.* Synthesis of mesoporous NiCo₂O₄ fibers and their electrocatalytic activity on direct oxidation of ethanol in alkaline media. *Electrochimica Acta*, 2015, **154**: 70–76.
- [77] CHEN J S, LOU X W. SnO₂-based nanomaterials: synthesis and application in lithium-ion batteries. *Small*, 2013, **9(11)**: 1877–1893.
- [78] ZHANG G Q, WU H B, HOSTER H E, *et al.* Single-crystalline NiCo₂O₄ nanoneedle arrays grown on conductive substrates as binder-free electrodes for high-performance supercapacitors. *Energy & Environmental Science*, 2012, **5(11)**: 9453–9456.
- [79] SU C. Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: a review of recent literature. *Journal of Hazardous Materials*, 2016, **322(Pt A)**: 48–84.
- [80] DUBAL D P, GOMEZ-ROMERO P, SANKAPAL B R, *et al.* Nickel cobaltite as an emerging material for supercapacitors: an overview. *Nano Energy*, 2015, **11**: 377–399.
- [81] JIANG H, MA J, LI C. Hierarchical porous NiCo₂O₄ nanowires for high-rate supercapacitors. *Chemical Communications*, 2012, **48(37)**: 4465–4467.
- [82] SHEN L, CHE Q, LI H, *et al.* Metal oxides: mesoporous NiCo₂O₄ nanowire arrays grown on carbon textiles as binder-free flexible electrodes for energy storage. *Advanced Functional Materials*, 2014, **24(18)**: 2736–2736.
- [83] CHEN R, WANG H Y, MIAO J, *et al.* A flexible high-performance oxygen evolution electrode with three-dimensional NiCo₂O₄ core-shell nanowires. *Nano Energy*, 2015, **1**: 333–340.
- [84] JI L, LIN Z, GUO B, *et al.* Assembly of carbon-SnO₂ core-sheath composite nanofibers for superior lithium storage. *Chemistry-A European Journal*, 2010, **16(38)**: 11543–11548.
- [85] LI L, PENG S, CHEAH Y L, *et al.* Electrospun eggroll-like CaSnO₃ nanotubes with high lithium storage performance. *Nanoscale*, 2013, **5(1)**: 134–138.
- [86] LI L, PENG S, CHEAH Y, *et al.* Electrospun porous NiCo₂O₄ nanotubes as advanced electrodes for electrochemical capacitors. *Chemistry*, 2013, **19(19)**: 5892–5898.
- [87] MA F X, YU L, XU C Y, *et al.* Self-supported formation of hierarchical NiCo₂O₄ tetragonal microtubes with enhanced electrochemical properties. *Energy & Environmental Science*, 2016, **9(3)**: 862–866.