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Semiconductor-metal core-shell nanostructures by colloidal heterocoagulation in aqueous medium

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ABSTRACT

In contrast to complex syntheses for the preparation of colloidal nanocomposites in a core-shell structure proposed in the literature, we present herein a facile colloidal route based on a heterocoagulation process promoted by the electrostatic interaction among ceramic NiO nanoplatelets and metallic Ni nanoparticles (NPs). Before the heterocoagulation process, NiO and Ni were synthetized separately in presence of ultrasound, by chemical precipitation and chemical reduction of the same nickel precursor, respectively. After that, NiO-Ni core-shell nanostructures were prepared forcing the electrostatic interaction among surfaces in aqueous medium. The surface charge balances of both types of particles were tuned effectively by adjusting the pH in a free-additives suspension. For the surface modification of NiO by Ni, the ceramic suspensions maintain a positive zeta potential at pH 9, while the surface of metallic particles is negatively charged. Then the uniform coating of NiO platelets, by the electrostatically induced coagulation with Ni NPs, was favors. The degree of coverage and the formation of NiO-Ni core-shell nanostructures were followed referring the evolution of zeta potential with the geometric calculation in terms of size and morphology of both nanoparticles, and then corroborated by field emission scanning electron microscopy (FESEM).

1. Introduction

In the last decade, the scientific community has paid a special attention to nanocomposites based on semiconductor/metal structures in order to profit from the plasmonic effect of metallic nanocrystals in relevant fields of materials technology, such as energy storage, optoelectronics, photocatalysis or optical bioimaging [1]. Changes in the local environment of semiconductors promoted by the electric field enhancement near the surface of the metallic nanoparticles can significantly increase sensitivity of ceramic semiconductors. In this sense, large commercial applications of such hybrid nanostructures have generated the idea to incorporate an increasing number of nanoplasmonic and magnetoplasmonic metals (i.e Al, Fe, Co or Ni) beyond Au and Ag [2–4]. Complementary, more recent studies show the relevance of the metal-semiconductor interface in the effectivity of the interfacial charge-transfer, and consequently tailoring of the heterostructure assembly to improve the electrochemical and/or catalytic response becomes new challenge [2,4].

In the area of particle engineering, core-shell nanostructures with non-symmetrical shapes and compositions [5,6] have been handled depending on the final application. Among all of them, inorganic/inorganic core-shells have been proved to be extremely useful [5]. The combination of Nickel oxide (NiO) and Nickel (Ni) in a core-shell nanocomposite has already been proposed for many authors, mainly in the configuration of Ni/NiO (Ni as core and NiO as shell) due to its particular advantages in the electrochemical performance of devices for energy storage [7–9]. However the opposite configuration, oxide semiconductor 1D or 2D nanostructures decorated with 0D metal nanoparticles, has paid a special attention because of the epitaxial growth of metal over the semiconductor nanostructure brings interesting plasmonic effects [1]. These semiconductor/metal hybrid nanostructures have been regularly fabricated by heteroprecipitation of the metal by the addition of a proper reducing agent. Moreover, the improved assembly of both nanostructures through an organic molecule has been successfully implemented. In this sense, this work proposes the assembly of Ni NPs onto NiO nanoplatelets by a direct heterocoagulation process. In a first step, both NiO and Ni NPs will be synthetized separately using two different routes, and later the core-shell assembly will be addressed when mixing both suspensions in the adequate ratio.

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2. Experimental procedure

All chemicals were of reagent grade and used without any further purification. The synthesis and annealing of NiO nanoplatelets have been described elsewhere [10]. NiO was obtained from the calcination of as-synthesized β-$Ni(OH)_2$ powder, prepared by chemical precipitation at room temperature using a high intensity ultrasonic horn (45 W/cm^2, 24 kHz, titanium T13 tip, Sonopuls HD 2200, Bandelin Electronic, Germany). The thermal treatment was conducted in air, maintaining a dwell temperature of 325 °C for 5 min, with heating and cooling rates of 10 °C/min.

Metallic Nickel nanoparticles (NP's) were synthesized by the chemical reduction of Nickel Nitrate Hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99,9% purity, Panreac, Spain) with monohydrate Hydrazine ($N_2H_4 \cdot H_2O$, Sigma-Aldrich, Germany), also sonicating with the same ultrasonic horn (Sonopuls HD 2200). The synthesis procedure can be described as follow: a desired amount of Ni precursor was dissolved into deionized water (solution A). Separately, one mixture was prepared by dissolving Potassium Hydroxide (KOH, Panreac, Spain) and monohydrate Hydrazine in water (mixture B). Then, mixture B was poured into solution A while US was applied. The temperature was controlled through the recirculation from a cryothermal bath. The products of synthesis were washed thoroughly for several times with deionized water at pH~9 (adjusting with tetramethyl ammonium hydroxide, TMAH, Sigma-Aldrich, Germany) to residues removal. Ammonium Citrate tribasic ($HOC(CO_2NH_4)(CH_2CO_2NH_4)$ Sigma-Aldrich, Germany) (CIT) was used in one case as synthesis modifier in a molar ratio [Ni^{2+}]: [CIT] of 120:1. It was previously dissolved in the solution A before the addition of the mixture B.

