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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 CH_4/Air/H_2 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[1] 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 be 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.

MATTERIALS 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

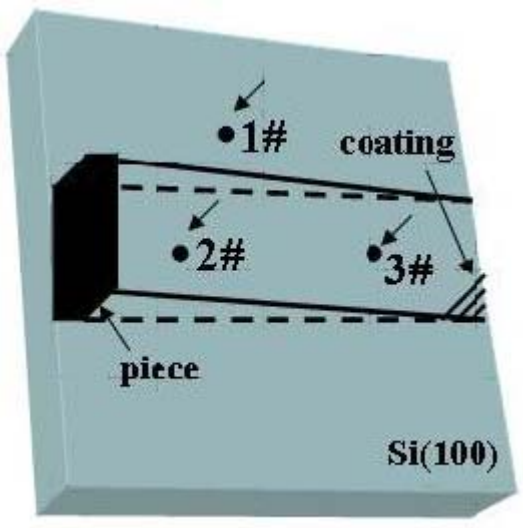

Fig. 1. Schematic figure showing the growth of Ni film

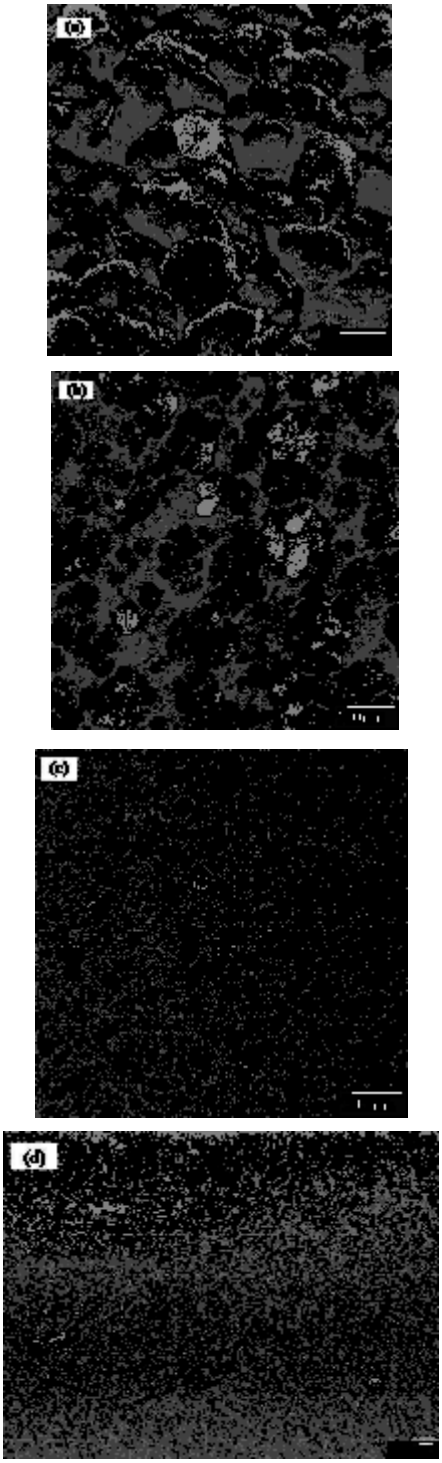

Fig. 2. SEM images of (a) 1#, the as-deposited Ni film by magnetron sputtering (b) 1#, the Ni film after being annealed treatment (c) 2#, the Ni film after being annealed treatment (d) 1#, Ni@C nanoparticles

