Efficient removal of transition phase from metal encapsulated carbon onions

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ABSTRACT

Transition metal encapsulated carbon onions with high crystallinity and economic scalability were fabricated by a facile chemical vapor deposition method. Then the as-prepared metal encapsulated carbon onions were subjected to microwave assisted acid digestion procedures to remove the metal impurities. High-resolution transition electron microscopic images and Raman spectrum demonstrated the efficient removal of metal phase and the formation of defective hollow carbon onions(HCNOs) under microwave assisted strong acid treatment. It was believed that the acid can corrode the outer carbon shell of onions while the microwave can induce local heating of metal impurities. Under the synergistic effect, the metal phase converts into soluble salt and leaves defective hollows in the center of onions.

1. Introduction

Carbon nano onions (CNOs, also called onion-like carbon OLC) are spherical carbon nanomaterials which consist of disordered concentric fullerene like multi-shells [1,2]. Since the observation of carbon nano onions (CNOs) in 1980 [3], tremendous efforts have been devoted to their synthesis, purification and property investigation [4,5]. So far, several types of CNOs have been identified, including spherical CNOs, polyhedral CNOs, HCNOs and metal encapsulated CNOs [6–9]. Among these magic onion architecture, HCNOs is one of the most promising carbon-based nanomaterials due to their high surface to weight and volume ratio, low toxicity, high biocompatibility, satisfactory chemistry stability and conductivity, thus exhibiting a multitude of application prospects in a couple of fields such as catalysis, biology, hydrogen and energy storage [10–16]. Several physical and chemical methods including chemical vapor deposition (CVD), template method, arc discharge, solvothermal synthesis and so on have been reported to fabricate HCNOs [4,8,10,17]. Some purification procedures such as acid refluxing, calcination, ultrasonic have also been proved to successfully convert CNOs to HCNOs [4,8,18]. In addition, HCNOs were occasionally obtained during the preparation of other nano-carbon materials [19], however, they are all hard to scale up.

Chemical vapor deposition (CVD) is one of the most optimal methods for producing CNOs with high crystallinity and economic scale up [20]. Meanwhile, the preparation process has been proved relatively safe, convenient and available for macroscopic industrial production. However, the catalyst is needed during CVD process and the catalyst will stay in or out of the as harvested carbon. In order to finally obtain HCNOs, some measures are needed to remove the catalyst particles. Chemical oxidation using traditional strong acid reflux is commonly used in literature for the removal of metal impurities of CNOs [19,21], but the strong oxidizing acid treatments is time-consuming and may damage the carbon shell. On the basis of pickling removal, auxiliary method need to be added to short the reaction time, increase the removal efficiency, improve the product quality and achieve mass production to a certain extent.

Ultrasound assisted method has been introduced for the purification of CNOs due to their energy providing for acid digestion procedure and it can accelerate the catalyst pickling rate, but the enormous ultrasonic energy acts on the surface only before opening the inside of the material, which will destroy the outer graphite structure extremely. Therefore, design a rational, efficient, energy-saving, environmental-friendly method for the effective removal of impurities in CNOs is necessary.

Microwave method could supply short-time-consuming and energy-saving benefits from the energy directly transmitted to the material through by an electromagnetic field [22]. Microwave energy preferentially excites the acid over the carbon, gives the acid greater kinetic energy and allows the acid to penetrate the carbon shell [23], and the pressure may assist in allowing the acid to penetrate the graphitic

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sheets, without any damages to the carbon as the pressures within the carbon structures are substantially higher [24]. On the other hand, microwave energy can effectively heat metal particles and cause carbon shell to burst. Actually, microwave-assisted acid method has been successfully used in the purification of CNTs and related nano carbon materials [25–27]. Based on this, it can be concluded that microwave assisted acid procedure for the metal particles removing from CNOs is theoretically feasible. However, the corresponding experimental research is rare in previous studies.

Herein a facile CVD procedure was employed to fabricate gram-scale NiCo@CNOs. Then, a series of microwave assisted acid digestive experiments were designed to remove metal phase, including the encapsulated metal nanoparticles in the carbon shell or the residual metal catalyst outside the onions.

2. Experimental procedure

2.1. Preparation of catalyst

Catalyst precursor solution was prepared by a sol-gel method. Co$(NO_3)_2$ and Ni$(NO_3)_2$ were added into a citric acid solution with 1:1 mol ratio and stirred at room temperature for 1 h. Then raised to 80 °C and stirred continuously about 2 h until a viscous syrupy was formed.

The 316 stainless steel mesh was cut into a cylinder of 5 mm as catalyst support. The mesh support was ultrasonic treated in ethanol and acid solution (V(H_2O):V(HNO_3) = 3:1) for 30 min in sequence in order to remove the stains of the mesh thoroughly. The treated stainless steel mesh was immersed in the as-prepared syrupy (Co-Ni$(NO_3)_2$·$6H_2O$) to achieve surface loading of catalysts. The loaded mesh was subsequently dried and calcined for 3 h at 600 °C.

2.2. Synthesis of NiCo@CNOs

NiCo@CNOs were fabricated by a CVD procedure. CH_4 was the selected as the carbon source and gradually deposited on the as-prepared catalyst at 800 °C until the catalyst particles are all coated with graphite to form NiCo@CNOs. Three sets of parallel experiments were carried out, in which two sets of quartz tubes were placed with as-prepared catalysts simultaneously to analyze repeatably, and the third was blank for benchmark and background analysis. The sample was heated in a tube furnace to 800 °C and purged with N_2 stream, in which the N_2 was continuously fed at a constant rate of 30 mL/min for 1 h to completely remove the air inside the tube. Then the tube temperature was programmed cooled to 600 °C at 10 °C/min and the H_2 with N_2 (1:4, V/V) was introduced at 30 mL/min to reduce the catalyst 1 h. Then the furnace temperature rose to 800 °C again, switch the gas to CH_4 at 30 mL/min for 60 h for CNOs growth. The tube reactor was cooled to ambient temperature in N_2 atmosphere after CVD process.

