Synthesis and Characterization of Ni-C Nanoparticles by Plasma-enhanced Chemical Vapor Deposition

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Nickel-carbon thin films have been deposited on silicon substrate in the CH₄/Air/H₂ atmosphere by plasma-enhanced chemical vapor deposition. Scanning electron microscopy, transmission electron microscopy, high resolution transmission electron microscopy and Raman spectroscopy were employed to investigate the morphology and microstructure of the samples. The results showed that graphitic carbon encapsulated nickel, nickel nanoparticles embedded in few-layer graphene, and entangled few-layer graphene nanoribbons were synthesized, respectively, corresponding to different diameter of nickel particles. The growth mechanism of the different microstructures has been discussed.

Key words: Ni-C, graphene, plasma-enhanced chemical vapor deposition.

Carbon materials, fullerenes (Kroto et al., 1985; Djordjevic et al., 2006), carbon nanotubes (Iijima, 1991; Gao and Xu, 2009), and graphene (Xu and Wang, 2009), are often used as support/shell for synthesis of metal-based nanoparticles that exhibit unique electronic (Chen et al., 2003), magnetic (Georgakilas et al., 2007), and optical properties (Chi et al., 2012) for desirable use in nanobiotechnology, including integrated imaging (Seo et al., 2006), nanothermotherapy (Gazeau et al., 2008; Vyalikh et al., 2008), and drug delivery without toxic adverse effects (Sherlock et al., 2011). Carbon materials encapsulated magnetic nanoparticles can help to protect the air-sensitive cores against degradation and preventing the magnetic nanoparticles from aggregation and magnetic coupling (Hayashi et al., 1996). Among various magnetic nanocrystals (Heutten et al., 2004; Moench et al., 2005; Cheng et al., 2006), Metallic nickel nanoparticles have attracted much attention not only because of their magnetic and conducting properties (Cheng et al., 2006), but also due to their unusually catalytic ability that has been demonstrated by Yu et al. in growth of graphene on 0.5 mm thickness Ni foils (Yu et al., 2008) and by Reina et al. with their few-layer graphene films on polycrystalline Ni film (Reina et al., 2009). According to Yu et al., the thickness and quality of graphene synthesized by a surface segregation process is strongly dependent on the cooling rates and gas atmosphere. Plasma-enhanced chemical vapor deposition (PECVD) is a simple, low cost, and reliable technique to obtain high-quality vertically aligned graphene nanosheets (Miller et al., 2010). In our previous work, it has also been employed to grow byproduct of graphite shell-encapsulated cobalt nanoparticles during producing carbon nanotubes (CNTs) (Qi et al., 2008) and vertically aligned graphene nanosheets catalyzed by Ni foam (Zhao et al., 2012),

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which has promising applications in biomedicine and electrochemical capacitors, respectively. However, for biotechnological applications, it is essential to produce high purity carbon-supported metal nanoparticles.

In the present work, we designed to grow Ni-C nanoparticles in CH$_4$/Air/H$_2$ atmosphere by PECVD that exhibit a significant size-morphology effect. Graphitic carbon shell encapsulated nickel, few-layer graphene supported-nickel nanoparticles, and few-layer graphene nanoribbons have a well correlation with size of nickel nanoparticle.

MATERIALS AND METHODS

Ni film preparation

First, Ni film on Si (100) substrate was synthesized by direct current magnetron sputtering. To investigate the size of Ni nanoparticles on the growth of nanostructured carbon, we design to grow Ni film that is schematically shown in Figure 1. Compared with region 1#, for region 2# and 3#, the Si (100) has been half-coated; the thickness of Ni film should be different among three different regions. The size of Si (100) substrate was 20×20 mm, the piece was chosen to be 2 mm. Prior to deposition, Si was ultrasonically cleaned in acetone, ethanol, and distilled water for 15 min, respectively. Before deposition, the vacuum chamber was pumped by a turbo-molecular pump to a base pressure of about 1×10$^{-4}$ Pa. During deposition, the Ar gas pressure and the sputtering current applied on Ni target were kept at 1.8 Pa and 0.2 A, respectively, for 15 s.

Synthesis of Ni-C nanoparticles

Then, the Si-supported Ni film without any coating was put into PECVD chamber, followed by etching pretreatment first in Air for about 10 min, then in H$_2$(10 sccm/20 sccm) for the same time and the Ni film was expected to anneal to some small islands. Finally, pure CH$_4$ (99.99%) with a flow rate of 80 sccm was introduced into the reaction chamber for the growth of Ni-C nanoparticles. During the growth, the total pressure and discharge power were maintained at 1300 Pa and 200 W, respectively. After 30 min deposition, CH$_4$ and Air inlets were shut off and the system was allowed to cool down to room temperature in H$_2$ gas.

Characterization

The morphology and structure for the synthesized samples were characterized by scanning electron microscopy (SEM) (JOEL JSM-6700F), transmission electron microscopy (TEM) (JOEL JEM-2010 at 150 V), high resolution transmission electron microscopy (HRTEM) (JOEL JEM-2010 at 300 kV) and Raman spectroscopy (Renishaw-invia with 514.6 nm excutatuib wavelength).

