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Letter to the Editor

In-situ generation of metal–metal oxide catalysts for the growth of highly oriented graphitic nanowiggles

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ABSTRACT

In this work we demonstrate an in situ generated growth catalyst that produces highly oriented graphitic nanowiggles (GNWs). GNWs are a new form of disordered nanocarbons with graphite domains stacked perpendicular to the filament axis. They had been prepared by acetylene decomposition at ~525 °C on Al–Mg mesh coated with iron-based nanoparticles. During CVD, inter-diffusion of Mg, Fe, and O between the electrodeposited Fe particles and the mesh generate flakes which become the active site for nanowiggle growth. The properties of this unique form of carbon were evaluated by TEM, HRTEM, SEM, Raman spectroscopy, XPS and cyclic voltammetry.

Low-dimensional crystalline nanocarbons such as graphene and carbon nanotubes offer the possibility of developing new types of materials for a wide range of technologically important applications [1,2]. Carbon deposition from gas phase precursors (i.e. carbon monoxide, acetylene, ethylene and methane) on transition metals has been shown to produce highly graphitic phases in a variety of morphologies [3]. In this work we describe the growth of a new form of nanocarbon, graphitic nanowiggles (GNWs), through the in situ formation of the active catalytic grain during chemical vapor deposition (CVD). The catalytic particle is obtained in two steps: first, electrochemical deposition of iron-based nanoparticles onto an Al–Mg mesh, and second, inter-diffusion of Mg, Fe and O during CVD. The plating media used was 0.03 M $FeCl_2$ in formamide (CH_3NO). The electrodeposits obtained were composed of a mixture of lepidocrocite-iron oxide, iron hydroxide (γ-FeO(OH)) and magnetite (Fe_3O_4) (Supplementary Fig. S1). Then, GNWs were prepared by CVD from 20 sccm (standard cubic centimeters per minute) of acetylene (C_2H_2) gas diluted in a mixture of 70 v% of helium (He, 700 sccm) as carrier gas, and 30 v% of hydrogen (H_2, 300 sccm) at 525 °C to 575 °C, during 10 min. Fig. 1 shows the morphology and structure of GNWs formed; transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Fig. 1a shows a bundle of GNWs on the TEM grid. Fig. 1b shows a group of filaments of ~5 nm of external diameter. Although a relatively low layer contrast is observed at the surface of these nanofilaments, the TEM image has enough resolution to verify that the surface nanostructure of the GNWs do not shows parallel graphene layers to the nano-filament axis, unlike multiwall carbon nanotubes. The GNWs appear to have adjacent

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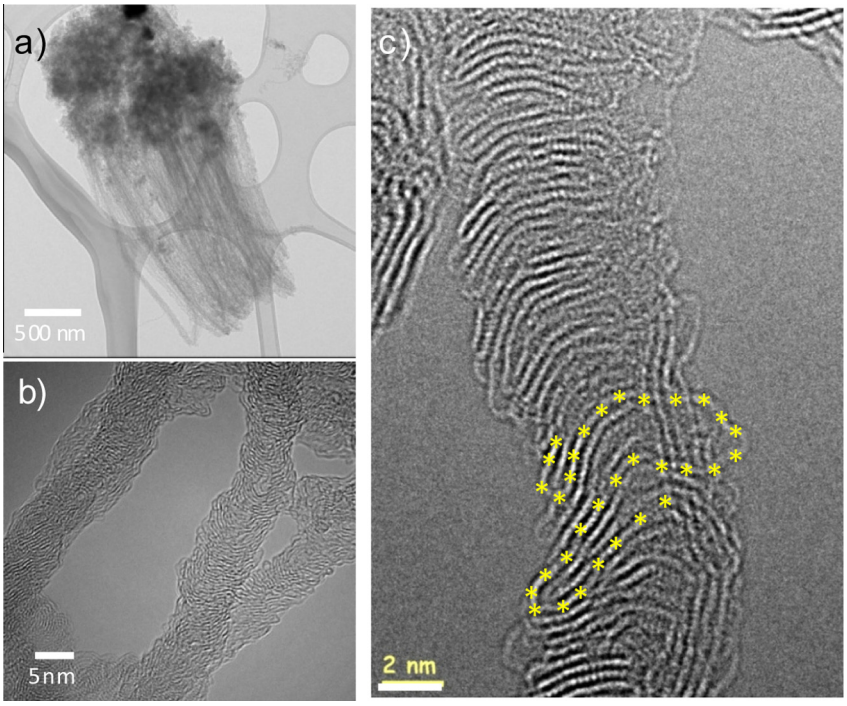