2.3. Transformation from NiCo@CNOs to HCNOs

10 mg as-prepared NiCo@CNOs were immersed in 10 mL 50 wt%, 70 wt% HNO_3 and mixed acid of concentrated H_2SO_4 and HNO_3 (1:1, V/V), respectively. Then the mixtures were placed in a microwave reactor. After the internal pressure of microwave reactor was increased to 15 bar, the temperature inside heated to 130 °C at 300 W for 5 min. Then the samples were washed thoroughly with deionized water until neutral. The final products were dried to constant weight to obtain HCNOs.

3. Results and discussions

SEM image of the as-prepared NiCo@CNOs is shown in Fig. 1(a), in which many irregular aggregations rich in spherical or ellipsoid nanoparticles can be observed. Fig. 1(b) is the energy spectra corresponding to the inserted figure. From the EDX pattern of the as-prepared

NiCo@CNOs, the metal elements Ni and Co are obviously detectable while the O signal was very feeble. The O signal may originated from the oxidization on the surface of outer graphitic layer [28], or amorphous carbon containing oxygen functional groups. Moreover, the presence of Cu peaks may result from the sample holder and should be ignored [29]. The EDX pattern indicates that the main components of the metal nanoparticles encapsulated in the carbon shell are Ni and Co.

Fig. 2(a) shows that the as-prepared CNOs are mainly consisted of several types of nanostructures, including NiCo@CNOs, HCNOs and uncurling CNOs, in which NiCo@CNOs nanoparticles are obviously dominated. As calculated from a survey of TEM images, examining 50 particles, catalyst particles are located in 98% of carbon onion particles, implying that almost all of the catalyst particles were encapsulated in the carbon shell. Roughly calculation, the single core-shell structure of NiCo@CNO has a particle size in the range of 40–120 nm and contains 10–40 nm metal particles inside. The HRTEM image of the as-prepared CNOs shown in Fig. 2(b) clearly depicts the core-shell configuration of a single NiCo@CNO, which is accord with the SEM and EDX analysis. The graphitic layers always follow the contour of the catalyst particle and where the contour is too sharp for the carbon to follow a dislocation is present. The graphitic layers are parallel to the outer edge of catalyst particles, it is recognizable that the lattice spacing values of the graphite layers in the observed CNOs (0.341 nm) are very close to the standard graphite (0.335 nm) [19]. In addition, the outermost shell of the onion was smooth without obvious defects. Combined with the XRD pattern shown in Fig. 3, it can be seen that the as-prepared CNOs showed distinct diffraction peak close to 26°, corresponding to the (002) crystal lattice of graphite carbon, and the obvious diffraction peaks appearing near at 42.9° corresponds to (100) crystal face of graphite [30]. From Fig. 3 it also can be found that the catalyst was exited in the as prepared CNOs obviously. In combination with the EDS analysis of Fig. 1(b), the diffraction peaks appearing near to 43.7°, 44.6° and 64.9° correspond to the internal NiCo alloy catalyst particles [31].

After microwave assisted 50 wt% HNO_3 treatment, the outer carbon shell of NiCo@CNOs were partially destroyed to form amorphous structures and the marked locations depict that the metal core tend to escape from the carbon shell and melt together, as shown in Fig. 2(c). On the other hand, the metal cores would be fused to a larger sphere, confirming by Fig. 2(d). Corresponding to Fig. 3, the diffraction peak of graphite at 26° is relatively enhanced compared with peak of the metal catalyst peaks, which is consistent with the electron micrographs of Fig. 2(c) and (d). This indicated that the metal particles encapsulated NiCo@CNOs are tend to be transferred, but cannot be completely removed with 50 wt% HNO_3 digesting. The TEM image of microwave heating under 70 wt% HNO_3 is shown in Fig. 2(e), almost all the metal impurities were removed from NiCo@CNOs. Fig. 2(f) clearly depicts that the original NiCo@CNOs successfully transformed into hollow structures with defects. Some of the perfectly closed ring was broken into a rip structure. The XRD pattern shown in Fig. 3 (70 wt% HNO_3) also certified that the catalyst was almost vanished and the graphic CNOs were gained. This is consistent with what founded in Fig. 2(e) and (f), indicating that the catalyst can be efficiently removed from NiCo@CNOs through microwave assisted 70 wt% HNO_3 purification process. As revealed in Fig. 2(g), under mixed acid treatment, metal impurities were completely removed from NiCo@CNOs, however, the (002) crystal lattice obviously destroyed and became discontinuous as shown in Fig. 2(h), this reflect to the diffraction peak at the (002) decreases significantly and slightly shifts (as shown in Fig. 3), indicating that the peripheral graphite layer of the material is seriously damaged under the treatment conditions. Combined Fig. 2 with Fig. 3, that means mixed acid (HNO_3 and H_2SO_4) is unsuitable to remove the metal impurities without CNOs destroying. In summary, the most effective method to obtain HCNOs is microwave assisted 70 wt% HNO_3 digestion. Under the synergistic effect of acid digestion and microwave heating, metal phase can be efficiently removed from NiCo@CNOs to form HCNOs.