Self-catalyzed Epitaxial Growth of Core-shell Ni@Graphene Nanoparticles from Ni(OH)₂-Graphene Composites

Wei Liu[1,2], Juwei Wu[1], Shaobo Han[1,2] and Kai Sun[2]

[1.] School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu, China.
[2.] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA.

In the past few years, graphene (Gr) based materials decorated with transition metals have aroused dedicated efforts of researchers in applications as electrocatalyst [1,2] and supercapacitors [3]. Specially, core-shell nanostructures denoted as M@Gr (M=Fe, Co, Ni) exhibits high structural stability benefitting for 3D symmetrical configuration in comparison with their 2D counterparts. To date, most of the reported M@Gr structures are in size of mesoscale (~200nm). Such symmetric sphere-like morphology, on one hand guarantees the uniform surface carbonization thus yielding homogenous multi-layered graphene shell, on the other hand, suppresses the crystallographic anisotropy of metal-core resulting in the loss of the diversity of facets-initiated epitaxial growth at the interface. In this work, we develop a facile synthesis of Ni(OH)₂-Gr composites in normal pressure and temperature followed by direct annealing treatment for growth of Ni@Gr core shell nanoparticles (NPs) in size of 10~20nm. Atom-resolved STEM microscopy evidences that the system follows a self-catalyzed epitaxial growth accompanied with kinetic phase transition from alpha-Ni(OH)₂, NiO to Ni. The crystallographic anisotropy nature of such core-shell nanostructure shall initiate distinct catalysis performance attributing to the asymmetric interactions between Ni and graphene layers. In a typical synthesis, 0.025g of reduced graphene oxides fabricated through Hummer's method and 0.015g of $Ni(NO_3)_2 \cdot 6H_2O$ were dispersed in 15 mL of deionized water under sonication for 2h. A $NaBH_4$ solution (0.4 ml, 1 M) was added drop-wise and stirred at room temperature (RT) for 2h. The powder dried at 60 °C was subject to annealing at 350 °C, 450 °C, and 770 °C, respectively, under 2% H_2 (in Ar) for 1h, yielding the Ni/RGO nanocomposites. The microscopy results were obtained on a JEOL JEM-2100F microscope operated in STEM mode equipped with a CEOS GmbH probe corrector. The collection angle for the spontaneously captured STEM-ADF and BF images are determined to be 50 mrad and below 20 mrad, respectively.

The morphology and microstructure details of the prepared nickel-graphene products are demonstrated in Fig. 1. For fresh products without annealing, it presents homogenous contrast similar to pure Gr and the EDS mapping (Fig. 1e) proves all the carbon, nickel and oxygen elements distributed uniformly. This product was further confirmed by X-ray diffraction to be alpha-Ni(OH)₂/Gr composite of low crystallinity. The low-magnified STEM-ADF images (Fig. 1a~1d) show the Ni nanoparticles form only after annealing and their sizes turn to increase with the promotion of annealing temperature. The NPs sizes grow rapidly from only several nanometers at 350 °C to ~20 nm at 450 °C. Majority of the NPs still maintain their sizes with only a small portion becomes larger as the annealing temperature increases from 450 °C to 770 °C. The encapsulation of Gr around Ni hybrid NPs accounts for such phenomenon as disclosed by high resolution STEM BF images. Ni/NiO NPs formed at 350 °C without Gr layers observed on the surface (Fig 1f). As the Ni/NiO phase grows during the annealing, the (111) facets dominate the NPs surface, which facilitates the Ni NPs catalyzed epitaxial growth of Gr layers (Fig. 1g). It should be noted that the corners of Ni NPs indexed to be (200) and (220) can not support the formation of Gr layers due to the lattice symmetry, resulting in the absence of Gr layers at these sites where NiO cluster nucleates serving as growth source of Ni NPs. As the Ni core further grows larger at 770 °C, a more uniform multilayer Gr shell forms attributing to the conjunction of Gr layers on the more symmetric (crystallographic isotropy) Ni surface. Figure 2 gives more details at atomic scale on self-

catalyzed formation of Ni@Gr NPs. The Gr layers grow epitaxially on Ni(111) facets with separation spacing of 0.22nm and the spacing of top two Ni layers is compressed to be 0.19nm (Fig. 2a), which is identical with typical configuration of Ni(111)/Gr interface as reported [4,5]. Besides, NiO clusters is observed to grow on Ni(111) facets following identical orientations with lattice distortions at the interface, where Gr is absent ascribed to the block of NiO phase. In addition, the Gr layers follow hexagonal stacking and "top-hcp" epitaxial growth on the Ni(111). The Gr layers from adjacent Ni(111) facets bridge together over the (200) facet (Fig. 2b). Moreover, it is intriguing to note that the Ni island on the Ni(111) facets can induce localized graphene buckling caused by atom stacking fault (Fig. 2c) [6].

