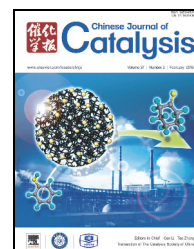


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Review

Carbon dioxide-expanded ethanol-assisted synthesis of carbon-based metal composites and their catalytic and electrochemical performance in lithium-ion batteries

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ABSTRACT

Highly dispersed metals, metal oxides and their composites on substrates have received considerable interest in catalysis and lithium-ion batteries, because of their superior properties compared with their single-component counterparts. In this review, we introduce the properties of supercritical carbon dioxide (scCO₂) expanded ethanol, such as low viscosity, near-zero surface tension and high diffusivity. We discuss the deposition procedure and formation mechanism of carbon-based composites in scCO₂-expanded ethanol. This method has been used to fabricate several carbon-based composites, such as metal and metal oxide composites deposited on zero-dimensional colloidal carbon, one-dimensional carbon nanotubes, two-dimensional graphene, and three-dimensional hierarchical porous carbon. These materials and their performance as anodic materials for lithium-ion batteries will also be reviewed.

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1. Introduction

Functional composites have attracted much recent interest in various areas. This is because they often behave differently from bulk materials, and exhibit improved properties compared with their single-component counterparts. For example, precious metal seeds encapsulated by metal and metal oxides, such as Pt@CoO [1], Au@ZrO₂ [2], and Pd@Au [3], exhibit higher stability, activity, and selectivity than their bare metal nanoparticles. This is because of the local effect and synergistic

interactions between the core metal particles and shell metal oxides. Various carbon-based composites, such as SnO₂/graphene [4], Fe₃O₄/C [5], and Co₃O₄/graphene [6], have been investigated for use in lithium-ion batteries (LIBs), in which they exhibit better electrochemical performance than their single metal oxide components. Carbon-based composites have been much studied as catalysts or catalyst supports, and favorable catalytic performance have been reported [7–10]. Bao's group [7] reported that reduced graphene oxide could be used as a catalyst for the hydrogenation of nitrobenzene at

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room temperature, and high catalytic activity and stability were obtained. Wang's group [8] prepared ultrafine Pd nanoparticle monolayers on graphene oxide, which exhibited high electrocatalytic ability in the oxidation of formic acid and ethanol. Liu' group [9] deposited Pt nanoparticles on multi-walled carbon nanotubes, which exhibited a turn-over frequency (TOF) of 69900 h^{-1} in the hydrogenation of nitrobenzene.

Synthesizing these composites usually requires uniformly coating or dispersing metal and metal oxides onto the core particles. Cao' group [11] reported that Ni-graphene nanocomposites with uniformly distributed nickel particles significantly lowered the decomposition temperature of ammonium perchlorate (AP). This was because of the reduced activation energy of the decomposition of AP, which enhanced the rate of decomposition of deprotonated HClO_4 gas. Balaya [12] reported that reducing the size of nanocrystals, which increases their surface-to-volume ratio, could reduce the scale of transport lengths for mass and charge transport. Nanoscale effects promoted the thermodynamic properties, because of excess surface contributions enhancing the cell voltage in LIBs. Controlling the loading of active materials is important, because it significantly influences the performance of the resulting composite. For example, Lee and co-workers [13] reported that Fe_3O_4 nanocrystals confined in mesocellular carbon foam (MSU-F-C) exhibited excellent rate performance compared with micro- Fe_3O_4 . The higher Fe_3O_4 loading (61%) decreased the rate performance, which was attributed largely to the lower pore volume.

Several approaches have been reported for impregnating or attaching active metal and metal oxide nanoparticles into the cavities or on the external walls of supports. Incorporating metals or metal precursors and a carbon source for carbon nanotube (CNT) growth is one approach for impregnating metals into the hollow interior of CNTs. However, harsh conditions such as high temperatures or arc evaporation are usually required, and impurities are produced as encapsulated carbon clusters and soot. Capillary drawing of low-melting point metals into CNTs is a simple approach. However, CNTs are not wetted by liquids with surface tensions higher than 0.1–0.2 N/m, which excludes most common metal catalysts [14]. The most promising and flexible approach is to deposit metals into the cavities or onto the external walls of CNTs through reactions such as chemical vapor deposition (CVD) or wet chemical processing. The small inner diameter and extremely high aspect ratio of CNTs means these approaches require high temperatures or long reaction time to fill metals into the inner cavities. As a consequence, the filling percentage of the CNTs is often low. Pristine CNT surfaces are rather inert and poorly hydrophilic, so this approach also results in unsatisfactory adhesion, and poor control of the coverage of the metal nanoparticles on the CNT outer walls. Most catalysis application prefers catalyst particles loaded onto the exteriors of CNTs, where they are more accessible to reactant molecules than those on interior surfaces. To obtain specific nucleation of metals on the outer surface with good adhesion and dispersion, CNTs are usually functionalized by chemical treatment with oxidants such as HNO_3 , KMnO_4 , $\text{HNO}_3/\text{H}_2\text{SO}_4$ and RuO_4 . This generates $-\text{COOH}$,

