Preparation of nickel and Ni₃Sn nanoparticles via extension of conventional citric acid and ethylene diamine tetraacetic acid mediated sol-gel method.

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ABSTRACT

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 N₂ atmosphere. Ni and Ni₃Sn alloy nanoparticles were obtained by this sol-gel method in the range of 623-823 K. The as-prepared Ni and Ni₃Sn 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.

Key Words: Sol-gel; Citric acid; EDTA; Ni nanoparticles; Ni₃Sn nanoparticles.

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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 SiO₂ 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 Ni₃Sn 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 ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), nickel formate ($\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$), nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$), nickel aminosulfonate ($\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$), stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), sodium dodecyl sulfonate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, 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 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 3h under N_2 protecting atmosphere, followed by cooling down to room temperature. The heating rate of the calcination was 3K/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. For the preparation of Ni-Sn alloy nanocrystals, 0.003 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.001 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and 0.02 mol CA were dissolved into 100 ml de-ionized water where SDS was used as surfactant and N_2 was used as protecting atmosphere. The initial atomic ratio of Ni: Sn was 3:1 and the pH of the solution was adjusted to 2. In order to

determine the yield of the nanoparticles, the as-obtained nanoparticles were calcined at 1273 K in air to remove the supporting media of carbon. The metallic phase was transformed into oxide phase and the yield of the nanoparticles could be obtained from the initial concentration of the metallic ions and the final mass of the oxides. For comparison, CA was replaced by EDTA and SDS was replaced by tween 20 for preparation of Ni₃Sn alloy nanoparticles. In view of possible applications, the scale up experiment was conducted where 0.03 mol NiCl₂·6H₂O, 0.01 mol SnCl₄·5H₂O, 0.2 mol CA and ten drops of tween 20 were dissolved into 250 ml de-ionized water. The solutions were then dried to form sol and gel, followed by calcinations under N₂ protecting flowing. Fortunately, the calcined product didn't burn when it was exposed in air. SnCl₄·5H₂O, PVP and CA were also dissolved into aqueous solution where the molar ratio of SnCl₄·5H₂O: CA was 1:5 and the other procedures were the same as those by using nickel nitrate, CA and PVP.

The crystalline phase structures of the as-prepared products were detected by X-ray diffraction (XRD, D8-advance) with Cu K_α radiation in a scanning rate of 10°/min. Before characterization, all the as-obtained products were kept in a drying dish in air and no other protecting method was applied to prevent the oxidization of nanoparticles. The elemental analysis of the as-prepared products were conducted on an energy dispersive X-ray spectroscopy (EDX, Oxford-2500) attached to a scanning electron microscopy (SEM, S-3400) with accelerating voltage being 20 kV. The microstructures of the as-prepared nanocrystals were investigated by transmission electron microscope (TEM, JEM-2100, 200 kV). First, the sample of the calcined

products was dispersed in ethanol, and then was dropped on copper-grid where carbon supporting film located on the copper grid. The magnetic hysteresis loop of the nickel nanoparticles were investigated by vibrating sample magnetometer (VSM, Models EV5) at room temperature in the magnetic field range from -1.25 T to 1.25T.

3. Results and discussion

Figure 1 shows the XRD analysis results of products calcined at 623, 723 and 823 K by using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CA and SDS at pH=2, respectively. The content of SDS is larger than its critical micelle concentration in aqueous solution. In **Fig. 1**, three diffraction peaks can be observed with diffraction angles being 44.40, 51.85, and 76.73°. The Miller indexes of the three peaks are calculated to be (111), (200), (220), and the lattice constant of the crystalline phase is calculated to be about 0.352 nm. This value is in agreement with that of face-centred-cubic (fcc) Ni [16]. The three diffraction peaks are very broad, indicating the small grain size of the as-prepared Ni nanoparticles.

Figure 2 displays the TEM images and corresponding selected area electron diffraction (SAED) analysis results of the products calcined at 623 (a and b), 723 (c) and 823 K (d) by using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CA and SDS. In Fig. 2a and 2b, ultrafine grains with grain sizes of 6-10 nm in diameter can be observed. The SAED result in Fig. 2a confirms the occurrence of fcc phase and the lattice constant of the fcc phase is calculated to be about 0.353 nm, showing that fcc Ni has been obtained by this sol-gel process. In Fig. 2c and 2d, the SAED results also indicate the formation of fcc Ni phase. The grain sizes of nickel nanoparticles in Fig. 2c and 2d are almost the same

as those in Fig. 2a, meaning that grain growth does not occur in the temperature range of 623-823 K.

