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Preparation of nickel and Ni_3Sn nanoparticles via extension of conventional citric acid and ethylene diamine tetraacetic acid mediated sol–gel method

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A B S T R A C T

This work aims to extend the application field of sol–gel process from conventional oxides, carbides, sulfides to metallic nanocrystalline materials. Metallic ions were coordinated with chelating agents of citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) in aqueous solution. Then the solutions were dried at 383 K, resulting in the formation of sol and gel. Heating treatments of dried gels were then carried out with protection of N_2 atmosphere. Ni and Ni_3Sn alloy nanoparticles were obtained by this sol–gel method in the range of 623–823 K. The as-prepared Ni and Ni_3Sn alloy nanoparticles have average grain sizes of 15 and 30 nm, and have face-centred-cubic (fcc) crystalline phase. Our results provide new insight into the application of conventional sol–gel method.

1. Introduction

Sol–gel method is a conventional way for preparation of functional materials such as oxides [1], carbides [2], and sulphides [3] because this method can ensure homogeneous molecular level mixture of different components [4]. Homogeneous mixing can be accomplished by combination of chemicals with chelating agents in aqueous or organic solutions [5]. Citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) are often operated as chelating agents in aqueous solution for the preparation of materials [5–7] due to the strong chelating capacity of CA and EDTA.

Recently, new phenomena of sol–gel method have been discovered [8,9]. For instance, by extension of traditional StÖber method, monodisperse carbon spheres instead of SiO_2 spheres can be obtained [8]. Metallic nanoparticles can also be obtained by CA mediated sol–gel method [9]. The CA mediated process can be performed in aqueous as well as organic solutions [10–13]. Since EDTA have been widely used in sol–gel method, it is still necessary to explore the possibility of preparation of metallic nanoparticles by applying EDTA. In addition, pH value is an important parameter in aqueous solution that can determine the crystalline phase and grain size of the final products [14]. The effect of pH on the crystalline phase of metallic nanoparticles prepared by sol–gel method has not been reported yet. In this work, we show for the first time that EDTA is also an effective chelating agent for preparation of nickel nanoparticles and the grain sizes of nickel nanoparticles can be controlled at different pH values, and we also show that Ni_3Sn alloy nanoparticles can be obtained by this sol–gel method.

2. Experimental

The initial chemical agents were CA, EDTA, nitrilotriacetic acid (NTA), diethylene triamine pentacetate acid (DTPA), nickel nitrate ($Ni(NO_3)_2\cdot6H_2O$), nickel sulphate ($NiSO_4\cdot6H_2O$), nickel chloride ($NiCl_2\cdot6H_2O$), nickel formate ($Ni(HCOO)_2\cdot2H_2O$), nickel acetate ($Ni(CH_3COO)_2\cdot4H_2O$, $Ni(ac)_2\cdot4H_2O$), nickel aminosulfonate ($Ni(NH_2SO_3)_2\cdot4H_2O$), stannic chloride ($SnCl_4\cdot5H_2O$), ammonia ($NH_3\cdot H_2O$), sodium dodecyl sulfonate ($C_{12}H_{25}SO_4Na$, SDS), polyvinylpyrrolidone (PVP, K-30), and tween 20. All these chemical agents had analytical purity and were used as-received without further purification. In a typical process, 0.004 mol nickel nitrate was dissolved in a beaker containing 100 ml de-ionized water, followed by addition of PVP. Then 0.02 mol CA was dissolved in the

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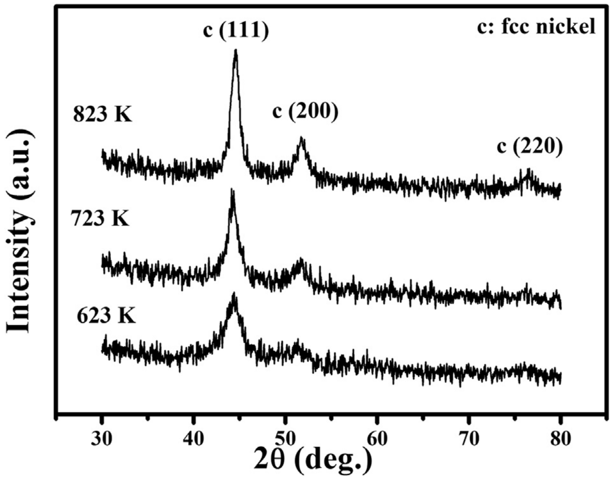

Fig. 1. The XRD analysis results of nickel nanoparticles prepared by using $Ni(NO_3)_2 \cdot 6H_2O$ and SDS, CA where the calcination temperatures are 623, 723 and 823 K, respectively.

