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Graphene/nickel nanoparticles composites from graphenide solutions

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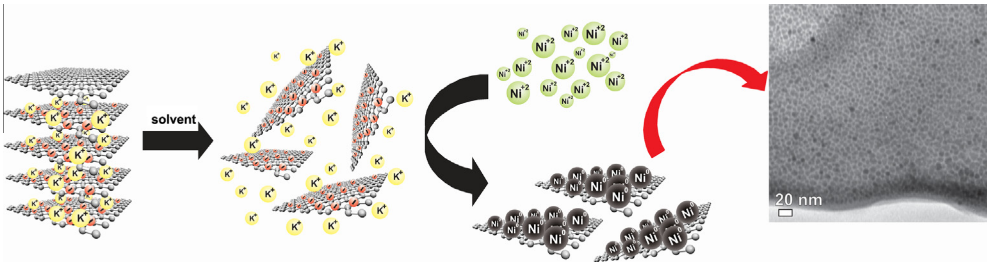
GRAPHICAL ABSTRACT



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ABSTRACT

Nanocomposites between nickel nanoparticles and graphene were obtained starting from nickel cations and graphenide solutions (negatively charged graphene layers) as both reducing agent to nickel cations and graphene source. Different nanomaterials were obtained in two different solvents, N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF), with different nickel/graphene ratios. The nanomaterials were characterized by UV–Vis spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). All the samples consist of large graphene layers highly decorated with crystalline nickel nanoparticles, of size ranging from 2 to 10 nm. Thin films of the samples were deposited on indium-tin oxide (ITO) substrates and electrochemically characterized in alkaline medium, leading to $Ni(OH)_2$/NiOOH redox pair, where the increase of the nickel proportion in the nanocomposites resulted in higher peak currents. The samples obtained in NMP showed the best performance with a fivefold increase of the peak currents, consistent with the lower charge transfer resistance as seen by electrochemical impedance spectroscopy (EIS).

1. Introduction

Nickel nanoparticles have received much interest in the last years due to their multifunctional properties, which allow their use in different fields like magnetic devices [1], batteries [2], catalysts [3], capacitors [4], etc. Regarding electrochemical applications, nickel-based nanomaterials are mainly employed in alkaline medium leading to $Ni(OH)_2$ and NiOOH species. The conversion of metallic nickel to those electroactive species is directly related to the morphological characteristics of the nickel nanomaterial. Thus, control and knowledge of the characteristics of the nickel nanoparticles are key-factors for their further application [5–8]. Many reports, however, relate a loss of performance during some

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applications [9,10]. This deleterious effect can be minimized combining metal nanoparticles with graphene, which avoid significant changes in the nickel morphology during the reduction process [9–12]. Besides enhanced stability, the use of graphene to prepare nanocomposites leads to higher conductivity and surface area, increasing its performance in many applications [13].

Different routes have been employed to obtain graphene, such as thermal rearrangement of SiC [14] and chemical vapor deposition (CVD) using metal catalysts [15], which produce high quality graphene, but with a low yield. Other methods are based on the chemical exfoliation of graphite, leading to a rather high yield of few graphene layers [16] or reduced graphene oxide containing defects as residual oxygenated groups [17]. A recent route to prepare graphene was described by some of us, which consists in the exfoliation of graphite intercalated compounds (GICs) in an organic solvent free of H_2O and O_2, leading to solutions of a negatively charged graphene salt [18–20], called graphenide [21,22]. The obtained solutions are solutions in the thermodynamic sense, i.e. the free energy of mixing GICs and NMP or THF is negative [20,23]. GIC's are known since the 1920s and they are composed of graphite intercalated with alkali metals. These materials are classified by their stage n, which is related to the number of graphene layers between two consecutive intercalant layers. KC_8 is a stage one compound, possesses one layer of graphene between two consecutive intercalant layers, and is the most negatively doped compound, presenting one negative charge for eight carbon atoms [24]. KC_8 is a strong reducing agent and so are graphenide flakes dissolved in a solvent. Likewise, carbon nanotube salts have been used as reducing agent to prepare Au and Pd nanoparticles [25]. However, there is no article that reports the use of KC_8 as reducing agent to metallic ions.

