Ionic Liquid-assisted Solvothermal Synthesis of Ni Particles and Study of Their Electrocatalytic Effect for Calcium Dobesilate Oxidation

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This article presents a simple ionic liquid-assisted solvothermal synthesis approach to the preparation of Ni particles from nickel acetylacetonate ($Ni(acac)_2$) as the precursor and N,N-dimethylformamide (DMF) as the solvent, where the ionic liquid, 1-methyl-3-ethoxyl imidazolium tetrafluoroborate ($[C_2OHmim]BF_4$), was used as the reducing agent and as stabilizer. The as-prepared Ni particles were characterized by means of X-ray diffracion (XRD) and scanning electron microscopy (SEM). The formation mechanism of the Ni particles during the solvothermal process is discussed. The electrocatalytic effect of Ni particles for calcium dobesilate (calcium 2,5-dihydroxy-benzenesulfonate, abridged as CDBS) oxidation on glassy carbon (GC) electrodes was investigated using cyclic voltammetry. It was found that the size of the Ni particles could be tuned by properly adjusting the concentration of the ionic liquid $[C_2OHmim]BF_4$ and of the reaction time and temperature. Moreover, the Ni particles prepared after reaction at 180 °C for 6 h in the presence of the ionic liquid had a strong electrocatalytic effect on CDBS oxidation, making them potentially applicable in electrochemical biosensors.

Key words: Ionic Liquid, Nickel, Electrocatalytic Oxidation

Introduction

As a class of important functional materials, magnetic metals such as Fe, Co, and Ni have been widely used in various fields including ferrofluids, solar energy absorption, permanent magnets, magnetic carriers for drug targeting, and catalysis [1 – 6]. Typically, nickel, as one of the non-noble metal materials, has promising applications in drug targeting and catalysis because of an effective electrocatalytic activity toward some organic compounds [7, 8]. Many methods such as metal carbonyl pyrolysis [8, 9], templated synthesis [10, 11], electrochemical deposition [12 – 15], and thermal reduction of Ni(II) salts with reducing agents in an organic solvent have been established for preparing Ni nanoparticles [16 – 18]. To date, however, few researches have been reported about the electrocatalytic oxidation of calcium dobesilate (calcium 2,5-dihydroxy-benzenesulfonate, CDBS) [19], a synthetic drug to treat chronic venous insufficiency and diabetic retinopathy, but with increased risks of adverse effects in pharmaceutical formulations and human biological matrices, on nanostructured electrodes.

Therefore, in the present research we focus on effectively increasing the electrocatalytic activity of nickel towards organic compounds by forming nanostructures [20], aiming to provide technical support for more efficient detection of CDBS. Our favorite choice is to prepare Ni nanostructures in the presence of room-temperature ionic liquids (RTILs), because RTILs have unique chemical and physical properties such as negligible vapor pressure, high chemical and thermal stability, high polarity, a wide electrochemical window, and the ability to dissolve a large variety of organic and inorganic compounds [21 – 24]. They have been used in various fields including organic synthesis, catalysis, electrochemistry [25 – 27], and inorganic synthesis [28 – 30]. The advantages of using RTILs in preparing metallic nanoparticles lies in the facts that they can act as stabilizers for the nanoparticles and are able to isolate metal nanoparticles, making it feasible to prevent the targeted metallic nanoparticles such as gold [31], palladium [32], iridium [33], and germanium [34] from aggregation and hence realize better catalytic function.