Figure 3a-3d represents the XRD profiles of the nickel particles being calcined at different temperatures by using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CA and PVP at pH=2, 4, 6, 8. It can be seen from Fig. 3 that fcc Ni phase occurs irrespective of the pH value. In Fig. 3a-3c, broad diffraction peaks can be observed when the heating temperatures are 623 and 723 K, showing that the as-prepared Ni particles have small grain size when the pH value of the solution is 2, 4 and 6. However, in Fig. 3d, narrow diffraction peaks appear when the calcination temperature is 723 K. Therefore, it is suggested that nickel nanoparticles can be obtained when the initial pH value of the solution is in the range of 2-6.

Figure 4 expresses the XRD results of Ni nanoparticles prepared by using CA, PVP, and different type of nickel salts at pH=2. In Fig. 4a-4d, the nickel salts are $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, respectively. In Fig. 4, broad diffraction peaks can also be observed, showing the occurrence of fcc Ni with small grain size. Figure 5 displays TEM images and corresponding SAED results of nickel nanoparticles being calcined at 823 K (a, b) using CA, SDS, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and being calcined at 623 K using CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP at pH=2. It can be seen from Fig. 5 that Ni nanoparticles with fcc crystalline phase have been prepared in the temperature range of 623-823 K.

Figure 6 shows the EDX results of as-prepared nickel nanoparticles being calcined at 623 K by using CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP (a), CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, SDS

(b). In Fig. 6, the signals of Ni, C and O can be observed. Oxygen is believed to be originates from the surface oxidized layer of Ni and carbon originates from CA since the molar of metallic Ni^{2+} : CA is 1:5. It is suggested that the excess amount of carbon acts as supporting media of nickel nanoparticles [11], as evidenced by the fact that the nanoparticles are dispersed in a supporting substance in Fig. 2 and 5. However, the carbon supporting media is amorphous and can't be identified by XRD measurements. In Fig. 6b, the signal of S also occurs, and this can be ascribed to the presence of SDS in the initial solution.

Figure 7 depicts the XRD patterns of the of supported nickel nanoparticles being calcined at different temperatures by using EDTA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP where the molar ratios of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: EDTA are 1:1 (a,b), 1:2 (c,d), 2:1 (e,f), and pH values are 5 (a), 8 (b), 5 (c), 8 (d), 5 (e), 8 (f), respectively. In Fig. 7, broad diffraction peaks of fcc nickel also can be observed, indicating that EDTA is also an effective chelating agent in fabricating nickel nanoparticles. The full widths at half maximum (FWHM) of the (111) diffraction peaks in Fig. 7b, 7d, 7f are 0.92° , 0.94° , 0.98° when the heating temperature is 773 K. While the FWHM is only 0.55° of the (111) diffraction peak in Fig. 3d when the heating temperature is 723 K. This implies that EDTA may be more effective in controlling grain size of the nickel nanoparticles. In Fig. 8, the XRD patterns of calcined products by using $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$, tween 20, EDTA (a and b), NTA (c and d), DTPA (e and f) where the molar ratios of $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: EDTA, $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: NTA, $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: DTPA are 1:1. The pH values of solutions of (b), (d), and (f) are adjusted to be 2, 6, 8, and the pH values of

solutions of (a), (c), and (e) are not modified. In Fig. 8, the main crystalline phase can be determined to be fcc nickel. This means that NTA and DTPA can also be served as chelating agent in this sol-gel method. However, diffraction peak of metastable Ni_3N [17] purity can also be determined, as shown in Fig. 8a-8f.

In many fields of application, bimetallic nanoparticles are required because their properties are often better than monometallic nanoparticles [18]. Here Ni_3Sn alloy nanoparticles are selected to be prepared by this sol-gel process. Figure 9a and 9b shows the XRD and EDX analysis results of Ni_3Sn alloy nanoparticles prepared under N_2 protecting gas where the initial molar concentration of Ni^{2+} and Sn^{4+} ions are 0.03 and 0.01 mol/L, respectively. It can be seen from Fig. 9a that the diffraction peaks of Ni_3Sn are quite different from those of pure Ni, and diffraction peaks locate at 33.89, 41.82, 48.68, and 71.30° when the calcination temperatures are 723 and 823 K. All these diffraction angles are in excellent agreement with those of Ni_3Sn alloy with fcc crystalline phase [19], and the Miller indexes of the diffraction peaks are ascribed to be (110), (111), (200) and (220). The occurrence of diffraction peak of (110) superstructure reflection plane is direct evidence of the formation of Ni_3Sn alloy crystalline phase obtained by this sol-gel method under N_2 protecting gas. In Fig. 9b, the elemental analysis of the Ni_3Sn particles calcined at 723 K is presented where atomic ratio of Ni:Sn is 3:1, also in consistent with the initial ratio of Ni:Sn in aqueous solution. The signal of Cl comes from the remnant Cl in the calcined product. The microstructure and SAED investigation results of Ni_3Sn alloy are shown in Fig. 9c and 9d where the grain sizes of Ni_3Sn alloy particles are in the range of 30-40 nm.