Several examples in the recent literature can be found concerning the preparation of nickel nanoparticles/graphene nanocomposites, as well as the application of these materials as sensors [12], electrodes for batteries [26], catalyst [27], materials for hydrogen storage [28], among others. The most common experimental route to get these nanocomposites is based on the direct reduction of both nickel salt and graphene oxide [27] or the reduction of nickel salt in the presence of graphene. Thermal decomposition of precursors [28] and electrochemical deposition [12] have also been commonly employed. It is well known that different synthetic approaches to nanocomposite materials lead to important modifications in their structure, morphology and properties.

Herein, we report a novel route to synthesize nickel/graphene nanocomposites starting from graphenide solutions, used as both graphene source and direct reducing agent for nickel ions. The characterization of the materials is reported, and the results indicate potential application as electrodes in Li-batteries and electrochemical sensors.

2. Experimental

THF (Sigma Aldrich) was passed through a purification system to remove water and oxygen, and was then distilled inside the glove

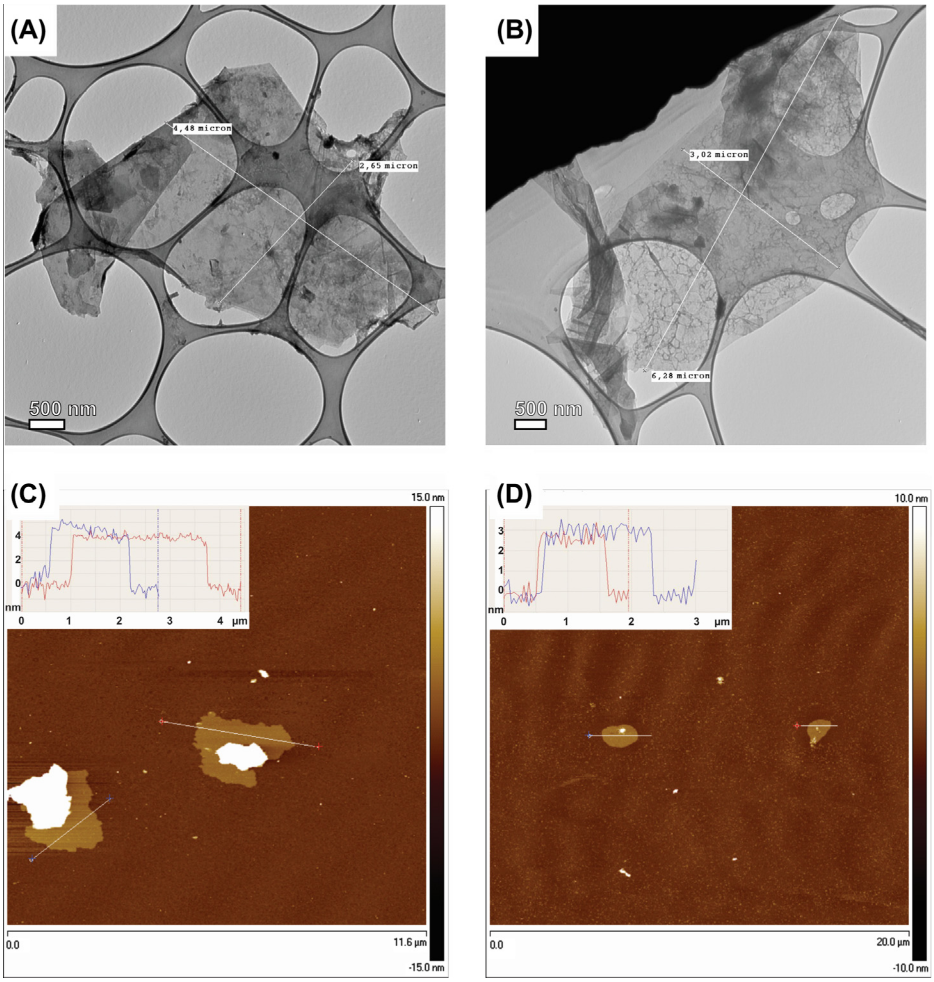

Fig. 1. (A, B) TEM and (C, D) AFM images of few graphene layers prepared in (A, C) NMP and (B, D) THF.