With those perspectives in mind, we have established an ionic liquid-assisted solvothermal route for the preparation of Ni nanoparticles using $Ni(acac)_2$ as

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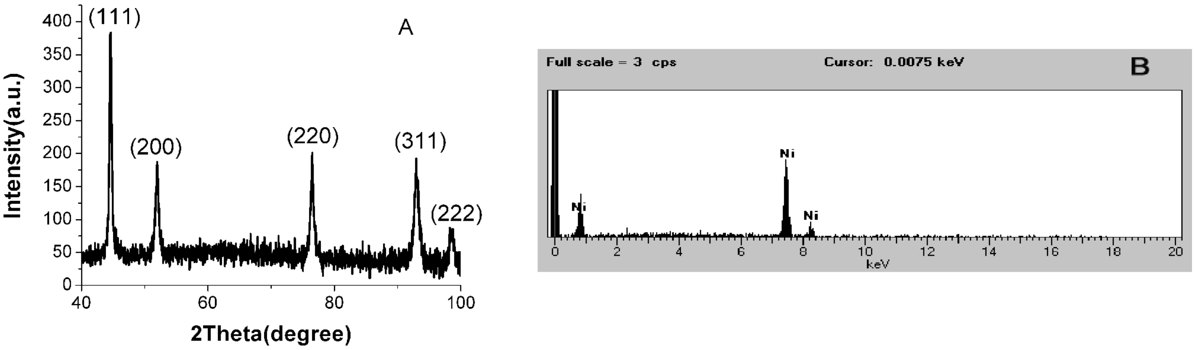

Fig. 1. A) XRD pattern and B) EDS spectrum of Ni particles obtained after reaction at 180 °C in an ionic liquid system (100 mM) for 6 – 12 h.

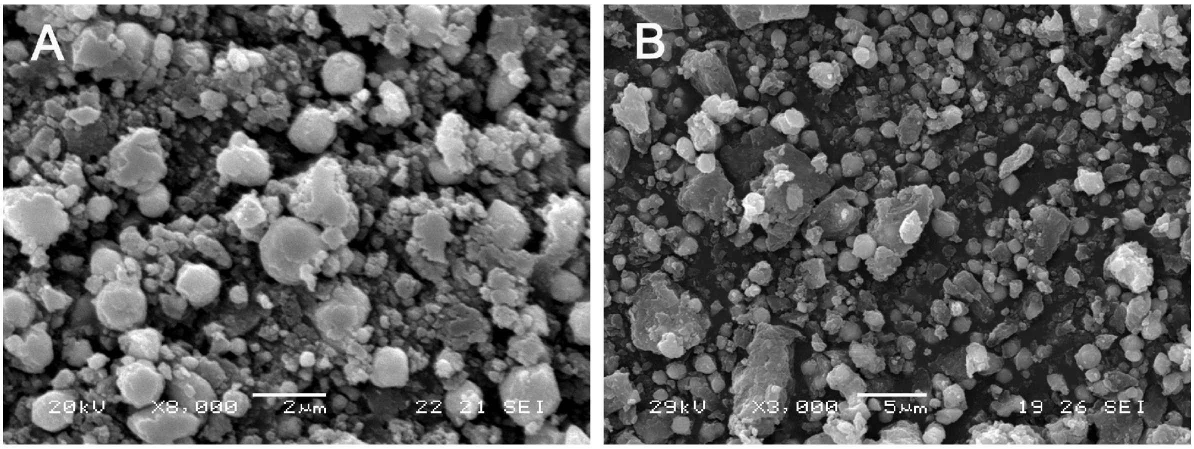

Fig. 2. SEM images of Ni particles obtained without ionic liquid.

the precursor and DMF as the solvent. And furthermore, we have investigated the electrocatalytic oxidation process of CDBS on a glassy carbon electrode modified with Ni nanoparticles.

Results and Discussion

Fig. 1 presents the XRD pattern and EDS spectrum of Ni particles prepared after reaction of Ni(acac)$_2$ in DMF at 180 °C in an ionic liquid system (100 mM) for 6 – 12 h. All the diffraction peaks of the Ni particles match well with that of face-centered cubic (fcc) Ni (Joint Committee on Powder Standards file No. 04-0850). Namely, the peaks at 44.51°, 51.84°, 76.37°, 92.94°, and 98.44° are assigned to (111), (200), (220), (311), and (222) planes (Fig. 1A), respectively, of Ni. This indicates that the Ni particles prepared are well crystallized, which could be closely related to their refining by the ionic liquid. The broadening of the diffraction peaks implies that the addition of the ionic liquid leads to a decrease of the size of the Ni particles. The EDS result (Fig. 1B) indicates that the as-prepared Ni particles are composed of elemental Ni alone, since no signals of other impurities are visible.