References

[1] XJ Fan *et al.*, ACS Nano **9**(2015) p. 7407-7418.
[2] MR Gao *et al.*, J. Am. Chem. Soc. **136**(2014) p. 7077-7084.
[3] HL Wang *et al.*, J. Am. Chem. Soc. **132**(2010) p. 7472-7477.
[4] A Dahal and M Batzill, Nanoscale **6**(2014) p. 2548-2562.
[5] J Lahiri *et al.*, New J. Phys. **13**(2011) p. 025001.
[6] The authors acknowledge funding from the JEOL JEM-2100F probe-corrected TEM was under the support of the University of Michigan College of Engineering and the NSF grant #DMR-0723032.
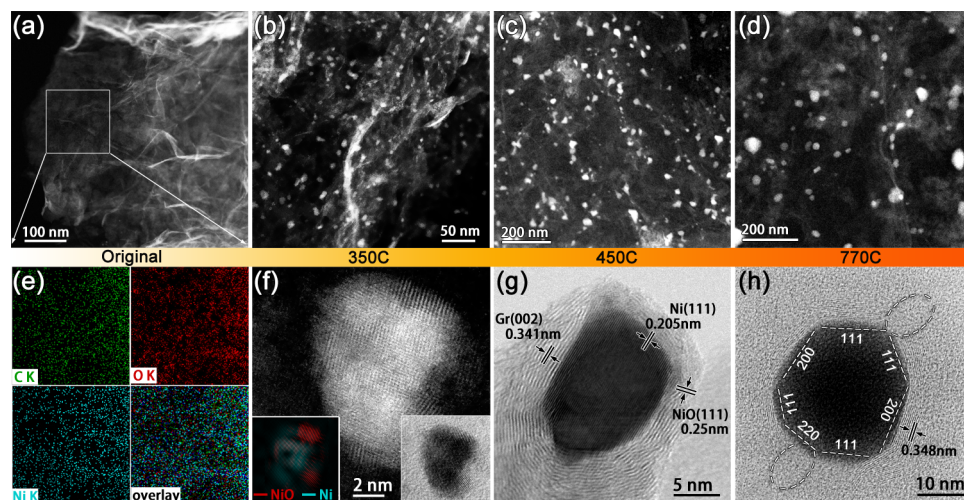
Figure 1. Low magnification (a~d) and magnified (f~h) STEM-ADF images of Ni/Gr composites evolving with temperatures; (e) the EDS mapping of C, O, and Ni elements from area marked in (a).
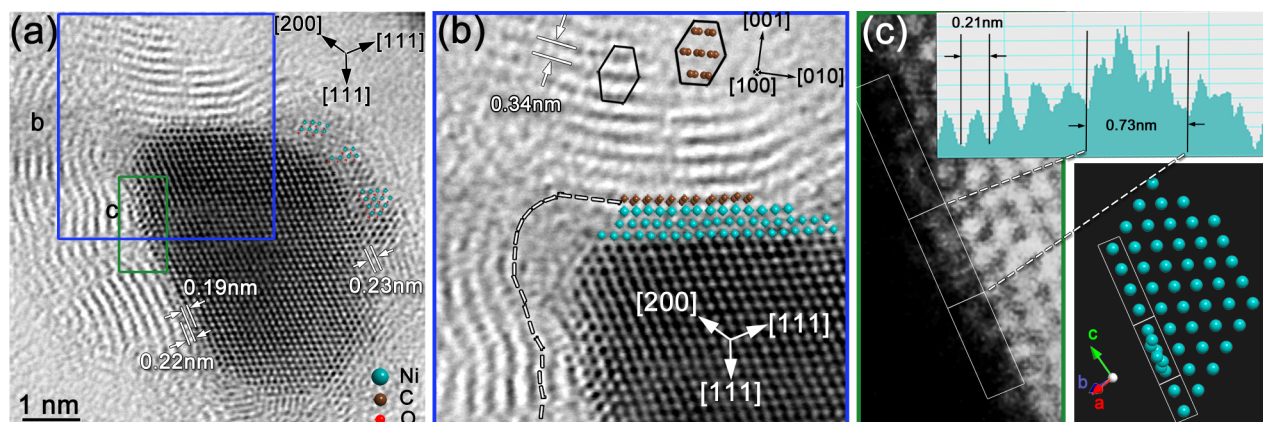

Figure 2. Atom-resovled STEM-BF (a~b) and STEM-ADF (c) images of an individual Ni@Gr particle.