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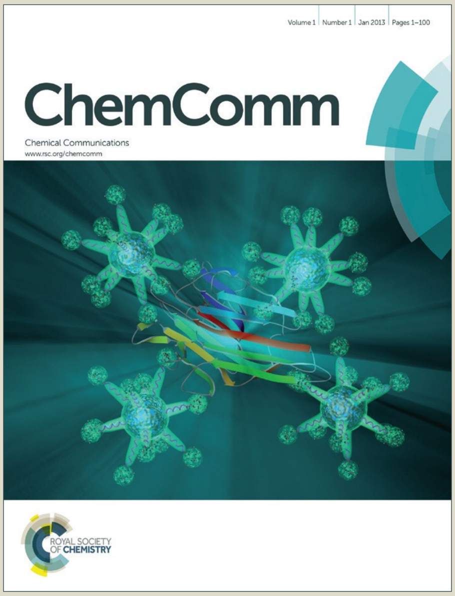

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Polymerized complex method for preparation of supported bimetallic alloy and monometallic nanoparticles

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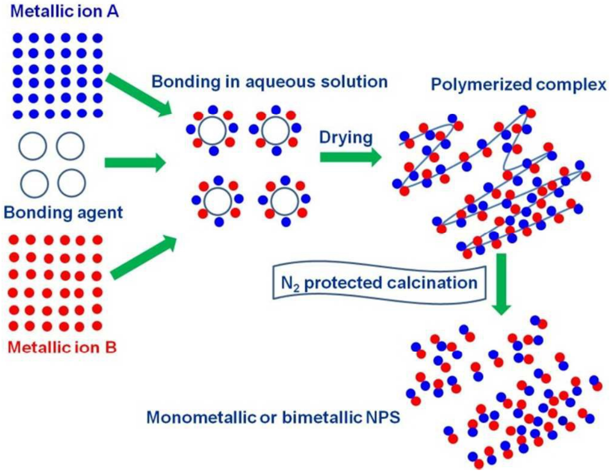
Here we report a novel polymerized complex method for preparation of Ni-Pd, Ni-Pt, Cu-Pt alloy, Pt, Pd, Ag, Ni, Cu nanoparticles. The grain sizes and crystalline phases of these nanoparticles can be controlled. These nanoparticles occur through formation of polymerized complex and releasing of reducing gases during N_2 protected calcinations.

Much attention has been paid to metallic nanoparticles (NPS) because of their excellent optical, catalytic, magnetic properties and potential applications in catalytic, biological, and magnetic fields.[1-4] For instance, Pd NPS have excellent catalytic capacity of Suzuki reaction.[5] Cu-Pt alloy NPS have superior activity for CO oxidization than pure supported Pt NPS.[6] In general, several strategies have been developed to prepare metallic NPS, including controlled reduction of metallic ions,[7] thermo-decomposition of organometallic precursors,[8] and electro-deposition.[9] However, these methods are not effective in controlling crystalline phase of intermetallic alloy NPS. The reason being that it is difficult to synchronously control nucleation and growth of two different kinds of metallic nuclei because of the distinction between thermodynamic and kinetic behaviors at the same experimental conditions.[9,10] For instance, In conventional aqueous reducing method,[11,12] the reducing reaction depends on the standard electrode potential of the different metallic ions. When two kinds of metallic ions exist in solution, the ions with higher potential are often reduced first, followed by the reduction of the other metal species, resulting in the formation of core-shell bimetallic NPS.[10] In order to induce the formation of alloy NPS, annealing at high temperature should be carried out to enhance the diffusion rate of two different kinds of metallic atoms and to provide sufficient energy to induce formation of alloy crystalline phase.[10, 11] However, grain growth often occurs at high annealing temperature,[13] and thus it is difficult to control grain size distribution of the alloy NPS.[14] In the co-reducing method, the redox potentials of two species should be tuned to be the same as each other, to ensure that the two different kinds of ions are reduced at the same time, which is extremely difficult.[9,10] In organic solutions, an effective way is the polyol process.[15] In this method, the polyol alcohol such as ethylene glycol acts as solvent and reducing agent at the same time, the metallic salt and extra reducing agent are often dissolved into the solvent, and then the solution is heated up to the boiling point of the solvent.[16,17] Metallic ions are thus reduced to metallic NPS near the boiling point of the solvent. In polyol and thermo-decomposition process, the reduction rates of different ions are also different,[18,19] leading to the formation of bimetallic core-shell NPS when two types of metallic ions are reduced, similar to the situation where different metallic ions are reduced in aqueous solution. Recently, the octadecylamine mediated reducing process has been developed for preparation of Pd, Ag, NiO, ZnO NPS.[20] However, Ni and Cu NPS can't be obtained by this method.[20] Therefore, it is necessary to develop an effective method for preparation and application of metallic alloy and monometallic NPS.