The yield of the Ni_3Sn nanoparticles was calculated to be 74.55%, which is lower than the theoretical yield of 100%. The reason can be ascribed to the fact that there are mass losses during the transformation of the porous dried gel from beaker to heating treatment oven and collecting of the calcined product. When CA was replaced by EDTA, the (100), (110), (111), (200), (211) and (220) diffraction peaks of Ni_3Sn could also be observed, as shown in Fig. 10a. Figure 10b displays the XRD profile of the product being calcined at 723 K where the beginning molar concentrations of Ni^{2+} and Sn^{4+} ions are increased to 0.12 and 0.04 mol/L. Fig. 10c denotes an image of the as-prepared product. In Fig. 10b, the diffraction peaks of Ni_3Sn can also be identified. However, diffraction peaks of purities of SnO_2 and Ni_3Sn_2 also occur in Fig. 10b. The reason for the occurrence of the purities may be that N_2 atmosphere can't protect the metallic nanoparticles in large scale experiment. If nickel ions are absent from the solution and only $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, PVP and CA are used, the crystalline phase of the final product is body-centred-cubic SnO_2 instead of Sn, as shown in Fig. 11 where the (110), (101) and (211) diffraction peaks of SnO_2 (JCPDF: 41-1445) can be observed.

Based on the results from Fig. 1-Fig. 10, it is claimed that Ni and Ni_3Sn nanoparticles can be prepared by this sol-gel method under protecting N_2 gas. These results introduce the conventional sol-gel method into the field of metallic nanoparticles. CA and EDTA are popular chelating agents that can be applied to chelating with metallic ions, and these two chelating agents can also be operated to prepare Ni and Ni_3Sn alloy nanoparticles. It seems that EDTA is more effective in controlling grain sizes of Ni nanoparticles than CA since broad diffraction peaks of

fcc Ni can be obtained by using EDTA with pH being equal to 8 while sharp diffraction peaks of fcc Ni emerge by using CA with pH equals to 8. However, EDTA can't be used in organic solution because it doesn't soluble in organic solvents. Therefore, the application range of EDTA is confined in aqueous solution while CA can be employed in organic solutions such as ethanol and acetone [12,17,20]. In EDTA, amine and carboxyl groups serve as chelating groups in aqueous solution, and hydroxyl and carboxyl groups play the role of chelating groups in aqueous solution. These groups form chemical bond with metallic ions and then the bonds are broken during calcination process. For preparation of bimetallic ions, the two kinds of different metallic ions are linked by these organic groups, resulting in the formation of alloy nanoparticles during the heating treatment. Since many functional groups can interact with metallic ions, it is expected that other kinds of chemical agents which contain amine, hydroxyl or carboxyl groups can act as chelating agent in aqueous solution, and then metallic nanoparticles can be prepared. Up to now, lactic acid [21] and acrylamide [22] are successful in preparation of metallic nanoparticles. Further investigations on other kinds of chelating chemicals with different functional organic groups are underway.

It should be pointed out that the type of metallic ions has great effect on the decomposition of the dried gels and the final products. For instance, if the nickel chloride was replaced by stannic chloride, the crystalline phase in the calcined powders is not Sn metallic phase, but SnO₂ oxide phase. However, if nickel chloride and stannic chloride are mixed with CA and PVP in aqueous solution, the fcc Ni₃Sn

phase is obtained instead of metal oxides. The reason why SnO₂ occurs may be explained from thermodynamic point of view noted that the standard enthalpy change ($\Delta_f H_m^\circ$) of SnO₂ (-580.823 KJ·mol⁻¹) is much lower than that of NiO (-241.818 KJ·mol⁻¹). For simplicity, the formation of metallic phase is divided into two subsequent processes. The first is the formation of metal oxides during the N₂ protected heating treatment, as evidenced by the occurrence of SnO₂ in Fig. 11. The second process is transformation from metal oxides to metallic crystalline phase, which can be identified by the detection of reducing gases of H₂ by mass spectroscopy [9,10]. Then the reaction of the transition from oxide to metallic phase can be expressed as:

The $\Delta_f H_m^\circ$, standard entropy (S_m°) of NiO, Ni, H₂, H₂O(g), SnO₂, Sn and Ni₃Sn [23] at 298 K are shown in Table 1. Then the standard Gibbs free energy change ($\Delta_f G_m^\circ$) of reactions 1-3 are presented in table 2. It can be seen from Table 2 that the $\Delta_f G_m^\circ$ of reaction 1 is negative, meaning that this reaction is spontaneously favourable at high temperatures. Considering kinetic fact that decomposition of the dried gel takes place at high temperatures [17], nickel crystalline phase can be readily obtained by this sol-gel process. However, the $\Delta_f G_m^\circ$ of reaction 2 is positive when the heating temperature (T) is lower than 844 K. Consequently, the reaction 2 is not thermodynamic favourable in the range of 623-823 K, and SnO₂ instead of Sn can be

formed in the XRD profiles in Fig. 11. Interestingly, the $\Delta_f G_m^\circ$ of reaction 3 is negative at any temperatures. This can be ascribed to the low value of $\Delta_f H_m^\circ$ of Ni_3Sn ($-93.701 \text{ KJ}\cdot\text{mol}^{-1}$). Combined with kinetic factor, it is not surprising that Ni_3Sn alloy crystalline phase can be observed in Fig. 9a and 10a. Moreover, the XRD analysis results in Fig. 9 and Fig. 10 provide a novel strategy for designing and preparation of alloy nanoparticles with metallic elements even though one element can bond with oxygen with relative low negative standard formation enthalpy. In addition, it is worth noting that N_2 flow is not effective in preventing the oxidization of scale up Ni_3Sn alloy nanoparticles and more effective protecting gas flow is required to avoid oxidation of metallic nanoparticles.

Figure 12 shows the room temperature hysteresis loops of Ni nanoparticles being calcined at 623 and 823 K by using CA, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, PVP. In Fig. 12a and 12b, the magnetization does not saturate in the range of -1.2 to 1.2 T, and the remnant magnetization is zero. These two facts show superparamagnetic character of the as-prepared Ni nanoparticles being calcined at 623 K. In general, superparamagnetic of nanoparticles originates from the fact that thermal fluctuation energy of the nanoparticles becomes comparable with that required for spin to flip directions when the grain size is below a certain critical value (r_0) [24], which can be estimated from the equation: $r_0 = \left(\frac{6k_B T}{K_u}\right)^{1/3}$ where k_B is Boltzmann constant, T denotes the temperature, and K_u represents the crystalline magnetoanisotropy [24,25]. With K_u being $8 \times 10^4 \text{ J/m}^3$ [24,25], r_0 is calculated to be 7 nm. If the grain size is larger than the critical value, typical ferromagnetic behaviour can be observed, as shown in Fig. 12c and 12d

since the magnetization is saturated in Fig. 12c and the remnant magnetization is not zero in Fig. 12d.

4. Conclusion

In summary, we have shown an effective aqueous sol-gel process for the preparation of Ni nanocrystals under N₂ protecting atmosphere where conventional CA and EDTA are used as chelating agent. These nanocrystals can be obtained by using different initial chemical agents, suggesting that this sol-gel process can be widely used in the preparation of metallic nanocrystals. The as-prepared Ni nanocrystals have ultrafine grain sizes and narrow grain size distributions. Ni₃Sn alloy nanoparticles can also be obtained by this sol-gel method, as confirmed by the XRD investigation and the composition of the alloy nanocrystals can be controlled. EDTA seems more effective than CA in controlling grain size of Ni nanoparticles in this sol-gel method, and Ni nanoparticles can be obtained in different pH values in aqueous solution. Depending on the grain size of nickel nanoparticles, nickel nanocrystals with superparamagnetic or ferromagnetic character can be obtained. Our results provide new insight into the application field of conventional CA and EDTA mediated sol-gel method. Our results also provide a new design strategy for preparation of alloy nanoparticles.

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Figure captions

Figure 1 The XRD analysis results of nickel nanoparticles prepared by using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and SDS, CA where the calcination temperatures are 623, 723 and 823 K, respectively.