$-\text{OH}$ and other functional groups on the external walls of the CNTs. The conventional wet chemical decoration processes usually involve tedious and time-consuming treatments of the CNTs, which generates significant aqueous waste.

An effective and green approach for uniformly dispersing metal and metal oxides or composites nanoparticles on carbon-based matrices has recently been developed. This approach involves assistance by CO_2 -expanded ethanol, and the carbon-based matrix can be used directly without tedious pretreatment. Several metal oxides have been deposited on the outer surfaces of CNTs, such as $\text{Co}_3\text{O}_4/\text{CNT}$ [15], $\text{Eu}_2\text{O}_3/\text{CNT}$ [16], $\text{Al}_2\text{O}_3/\text{CNT}$ [17], $\text{Fe}_2\text{O}_3/\text{CNT}$ [18], ZrO_2/CNT [19], and $\text{La}_2\text{O}_3/\text{CNT}$ [20], in a solution of supercritical CO_2 (scCO_2)-modified ethanol. The coating thickness could be tailored by tuning the ratio of the initial mass of precursors to CNTs. The metal or metal oxides nanocrystals or nanoalloys, and complex metal oxide nanoparticles were dispersed on carbon-based matrices with different dimensions, in scCO_2 -expanded ethanol without using precipitants. Matrices have included zero-dimensional (0D) carbon colloids (C@Ni , CoO/C , C@Ni\&Co , C@Ni\&Pd [21], Pd/C [22]), one-dimensional (1D) CNTs ($\text{Co}_3\text{O}_4/\text{CNTs}$ [23], $\text{CoFe}_2\text{O}_4/\text{CNTs}$ [24]), two-dimensional (2D) graphene (NiO@GNS [25], $\text{Fe}_3\text{O}_4@\text{GNS}$ [26], $\text{CoFe}_2\text{O}_4@\text{GNS}$ [27]), and three-dimensional (3D) hierarchical porous carbon ($\text{Fe}_3\text{O}_4/3\text{DHPC}$ [28], $\text{NiO}/3\text{DHPC}$, $\text{Co}_3\text{O}_4/3\text{DHPC}$, $\text{NiCo}_2\text{O}_4/3\text{DHPC}$ [29]). These nanocomposites have exhibited good performance in catalytic hydrogenation, or good electrochemical performance in LIBs.

2. scCO_2 -expanded ethanol deposition

scCO_2 deposition is a green and sustainable technique for efficiently synthesizing and processing nanomaterials. scCO_2 is an attractive alternative to organic solvents, because it is nontoxic, nonflammable, inexpensive, naturally abundant and chemically inert. Its physical properties such as density and solvent power can be tuned via the operating temperature and pressure [28]. Its low viscosity, near-zero surface tension and high diffusivity are favorable for synthesizing ultrafine uniform nanomaterials, and for enhancing reaction rates [30]. scCO_2 deposition also has advantages for processing cellular materials, because it can mitigate mass transfer limitations, facilitate the infiltration of precursors into complex geometries, and maintain a porous nanostructure without collapse. scCO_2 as a reaction medium could also reduce the solvent strength caused by hydroxyl groups originating from ethanol and water, and thus suppress aggregation of the final particles [20]. Polar organic solvents are usually used as cosolvents to enhance the solvent strength of scCO_2 , resulting in scCO_2 -based solutions. For example, metal nitrates (e.g. cobalt, iron, and aluminum nitrates) are insoluble in scCO_2 , but are soluble in $\text{scCO}_2/\text{ethanol}$ under the appropriate conditions. These nitrates can decompose into their respective metal oxides at relatively low temperatures in the presence of scCO_2 [31].

In the general procedure, a nitrate ethanol solution containing carbon-based supports is loaded into a high-pressure stainless-steel vessel, as the vessel is preheated to a certain

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