Fig. 1 – Morphology and structure of the GNWs by TEM and HRTEM. (a) A bundle of nanowiggles attached to the catalytic flake. (b) High-magnification image showing the connection between GNWs filaments. (c) HRTEM showing the characteristic pattern of graphitic domains in a single nanowiggle. (A colour version of this figure can be viewed online.)

graphene layers folded and twisted perpendicular to the nanofilament axis. The HRTEM image in Fig. 1c revealed that the GNWs have a novel structure when compared with previously reported filamentous carbons (e.g. platelet, herringbone, and tubular-type) synthesized by decomposition of hydrocarbons [4,5]. The interpenetrated single graphene nano-ribbon layers appear from side to side (wiggling) of the filament (yellow trace in Fig. 1c). Fig. 2a shows the morphology of the GNWs-Fe-MgO complexes after CVD. The higher magnification SEM image (Fig. 2b) shows that the GNWs bundles are aligned perpendicular to the flakes of the catalyst. The highly-oriented nano-filaments are grouped in bundles of ~1 μm length, and are attached to the substrate and the catalytic flake. This flake has a thickness of up to 100 nm. Fig. 2c shows a transmission electron microscopy (TEM) image and the EDX elemental maps of one bundle of GNWs and end-attached catalytic flake. The analysis revealed the presence of Fe, Mg and O. The selected area electron diffraction pattern (SAED) (Fig. S2) shows that Fe nanoparticles are embedded in a matrix of MgO. During the CVD synthetic step, carbon diffuses through the in situ formed flakes originating the GNWs bundles.

In order to investigate the mechanism of formation of these flakes, we performed several thermal treatments at 525 °C on the as-received Al–Mg mesh with and without any carbon precursor. The results were analyzed by EDX (Fig. S3) and XPS (Fig. S4). From these results we propose that interdiffusion between Fe and Mg can be the origin of the catalytic flake formed during the CVD synthesis, which in turn promotes the growth mode of the GNWs. To further confirm

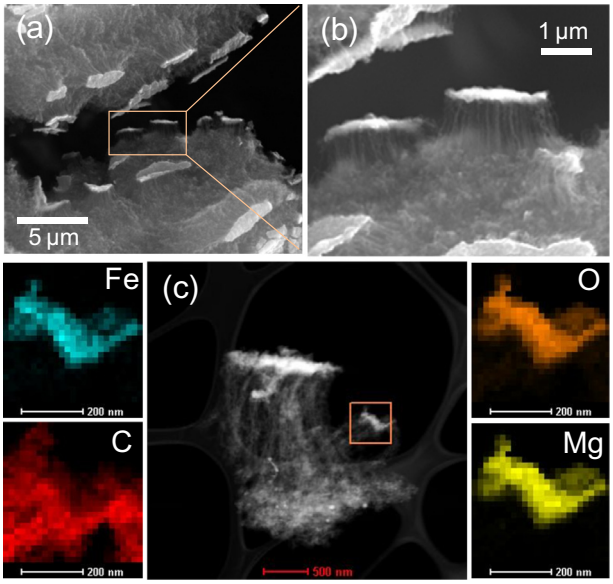

Fig. 2 – Morphology and composition of carbon nanowiggles-catalyst complexes. (a–b) SEM images showing the GNWs bundles that growth oriented perpendicular to the catalytic Fe–MgO flakes, (c) HAADF image and EDX mappings of a bundle of GNWs. (A colour version of this figure can be viewed online.)

our proposed growth mechanism we tested the effect of C_2H_2 (20 sccm) on outer surface components of the bare