Fig. 2 shows the SEM morphologies of the Ni particles prepared in the absence of an ionic liquid. It is seen that the Ni particles prepared in the absence of the ionic liquid have irregular shapes and relatively large sizes from hundreds of nanometers to a few micrometers. Thus it can be inferred that Ni micro-crystals were liable to grow up and aggregate as well when no ionic liquid was introduced in the reactant system.

Fig. 3 shows the SEM images of the products obtained in the presence of an ionic liquid system (100 mM) after reaction at 180 °C for different durations. It is seen that the Ni particles prepared in the presence of the ionic liquid are spherically shaped and much smaller in size than those prepared in the reactant

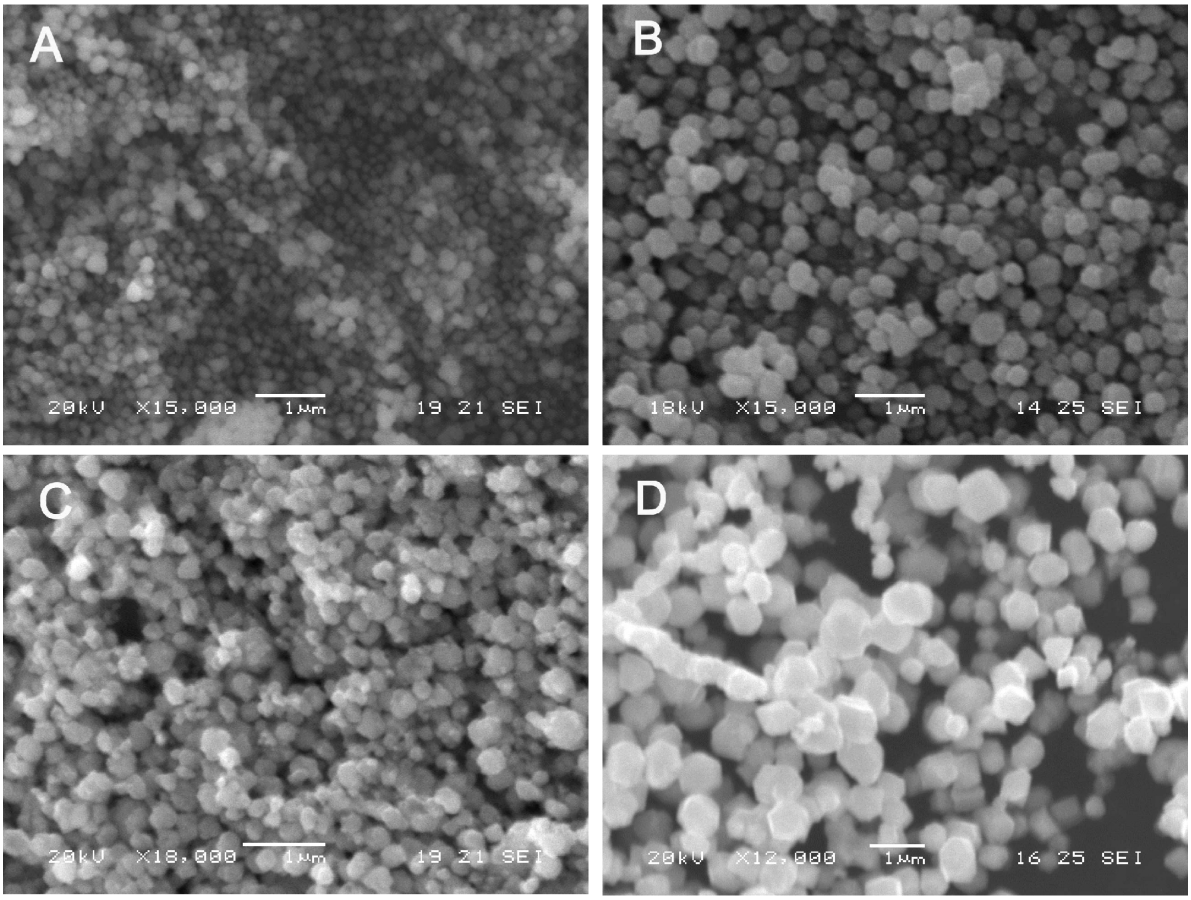

Fig. 3. SEM images of Ni particles obtained after reaction at 180 °C in an ionic liquid system (100 mM) for different time intervals. (A) 6 h; (B) 8 h; (C) 10 h; and (D) 12 h.

system without ionic liquid. For example, the Ni particles synthesized after reaction at 180 °C for 6 h in the ionic liquid system are well separated from each other and have a size of about 200 nm (Fig. 3A). Moreover, the size of the Ni nanoparticles increases with increasing reaction time. Namely, the Ni particles prepared at a reaction time of 8, 10, and 12 h have increased sizes of 300, 400, and 800 nm (Figs. 3B, C, and D, respectively). Therefore it is to be recommended to select a reaction time of 6 h for the reactant system containing an ionic liquid in order to obtain Ni particles with smaller sizes, resulting in better electrocatalytic activity. No nanoparticles are obtained at reaction times > 8 h.

