



New route toward integrating large nickel nanocrystals onto mesoporous carbons



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ABSTRACT

Integrating large and magnetic transition metal nanocrystals onto mesoporous carbons is of great importance owing to their low cost, easy separation and great potential in various applications. Herein we firstly report large nickel nanocrystals (Ni NCs, 30–75 nm) *in situ* integrated onto mesoporous carbons (MC), synthesized *via* block copolymer-directed self-assembly of nickel acetate and 8-quinolinol modified chitosan under neutral conditions assisted by tetraethyl orthosilicate before pyrolysis and silica removal. This neutral one-pot synthesis not only renders evenly dispersed Ni NCs firmly attached on the mesoporous carbonaceous framework without using any stabilizer, but also creates larger Ni NCs as compared to those prepared by acidic and basic synthetic routes. It is found that all nickel catalysts can be magnetically separated easily; and the Ni NC size, microstructure and the carbonaceous support morphology are well adjusted by variation of the pyrolysis temperature, which in turn affects the catalytic properties of Ni NCs towards 4-nitrophenol reduction. The Ni NC functionalized mesoporous carbon pyrolyzed at 750 °C (Ni-MC-750) simultaneously possessing twinned microstructure and carbon nanotube morphology, exhibits the highest catalytic efficiency. High-energy X-ray diffraction, N₂ adsorption/desorption, transmission electron microscopy, infrared spectroscopy, X-ray absorption fine structure and Raman spectroscopy studies, as well as the comparative catalytic tests have demonstrated these points.

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1. Introduction

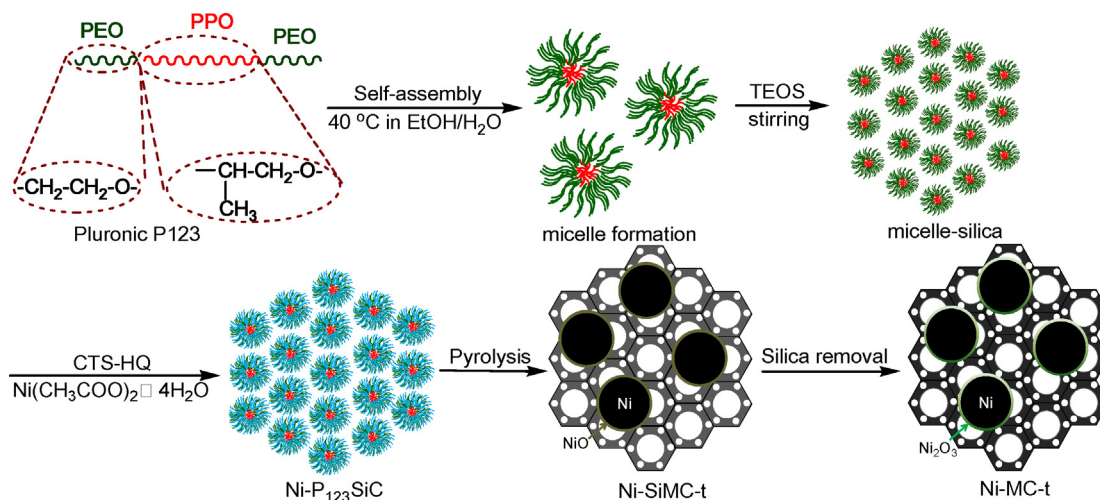
To overcome the problem pertaining to the environmental pollution, green processes have been recently achieved *via* chemical transformations by using green solvents, nontoxic chemicals and ambient reaction conditions. In this aspect, the disposal of nitro compounds is an area of intensive research [1–6]. Nitrophenols are among the most common organic pollutants in industrial and agricultural wastewaters. In particular, 4-nitrophenol (4-NP) is a notorious industrial pollutant exhibiting high solubility and stability in water [7,8]. It is therefore important to develop effective methods for its removal. There are various methods including microbial degradation, catalytic oxidation and electrochemical treatment, have been well developed for its disposal [9–11]. However, the catalytic reduction of 4-NP to 4-aminophenol (4-AP) by using sodium borohydride, which is widely used in sewage

treatment, is considered to be the most efficient, green and economical approach [12–15], and the reduction product namely, 4-AP, has great industrial relevance such as for aniline and paracetamol production [16]. Hence, various catalysts, including precious or doped precious metals [17–21], non-precious metals, mainly Ni-containing nanostructures [17,22–25], and metal-free catalysts [26], have been investigated for this process. Among which, magnetic transition metal nanocrystals (NCs) are much favored since they are low cost, and make the separation process easy by means of an external magnetic field, avoiding the conventional filtration or centrifugation procedures, which is a key obstacle preventing the industrial scale application. In spite of their significant virtues, these magnetic NCs, especially in small size, are prone to agglomeration during usage owing to their high surface energy, which will remarkably lower their catalytic activity and reduce the lifetime. Therefore, creating large NCs and dispersing them on porous supports are vital for construction of economical and persistent nanocatalysts for wastewater treatment.

Magnetic NCs are always immobilized on porous supports, including silica, alumina, titania, zirconia, magnesia and carbon

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Scheme 1. Schematic description of the Ni-MC-t synthesis.