The studied variables have been: i) [Ni^{2+}] concentration (0.02 M, 0.05 M, 0.075 M and 0.1 M), ii) N_2H_4/Ni^{2+} Ratio (6, 20, 60), iii) Temperature (40 °C, 50 °C), iv) Ultrasound Time (5 and 60 min), v) Ultrasound Power (100% (63 W) – 50% (31.5 W)) and vi) Synthesis modifier (CIT).

Core-shell nanostructures preparation was carried out by inducing heterocoagulation of Ni and NiO suspensions. 1 g/L and 10 g/L suspensions of the calcined NiO and as-synthesized Ni nanopowders were prepared, respectively, at the tailored pH in deionized water. Different aliquots of the Ni suspension were added to a beaker where the NiO suspension was being beaten with a mechanical stirrer at 200 rpm. Later, suspensions were rolled overnight to promote the heterocoagulation between NiO nanoplatelets (with positive charge) and NP's (with negative charge).

The surface charge of NiO platelets and NPs was evaluated in terms of zeta potential. A Zetasizer Nano ZS (Malvern, UK) was used in order to determine the particle size distribution and zeta potential of all particles using Dynamic Light Scattering (DLS) and laser Doppler velocimetry, respectively. Suspensions used for determination were prepared with concentrations of 0.1 g/L using 10^{-2} M KCl as solvent and inert electrolyte, so as to maintain the ionic strength of the medium. The pH adjustments of the suspensions were carried out by addition of small aliquots of 0.1 M HNO_3 or TMAH and controlled with a pH probe (Metrohm AG, Germany). Subsequently, homogenization was achieved by sonication, using a UP400S Ultrasonic probe (Hielscher, Germany) for an optimized period of time.

Crystalline phases were characterized by X-Ray diffraction (Siemens-Bruker D8 Advance, Germany) using Cu Kα radiation (λ = 1.540598 Amstrongs). The diffraction patterns were measured step by step (0.05° in 2Θ). Finally, particle size, morphology and crystallography were also examined by field emission scanning

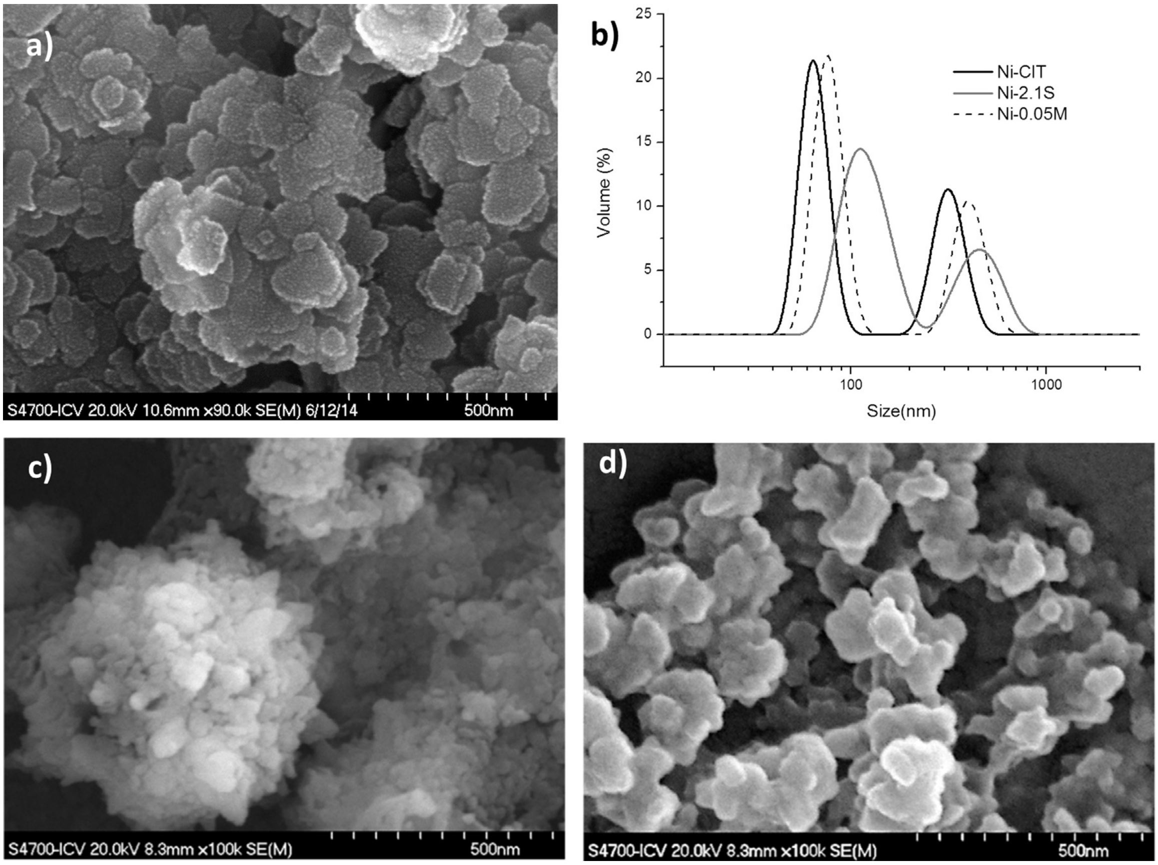

Fig. 1. (a) FESEM image of NiO nanoplatelet, (b)Particle size distribution of the syntheses Ni-CIT, Ni-2.1 S and Ni-0.05 M. And FESEM image of the clusters of Ni NPs synthesized without (c) and with (d) citrate.