Fig. 4 shows the SEM images of the products obtained after reaction at 200 °C for different time intervals in an ionic liquid system (100 mM). As shown in Fig. 4A, the Ni particles synthesized after reaction at 200 °C for 5 h have a size of approximately 400 nm. When the reaction time was prolonged to 8 h, the corresponding Ni particles have an increased size of about 800 nm. In combination with Fig. 3, it can be concluded that the size of final Ni particles increases with increasing reaction time and temperature. It would therefore be infeasible to obtain nanoscale Ni particles at extended reaction duration or increased reaction temperature even though an ionic liquid was used as a stabilizer in the synthesis.

The reactions involve the chemical reduction of $Ni(acac)_2$ and the nucleation and growth of Ni nuclei into microspheres, and the size of the Ni particles is dependent on the reduction rate as well as on the nucleation and growth rate. It can be rationally anticipated that the formation rate of nickel nuclei depends on their precipitation rate from the reactant solution, which should be closely related to the concentration of

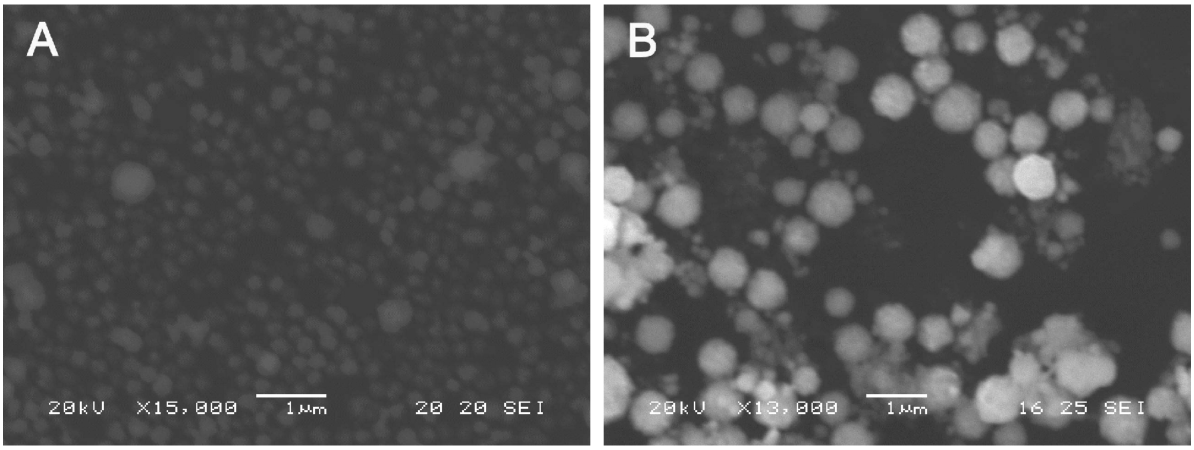

Fig. 4. SEM images of Ni particles obtained after reaction at 200 ℃ in an ionic liquid system (100 mM) for (A) 5 h and (B) 8 h.