[27–32]. Amongst them, porous carbonaceous supports are the most frequently used, and proved to be superior to oxide carriers, due to their chemical inertness and excellent stability under both acid and basic conditions. So activated carbon, because of its large specific surface area and high pore volume, is widely used as the support. However, the micropore size restricts its further application owing to the difficulty in large molecule transportation [33]. Therefore, mesoporous carbons (MC) with uniform large pores and high surface area are much in demand. Recent advances in the fabrication of NCs onto MC focus on the hard-templating approach to infiltrate an appropriate carbon precursor (e.g. furfuryl alcohol, sucrose) and metal source (Fe, Co and Ni compounds) into the mesopores of the silica template, followed by thermal polymerization, carbonization and subsequent silica dissolution [34–37]. It is demonstrated that SBA-15 coated with 2,3-dihydroxynaphthalene (DHN) and then impregnated with nickel salt and heated, results in mesoporous carbons with evenly dispersed Ni NCs [38]. However, this multi-step synthetic procedure is time-consuming, including repeated impregnation with carbon and/or metal precursors, which may severely hamper the broad application of these composite materials. Recently, in the case of soft-templated carbons, the incorporation of inorganic species to the carbon framework can be done directly during the self-assembly process. So adding the metal salt to the reaction mixture involving the polymerizable precursors and block copolymer templates, can facilitate its transformation into metal NCs embedded in the carbon matrix during thermal treatment. This concept is well demonstrated by Zhao's group; they use nickel nitrate as the metal precursor, resol as the carbon source, and Pluronic F127 as the template in the one-pot synthesis to obtain MCs with evenly distributed Ni NCs (16–20 nm, 10 wt% Ni) [39]. However, more nickel precursor has to be introduced to prepare large Ni NCs, since possible Ni leaching cannot be avoided under the acidic synthetic condition. Our previous studies demonstrate that larger Ni NCs (25–40 nm) can be realized by CTAB-directed self-assembly of modified chitosan and nickel nitrate (10 wt%) under basic conditions [40,41]. Unfortunately, the particle size cannot be further improved even increasing Ni percentage to ca. 20 wt%. It is probable that in the presence of ammonia, the formed nickel ammine was dissolved into the reaction mixture, lowering the Ni loading. Therefore, it is speculated that under neutral synthetic conditions, much larger Ni NCs would be prepared since more Ni species could be captured.

We herein firstly report large nickel nanocrystals (Ni NCs, 30–75 nm, ca. 20 wt%) *in situ* integrated onto mesoporous carbons

(MC), synthesized *via* Pluronic P123-directed self-assembly of nickel acetate and 8-quinolinol modified chitosan under neutral conditions assisted by tetraethyl orthosilicate before pyrolysis and silica removal. This silica-assisted strategy strengthens the interaction between chitosan and P123 *via* the polymerization of chitosan with silica, rendering “homogeneous” interpenetrating silica–chitosan frameworks with evenly dispersed nickel complexes inserted, leading to homogeneously distributed Ni NCs on the silica–carbon frameworks in the resulting pyrolyzed samples. Silica removal created more exposed and magnetically recoverable Ni NCs, and their size, microstructure, carbonaceous support morphology, and the corresponding catalytic performances towards 4-nitrophenol reduction can be facily tuned by variation of the pyrolysis temperature.

2. Experimental

2.1. Materials preparation

Ni NCs were *in situ* integrated onto the MCs *via* construction of P123-directed silica–chitosan–nickel assemblings (Ni-P₁₂₃SiC) before pyrolysis and silica removal. First, 8-quinolinol modified chitosan, CTS-HQ, was facily synthesized from 5-chloromethyl-8-quinolinol hydrochloride (1), involving a two-step chemical transformation from 8-quinolinol (see Supporting Information and Figs. S1–S6). Then, TEOS, CTS-HQ and $Ni(CH_3COO)_2 \cdot 4H_2O$ were respectively used as silica, carbon and metal precursors, and added stepwise to synthesize P123-directed precursor composite before pyrolysis and silica removal (Scheme 1). The molar ratio of the precursor gel in the preferred preparation is: 1 CTS-HQ:0.5 $Ni(CH_3COO)_2 \cdot 4H_2O$:0.017 P123:0.55 TEOS:66.5 H₂O:19.6 EtOH. The mixture was stirred at 40 °C for 20 h and then transferred into a polypropylene bottle and reacted at 100 °C under static conditions for 48 h. The as-made product was washed, dried and pyrolyzed in a tubular furnace under N₂ atmosphere. The heating rate was 2 °C/min below 250 °C and 5 °C/min above 250 °C, and the pyrolysis was carried out at 550, 750 and 950 °C for 2 h, respectively. The resulting solid were denoted as Ni-SiMC-*t*, and were subjected to alkaline etching with 3.0 M NaOH solution to remove silica layers, affording Ni-MC-*t*, where *t* represents the carbonization temperature. For comparison, nickel-free mesoporous carbon (MC-750) was synthesized according to the above procedure with the maintenance of the total precursor compounds except for nickel acetate.

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