solution where ammonia was used to adjust the pH value of the solution. The molar ratio of Ni^{2+}: CA was 1:5. Transparent green solution was formed under magnetic stirring. Then the transparent solution was dried at 383 K, which was near the boiling point of de-ionized water. During the drying process, the viscosity of the solution was increased gradually as the solvent was evaporated, indicating the formation of sol and gel. Porous dried gel was obtained after the solvent was evaporated completely. Then some parts of the dried gel were calcined at different temperatures for 3 h under N_2 protecting atmosphere, followed by cooling down to room temperature. The heating rate of the calcination was 3 K/min and N_2 flow was applied during the whole calcination procedure, including cooling of the calcined product. In the heating treatment, the dried gel decomposed and reducing gases of H_2, CH_4 could be released [9,10], which could ensure the formation of metallic nanoparticles. Finally, black products were obtained and kept in a sample sack in a drying dish in air. It should be pointed out that the nanoparticles were supported by amorphous media main containing carbon [15] because the heating treatment should be carried out at temperature higher than 1073 K to eliminate carbon [14]. When nickel sulphate, nickel formate, nickel acetate, and nickel aminosulfonate were used, nickel nitrate was replaced by these nickel sources. The other procedures were the same as the procedures when nitrate and CA were conducted. When EDTA, NTA or DTPA were applied, CA was substituted by chelating agent of EDTA, NTA, DTPA, respectively. First, nickel nitrate and surfactant of PVP were dissolved in de-ionized water. Then chelating agent was added into the solution followed by drying the solution near the boiling point of water. During the drying procedure, the chelating agent was dissolved into the solution gradually until it was dissolved completely. According to the concentrations of Ni^{2+} ions and EDTA, the molar ratios of Ni^{2+}: EDTA were adjusted to be 1:1, 1:2 and 2:1, respectively. The molar ratios of Ni^{2+}: NTA and Ni^{2+}: DTPA were 1:1. Then ammonia was added into the solutions to adjust the pH value of the solutions. After the dried gel was obtained, calcinations of the dried precursors were carried out under N_2 protecting atmosphere. The as-obtained products were also kept in air.

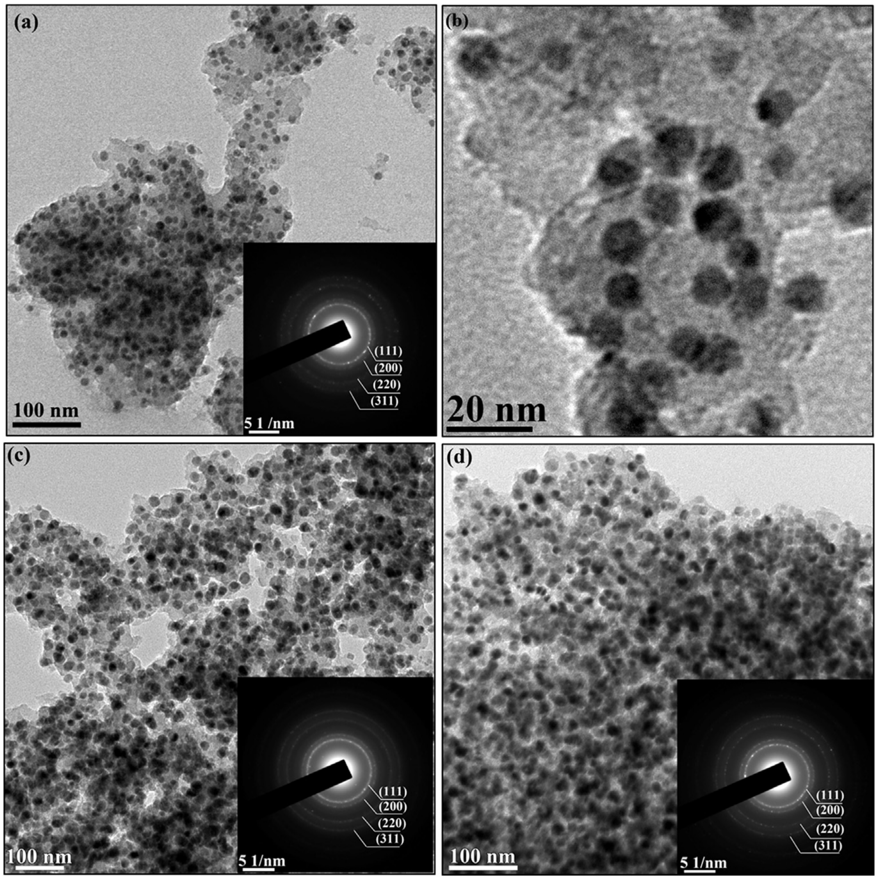

Fig. 2. The TEM images and corresponding SAED results of nickel nanoparticles calcined at 623 K (a, b), 723 K (c) and 823 K (d).