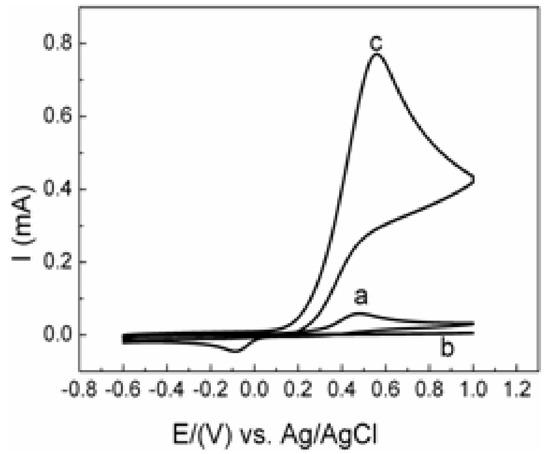

Fig. 5. CVs of 1 mM calcium dobesilate on (a) a bare GC electrode, (b) a buffer solution alone, (c) on a Ni/GC electrode (in 0.1 M phosphate buffer solution, pH = 6.0; scan rate: 100 mV s^{-1}; Ni particles as synthesized in the ionic liquid system after reaction at 180 ℃ for 6 h).

the solution. When other reaction conditions are fixed, Ni particles are generated as a result of rapid nucleation under the protection of the ionic liquid, while with the concentration of the ionic liquid fixed, the growth rate of Ni crystallites rises significantly with increasing temperature.

In order to examine the catalytic activity of the Ni particles prepared under different conditions, cyclic voltammetry (CV), a surface sensitive technique, was used to check whether these Ni particles had different effects on the electrochemical oxidation of CDBS. We found that the Ni particles which were obtained in the ionic liquid system with smaller sizes show better electrocatalytic activity. The Ni particles used in Fig. 5 were synthesized by reaction at 180 ℃ for 6 h and had a size of about 200 nm (Fig. 3A). Fig. 5 shows the CV of the bare GC electrode in the presence of 1 mM CDBS (curve a) and the CVs of the Ni/GC electrode in the absence (curve b) and presence (curve c) of 1 mM CDBS. No redox peak appeared on the CVs of the Ni/GC electrode (curve b) in blank buffer solution, indicating that the Ni particles were non-electroactive in the selected potential range. After co-immobilizing the Ni particles on the surface of the GC electrode, electro-oxidation of CDBS took place at +0.55 V (*vs.* Ag/AgCl; curve c), indicating that the Ni particles had electrocatalytic activity for the oxidation of CDBS on the GC electrode. On the GC electrode modified with Ni particles, the anodic peak current for CDBS significantly increased, while the cathode peak disappeared, indicating that CDBS on the modified GC electrode had a much larger catalytic anodic peak current than on the bare GC electrode, corresponding to electrocatalytic oxidation processes. Therefore, the present research has demonstrated a potential novel strategy for developing Ni microcrystal-based electrochemical biosensors. The study in that respect is underway.

Conclusion

A facile ionic liquid-assisted solvothermal method has been established to synthesize Ni microcrystals, using $Ni(acac)_2$ as the precursor and the ionic liquid 1-methyl-3-ethoxyl imidazolium tetrafluoroborate as a reductant and stabilizer. The electrocatalytic oxidation process of CDBS on a glassy carbon electrode modified with Ni particles was investigated using cyclic voltammetry. It was found that the size of the Ni microcrystals could be tuned by adjusting the concentration of the ionic liquid, the reaction time and temperature. With the protection of the ionic liquid, it was possible to obtain well-dispersed Ni particles. These Ni particles had a strong electrocatalytic effect for the oxidation of CDBS, making them potentially applicable in electrochemical biosensors.