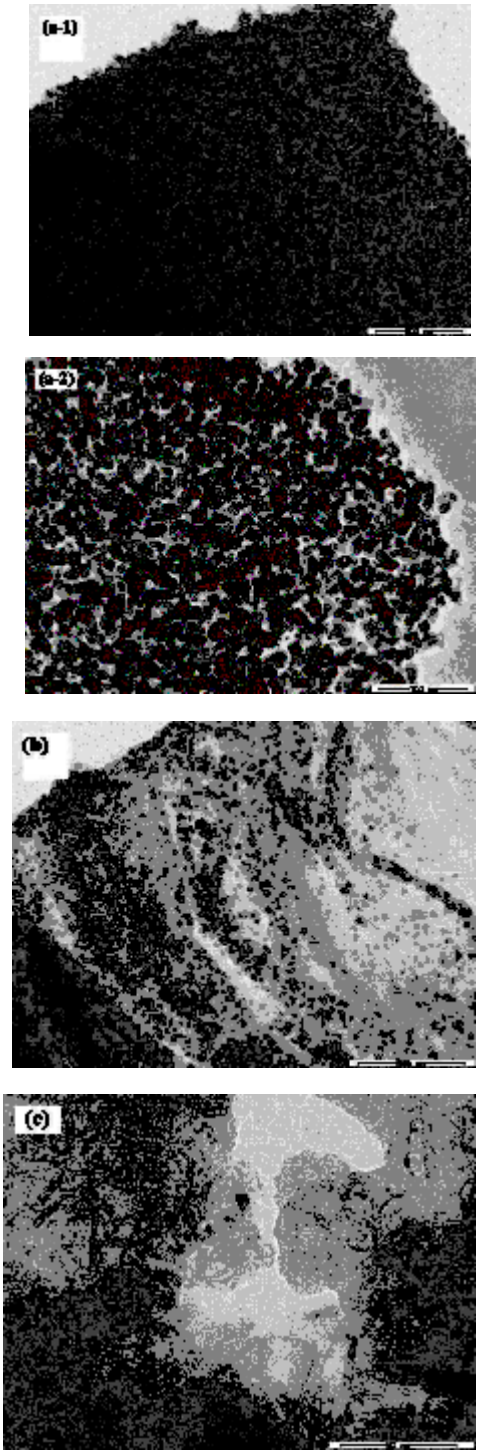

Fig. 3. TEM images of Ni@C (a-1) 1# (a-2) 1# (b) 2# (c) 3#

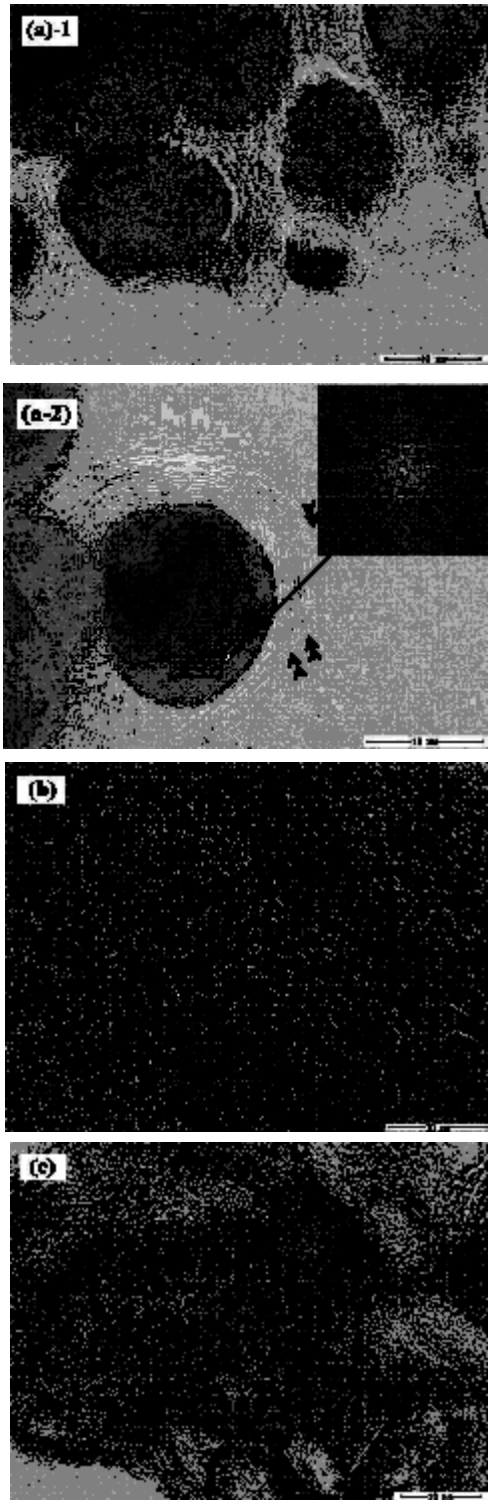

Fig. 4. TEM images of Ni@C (a-1) 1# (a-2) 1# (b) 2# (c) 3#

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 DigitalMcrograph 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) patters shown in Figure

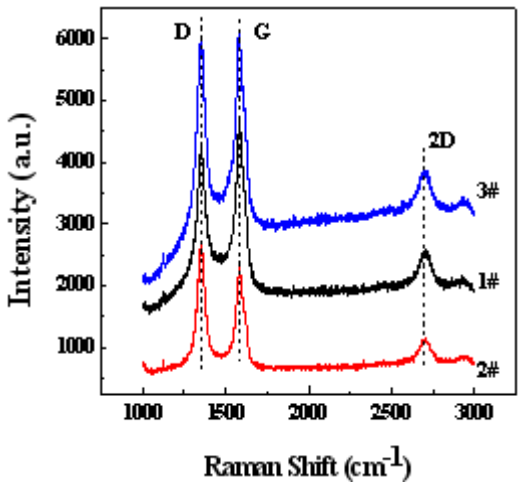

Fig. 5. Raman spectra (excitation 514.6 nm) for Ni@C composites in region 1#, 2# and 3#

4(a-2) are consistent with the polycrystalline NiC_x (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 CH_4 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 CH_4/Air/H_2 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 sp^2 and sp^3 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 and the decrease of 2D band (Rao *et al*., 2009). Also it may be from the discontinuous few-layer graphene structure with many steps or edges. From Figure 4(a) (c), it can be seen that the graphitic are well stacked, therefore the relevant defects should mainly come from the open graphitic edge planes, which has high surface activity for nanobiotechnological applications. The higher line-width of G-band for 2# compared with 1# and 3# also confirms the much more disorder structure in the sample. In addition, the I_{2D}/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 CH_4/Air/H_2. 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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REFERENCES

1. Chen RJ, Bangsaruntip, S. Drouvalakis KA, Noncovalent Functionalization of Carbon Nanotubes for Highly Specific Electronic Biosensors. Proceeding National Academ. Sci. U.S.A. 2003; **100**: 4984-89.
2. Cheng JP, Zhang XB, Ye Y., Synthesis of Nickel Nanoparticles and Carbon Encapsulated Nickel Nanoparticles Supported on Carbon Nanotubes.

