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Preparing Super-highly Dispersed Co_3O_4@SBA-15 with Controllable Morphologies with the Assistance of Dilute Acid in Supercritical CO_2

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Cobalt oxide nanostructures have been proved to have promising applications in energy storage fields. However, it is still challenging to obtain homogeneous metal dispersion and distribution due to low support-precursor interactions in the most commonly used impregnation method. Supercritical fluid deposition method is a new, effective and environmentally benign technique which has attracted growing attentions in recent years. Superior to traditional impregnation method, large aggregates of nanoparticles outside of the nanochannels could be usually avoided due to the near-zero surface tension of supercritical fluids.

Generally speaking, expensive organometallic compounds were used as precursors in this method because they had relatively large solubilities in the widely used $scCO_2$. Recently, our group have used cheap inorganic salts to instead of the expensive organometallic compounds. Inorganic salt is not soluble in $scCO_2$, therefore, co-solvents such as methanol, ethanol, acetone etc. are usually applied to modify the polarity of the solvent and to enhance the dissolution of precursor. In this study, a small amount of dilute nitric acid (HNO_3) or hydrochloric acid (HCl) was introduced into $scCO_2$ as co-solvent for the first time to synthesize Co_3O_4@SBA-15, using $Co(NO_3)_2 \cdot 6H_2O$ as precursor. The aim of adding dilute acid was not limited to the dissolution enhancement of precursor but also focused on the change of the interaction between the precursor and the substrates, which may consequently influence the dispersion and morphology of nanostructures. Super-highly dispersed Co_3O_4 nanoparticles were confined in the nanochannels of SBA-15 after deposition and calcinations when adding a small amount of nitric acid as co-solvent. As the concentration of nitric acid increased, more individual small nanoparticles in adjacent nanochannels aggregated through the micropores in the walls of the substrates, which favored the formation of large nanoparticles. Furthermore, only Co_3O_4 nanoparticles were obtained when adding nitric acid in supercritical CO_2-ethanol solution whereas nanowires were found instead when applying hydrochloric acid. It indicated that H^+ favored the adsorption and dispersion of the precursors on the substrates and Cl^- played a key role in dictating the nanowire morphology.

Keywords: supercritical carbon dioxide; mesoporous silica; dilute acid; highly dispersed; Co_3O_4

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超临界 CO_2 中稀酸辅助制备高分散可控形貌 Co_3O_4/SBA-15

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四氧化三钴纳米结构在储能方面应用前景广阔。采用传统浸渍法制备担载型纳米复合材料时，由于硝酸盐与载体之间的弱相互作用以及有机溶剂的表面张力，纳米相形貌难以控制并且纳米相很难分散均匀。超临界流体沉积法(SCFD)是近年来发展起来的制备担载型纳米复合材料新而有效的方法。该方法优于传统浸渍法，由于超临界流体零表面张力，能够避免纳米孔道外部的大颗粒聚集。一般说来，由于所使用的溶剂超临界二氧化碳($scCO_2$)非极性的限制，文献报道多使用昂贵有毒的有机金属盐作为前驱物。近年来本课题组提出用廉价的无机盐替代有机金属前驱物。无机盐不溶于 $scCO_2$，常用甲醇、乙醇、丙酮、氯仿等有机溶剂作共溶剂改善 $scCO_2$ 极性，增加无机盐在其中的溶解度。本文研究首次提出用少量稀硝酸或稀盐酸做共溶剂，$Co(NO_3)_2{\cdot}6H_2O$ 作前驱物，$scCO_2$ 作溶剂来制备 Co_3O_4@SBA-15。加入稀酸的目的不仅仅在于增加溶解度，同时着重于改变前驱物和载体之间的相互作用，从而改善纳米相分散度和形貌。用稀硝酸作共溶剂，在 SBA-15 中制备了高度分散的 Co_3O_4 纳米颗粒，随着硝酸浓度的增加，相邻孔道内的纳米颗粒通过载体孔壁上的微孔连接在一起，形成大的纳米颗粒。研究发现，用硝酸做共溶剂，得到 Co_3O_4 纳米颗粒，而用盐酸做共溶剂，得到 Co_3O_4 纳米线。分析认为 H^+对纳米相分散起到积极作用，而 Cl^-对纳米线的形成有诱导作用，进一步的机理正在研究中。

关键词：超临界二氧化碳；介孔氧化硅；稀酸；高分散；四氧化三钴