Experimental Section

Materials

Ni(acac)$_2$ (analytical grade, 99.3 %) was purchased from Xingye Zhuji Company Limited of Yangzhou City (Yangzhou, China). DMF and ethanol (both analytical grade) were purchased from Tianjing Chemical Reagent Company Limited (Tianjin, China). CDBS was purchased from Shandong Juye Lingfeng Chemical Materials Company Limited (Shandong, China). The ionic liquid [C$_2$OHmim]BF$_4$ was prepared at our laboratory according to the literature [35]: 1-Chloroethanol (64 mL, 0.95 mol) and 1-methylimidazole (50 mL, 0.63 mol) were added to a round-bottomed flask fitted with a reflux condenser and heated for 24 h at 80 °C with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted, and diethyl ether (50 mL) was added with thorough mixing. The diethyl ether was decanted followed by addition of fresh solvent, and this step was repeated twice. The bottom phase was washed with diethyl ether (4 × 25 mL), heated at 80 °C and stirred under vacuum for 2 d. [C$_2$OHmim][Cl] was obtained as a slightly yellow liquid which solidified on cooling. [C$_2$OHmim][Cl] (25.00 g, 0.15 mol) was transferred to a plastic Erlenmeyer flask (250 mL). Acetone (150 mL) was added followed by NaBF$_4$ (19.00 g, 0.17 mol). This mixture was stirred at r. t. for 24 h. The resulting waxy solid precipitate was collected by filtration and washed with acetone (2 × 100 mL). The combined layer was collected, dried (MgSO$_4$) and filtered, and the solvent removed in vacuum to give the product [C$_2$OHmim][BF$_4$] as a colorless liquid.

Synthesis of Ni particles

In a typical synthesis, 25 mL of a 20 mmol Ni(acac)$_2$ solution (a certain quantity of Ni(acac)$_2$was dissolved in DMF), and 100 mmol of ionic liquid were mixed and sealed in a Teflon-lined stainless steel autoclave (capacity: 50 mL). The mixture was then heated to different temperatures in an oven and held there for different reaction durations, allowing the generation of Ni particles. At the end of the reactions, the autoclave was taken out of the oven and cooled in tap water, generating dispersions of the primary products. The dispersions were purified by cycles of centrifugation and redispersion, where the supernatant was sequentially decanted and replaced with ethanol. Finally the purified powders were dried at r. t. in vacuum, to attain the final products. A small amount of Ni particles was dispersed in H$_2$O by ultrasonic agitation to give a black suspension, and a drop of the concentrated suspension was then dispersed onto a GC disc electrode (d = 3 mm) and dried in a desiccator to remove the solvent. To ensure good reproducibility, the GC electrode was sequentially mechanically polished with fine emery paper and alumina paste to obtain a mirror finish surface (surface roughness Ra below 0.05 μm), followed by sonication in Milli-Q water for 3 min. A counter electrode Pt ring and a reference electrode Ag/AgCl were used for measurement of the electrocatalytic activity, and all the potentials were quoted *vs.* Ag/AgCl. The standard stock solution, 1.0 mM CDBS, was prepared daily by dissolving CDBS in distilled water. Conventional Ni particles were prepared in the same manner except that no ionic liquid was used in the reactant system.

Characterization

Ni particles as the target products were characterized by means of scanning electron microscopy (SEM, JSM-5600LV, equipped with an energy dispersive spectrometer (EDS) attachment) and powder X-ray diffraction (XRD, Philips X'PertPro, CuK_α radiation). All electrochemical measurements were performed in a conventional three-compartment glass cell installed on an electrochemical workstation (CHI 660, CH Instruments).

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