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

Figure 3 The XRD analysis results of nickel nanoparticles being calcined at different temperatures by using nickel nitrate, PVP and CA at pH=2 (a), 4 (b), 6 (c), 8 (d), respectively.

Figure 4 The XRD analysis results of nickel nanoparticles being calcined at different temperatures by using CA, SDS, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (a), CA, PVP and $\text{Ni}(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (b), CA, PVP and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (c), CA, PVP, and $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ (d).

Figure 5 The TEM images and corresponding SAED results of nickel nanoparticles being calcined at 823 K (a, b) using CA, SDS, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and being calcined at 623 K using CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP.

Figure 6 The EDX results of carbon-supported nickel nanoparticles being calcined at 623 K where CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP (a), CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, SDS (b), have been used.

Figure 7 The XRD profiles of nickel nanoparticles being calcined at different temperatures by using EDTA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP where the molar ratios of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: EDTA are 1:1 (a,b), 1:2 (c,d), 2:1 (e,f), and pH values are 5 (a), 8 (b), 5 (c), 8 (d), 5 (e), 8 (f), respectively.

Figure 8 The XRD patterns of calcined products by using $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$, tween 20, EDTA (a and b), NTA (c and d), DTPA (e and f) where the molar ratios of $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: EDTA, $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: NTA, $\text{Ni}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$: DTPA are 1:1. The pH values of solutions of (b), (d), and (f) are adjusted to be 2, 6, 8, and the pH values of solutions of (a), (c), and (e) are not modified.

Figure 9 (a): XRD analysis results of Ni_3Sn alloy nanoparticles calcined at different temperatures, (b): EDX investigation result of Ni_3Sn alloy nanoparticles calcined at 723 K, (c) and (d): TEM images and SAED results of Ni_3Sn alloy nanoparticles calcined at 723 K.

Figure 10 XRD patterns of Ni_3Sn alloy particles (a) being calcined at 723 K using 0.003 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.001 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 0.004 mol EDTA, 2 drops of tween 20 and 100 mL de-ionized water, the XRD profile (b) and photograph image (c) of the scale up products (b) being calcined at 723 K using 0.03 mol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.04 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 0.2 mol CA, 10 drops of tween 20 and 250 mL de-ionized water.

Figure 11 XRD profiles of the products being calcined at different temperatures by using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, CA, PVP.

Figure 12 The room temperature magnetic hysteresis loop of nickel nanoparticles being calcined at 623 (a and b) and 823 K (c and d) by using CA, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, PVP.

Table 1 $\Delta_f H_m^\circ$, S_m° of H_2 , H_2O , NiO , Ni , SnO_2 , Sn , Ni_3Sn .

Table 2 $\Delta_f G_m^\circ$ of reactions (1)-(3) where T is absolute temperature.

Table 1

materials	$\Delta_f H_m^\ominus (\text{KJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$S_m^\ominus (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
H ₂	0	130.684
H ₂ O (g)	-241.828	188.825
NiO	-239.701	37.991
Ni	0	29.874
SnO ₂	-580.823	52.342
Sn	0	51.195
Ni ₃ Sn	-93.701	131.378

Table 2

Reaction	$\Delta_f H_m^\ominus$ (KJ·mol ⁻¹ ·k ⁻¹)	$S_m^\ominus$ (J·mol ⁻¹ ·k ⁻¹)	$\Delta_f G_m^\ominus$ (KJ·mol ⁻¹ ·k ⁻¹)
NiO+H ₂ →Ni+H ₂ O (g)	-2.127	50.024	-2.117-0.050×T/K
SnO ₂ +2H ₂ →Sn+2H ₂ O (g)	97.167	115.135	97.167-0.115×T/K
3NiO+SnO ₂ +5H ₂ →Ni ₃ Sn+5H ₂ O(g)	-2.915	255.768	-2.915-0.256×T/K

Sol-gel method is conventionally applied to prepare oxides, carbides, and sulfides. In this work, the application field of sol-gel method is extended to metallic nanoparticles. By using citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) mediated sol-gel method, metallic Ni (a and c) and Ni_3Sn (b and d) alloy nanoparticles can be prepared when the heating treatments are performed under N_2 protecting atmosphere. The Ni and Ni_3Sn nanoparticles have face-centered-cubic (fcc) crystalline phase and ultrafine grain sizes. Diffraction peaks of (110) superstructure reflection plane of Ni_3Sn nanoparticles can also be observed in Figure b, which can be considered as direct evidence of formation of alloy crystalline phase by performing this sol-gel method.