J. Solid State Chem. 2006; **179**: 91-95.
3. Chi XQ, Huang DT, Zhao ZH., Nanoprobes for in Vitro Diagnostics of Cancer and Infectious Diseases. *Biomaterial. J*. 2012; **33**: 189-206.
4. Djordjevic A, Bogdanovic G, Dobric S., Fullerenes in Biomedicine. J. B.U.ON.: official *journal of the Balkan Union of Oncology* 2006; **11**: 3910404.
5. Gazeau F, Lévy M, Wihelm C., Optimizing Magnetic Nanoparticle Design for Nanothermotherapy. *Nanomedicine J.,* 2008; **3**(6): 831-44.
6. Gao JH, Xu B., Applications of Nanomaterials Inside Cells. Nano Today 2009; **4**: 37-51.
7. Georgakilas V, Gournis D, Tzitzios V., Decorating Carbon Nanotubes with Metal or Semiconductor Nanoparticles. *J. Mater. Chem.* 2007; **17**: 2679-94.
8. Hayashi T, Hirono S, Tomita M, Umemura S., *Nature J*. 1996; **381**: 772-774
9. Huetten A., New Magnetic Nanoparticles for Biotechnology. *J Biotechnol*. 2004; **112**: 47-63.
10. Kroto HW, Heath JR, Brien SCO, Curl RF, Smalley RE., C60: Buckyminsterfullerene. *Nature J*. 1985; **318**: 162-3.
11. Iijima S., Helical Microtubules of Graphitic Carbon. *Nature J*. 1991; **354**: 56-58.
12. Miller JR, Outlaw RA, Holloway BC., Graphene Double-layer Capacitor with ac Line-Filtering Performance. *Science J*. 329: 1637-39.
13. Moench I, Meye A, Leonhardt A, Kraemer K, Kozhuharova R, Gemming T, Wirth MP, Buechner B., Ferromagnetic Filled Carbon Nanotubes and Nanoparticles: Synthesis and Lipid-Mediated Delivery into Human Tumor *Cells. J. Magne. Magne. Mater*. 2005; **290-291**: 276-8.
14. Qi JL, Wang X, Zheng WT, Liu JW, Tian HW, Li ZP, Liu C., Influence of Oxygen on the Growth of Carbon Nanotubes. *J. Phys. D: Appl. Phys.* 2008; **41**: 205306-1-6.
15. Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A., Grajphene: The Two-Dimensional Nanomaterial. Angew. Chem. Int. Ed. J.2009; **48**: 7752-77.
16. Reina A, Jia XT, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus MS, Kong J., Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett*. 2009; **9**(1): 30-35.
17. Seo WS, Lee JH, Sun XM, Suzuki Y, Mann D, Liu Z, Terashima M, Yang PC, Mcconnell MV, Nishimura DG, Dai HJ., FeCo/Graphitic-Shell Nanocrystals as Advanced Magnetic-Resonance-Imaging and Near-Infrared Agents. *Nature Mater. J*. 2006; **5**: 971-76.
18. Shang NG, Papakonstantinou P, McMullan M, Chu M, Stamboulis A, Potenza A, Dhesi SS, Marchetto H., Catalyst-Free Efficient Growth, Orientation and Biosensing Properties of Multilayer Graphene Nanoflake Films with Sharp Edge Planes. *Adv. Funct. Mater. J*. 2008; **18**: 3506-14.
19. Sherlock SP, Tabakman SM, Xie LM, Dai HJ., Photothermally Enhanced Drug Delivery by Ultrasmall Multifunctional FeCo/Graphitic Shell Nanocrystals. *ACS Nano J*. 2011; **5**(2): 1505-12.
20. Vyalikh A, Wolter AU, Hampel S, Haase M, Ritschel M, Leonhardt A, Grafe HJ, Taylor A, Kraemer K, Buechner B, Klingeler R., A Carbon-Wrapped Nanoscaled Thermometer for Temperature Control in Biological Environments. *Nanomedicine J*. 2008; **3**(3): 321-27.
21. Xu C, Wang X., Fabrication of Flexible Metal-Nanoparticle Films Using Graphene Oxide Sheets as Substrates. *Small J*. 2009; **5**(19): 2212-217.
22. Yu QK, Lian J, Siriponglert S, Li H, Chen YP., Graphene Segrated on Ni Surfaces and Transferred to Insulators. *Appl. Phys. Lett*. 2008; **93**: 113103-3.
23. Zhao CM, Wang X, Wang SM, Yang YY, Zhao YX, Zheng WT., Synthesis of Co(OH)2/ Graphene/Ni Foam Nano-Electrodes with Excellent Pseudocapacitive Behavior and High Cycling Stability for Supercapacitors. *Int. J. Hydrogen Energy* 2012; 37: 11846-852.