RESULTS AND DISCUSSIONS

Figure 2(a) shows the surface morphology of the Ni film (1# in Figure 1) deposited by magnetron sputtering. It can be seen that sputtering Ni target for 15 s can only get islands with the diameter about 100 nm instead of a continuous film. After etching pretreatment at 800 °C in Air/H$_2$ atmosphere, the islands were annealed into much smaller nanoparticles, with the diameters in the range of 6~21.7 nm and 4~8.5 nm, respectively, SEM images corresponding to the region of 1# and 2# in Figure 1, shown in Figure 2(b) and (c). The small size nanoparticles during etching treatment can be attributed to the oxygen in Air, which has been demonstrated in our previous work (Qi et al., 2008). When the Ni film was etched in Air, the region of grain boundary may be oxidized that limited the Ni particle coarsening but forming

![Fig. 1. Schematic figure showing the growth of Ni film](image-url)
Fig. 2. SEM images of (a) 1#, the as-deposited Ni film by magnetron sputtering (b) 1#, the Ni film after being annealed treatment (c) 2#, the Ni film after being annealed treatment (d) 1#, Ni@C nanoparticles

Fig. 3. TEM images of Ni@C (a-1) 1# (a-2) 1# (b) 2# (c) 3#
nickel oxide with smaller size. The small size oxide could be further reduced to nickel in the hydrogen atmosphere at high temperature. Figure 2(d), a side-view SEM image, presents the morphology of Ni-C nanoparticles in region 1#, from which a uniform distribution nanoparticles formed on the substrate can be seen.

To better understand the crystal phases and confirm the average size of the nanostructures, the Ni-C samples chosen from region 1#, 2#, and 3# were characterized by means of TEM. For region 1#, a black thin film of Ni-C could be easily peeled off from the silicon substrate, while to region 2#, especially region 3#, a hardly visible amount of Ni-C was obtained that were dispersed with a drop of ethanol on the top of carbon-supported Cu rings for TEM investigation. The TEM bright-field image shown in Figure 3(a-1) (a-2) are from region 1# that reveals graphitic carbon and Ni nanoparticle composited structure. The average diameter of the particles was analyzed through DigitalMicrograph image analysis software. The statistical results of the average particle size obtained from Figure 3(a-2) demonstrated an average particle diameter of approximately 16 nm. High-resolution TEM for 1# given in Figure 4(a-1) (a-2) clearly shows the graphitic carbon encapsulated nanoparticle cores. The lattice fringes of the cores reveal a mixed structure of single crystalline and polycrystalline of Ni-based nanoparticles in the samples. Fast Fourier Transform (FFT) patterns shown in Figure

![Fig. 4. TEM images of Ni@C (a-1) 1# (a-2) 1# (b) 2# (c) 3#](image)

![Fig. 5. Raman spectra (excitation 514.6 nm) for Ni@C composites in region 1#, 2# and 3#](image)
4(a-2) are consistent with the polycrystalline NiC,
(PDF#: 45-0979). The several-layer shells are from
graphite (002) plane. It can be noted that Ni
nanoparticles with size ~6 nm tend to catalyze CH₄
to form CNTs (marked by arrows in Figure 4(a-1)).
The CNTs are multi-walled structure with well
crystallinity. From Figure 4(a-2), the dense and
short black arrows show the open graphitic layers
and steps with sharp edge structure, which play a
special role for electrochemical applications (Shang
et al., 2008). From Figure 3(b), a semi-transparent
and flexible film supported nickel nanoparticles can
be observed. The nanoparticles are uniformly
dispersed in the film. The average diameter of the
particles was estimated to be 7.4 nm with a fairly
sharp size distribution. Nickel nanocrystals in 1#
and 2# after PECVD in CH₄/Air/H₂ are completely
isolated from each other by graphite-like carbon.
The HRTEM image of region 2# in Figure 4(b)
exhibits the few-layer graphene with discontinuous
structures. The size of nickel particles after etching
treatment for region 3# is much smaller than 4 nm,
which could hardly be seen in TEM image, shown in
Figure 3(c) and Figure 4(c). The HRTEM image
of Figure 4(c) reveals few-layer graphene
nanoribbons with the number of layers fewer
than 10.

Raman spectroscopy is a powerful probe
for characterizing sp² and sp³ hybridized carbon
atoms (Rao et al., 2009). Figure 5 gives the Raman
spectra of sample 1#, 2#, and 3#, shown in Figure
1, which were used to identify a graphitic carbon G
peak at ~1580 cm⁻¹ and a disordered D peak at ~1350
cm⁻¹ (Figure 5), providing evidence for the graphitic
carbon. Normally, the ratio I_D/I_G provides
information about the presence and crystallinity
of carbon, i.e. the disorder, such as edges, charge
puddles, ripples, or any other defects existed in
the sample. In this work, the I_D/I_G for the 1#, 2#,
and 3# samples is measured to be 0.87, 1.21, and
0.95, respectively. The high ratio of 1.21 for sample
2# is probably due to the nickel nanoparticles
coating on the graphene that will arise Columbic
charge transfer and result in the increase of the
intensity of the Raman D band for 2# compared with
1# and 3# also confirms the much more disorder
structure in the sample. In addition, the I_D/I_G
of the sample 1#, 2#, and 3# was measured to be 0.23,
0.21, and 0.21, respectively, which can provide a
good correlation with the stacking of graphene
layers (Reina et al., 2009). All the obtained values
are given in Table 1.

CONCLUSIONS

Carbon-supported nickel-based nanoparticles have been synthesized by PECVD
technique in the atmosphere of CH₄/Air/H₂. Air was essential for obtaining small size metal
nanoparticles during etching treatment. The grain
size and the crystal structure of the Ni@C
composites depended on the diameter of Ni
particles. As carbon can diffuse into the Ni
nanoparticles during heating treatment and
segregate at the nickel surface during cooling, the
size of nickel particles is expected to influence the
morphology and nanostructure of carbon. Wafer
Si might be replaced by other materials as substrate
to grow Ni@C or other metal nanoparticles and
nanostructured carbon composites for various
uses in nanobiotechnology.

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