Scheme 1. Schematic illustration of the polymerized complex method where A and B denote different metallic ions.

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Electronic Supplementary Information (ESI) available: Experimental details and XRD, TEM, EDX analysis results of Pt, Pd, Ag, Cu-Pt, Cu-Pd, Ni-Pd nanoparticles.

In this work, we report a novel method for preparation of supported bimetallic alloy and monometallic NPS. The principle of this method is not reducing or thermo-decomposition of two different organometallic precursors, but bonding metallic ions with appropriate agent in an aqueous solution to form a polymer/metal complex, as shown in scheme 1 where colour A and B circles denote different metallic ions, and white circles represent bonding agent. Then the metallic ions in the polymer/metal complex transform to NPS during calcination of the polymerized complex under N_2 protecting atmosphere. In a binary system where two types of metallic ions are bonded together with the polymer, they are positioned adjacent to each other within the polymer complex. In this circumstance, the two different metallic ions would receive electrons simultaneously, forming bimetallic crystalline phase. Kinetically, the nucleation and growth of two different metals are synchronously controlled by decomposition of the complex during heat treatment. As a result, the differences between electrode potentials of the metallic species no longer pose as a problem in forming homogeneous bimetallic alloy NPS. In other words, alloy crystalline phase rather than core-shell phase can be obtained by this method. Moreover, grain growth does not take place in this method. These two features can be considered as the advantages of this method. Here we show that by forming such polymerized complex, the NPS of Cu-Pt, Ni-Pd, Ni-Pt, Pt, Pd, Ag, Ni, and Cu can be conveniently prepared.

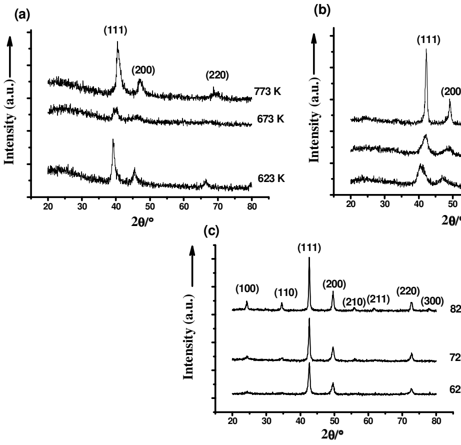

Figure 1. X-ray diffraction (XRD) patterns of Ni-Pd (a), Ni-Pt (b), Cu-Pt (c) bimetallic NPS being calcined at different temperatures.

Figure 1 shows the X-ray diffraction (XRD) patterns of Ni-Pd (a), Ni-Pt (b), and Cu-Pt (c) NPS being calcined at different temperatures, respectively. In Fig. 1a and 1b, diffraction peaks of (111), (200) and (220) reflection planes can be observed. In Fig. 1c, diffraction peaks can be observed at 24.22, 34.62, 42.62, 49.65, 55.83, 61.76, 72.82, 77.95°, respectively. These diffraction angles are in agreement with those of ordered face-centred-cubic (fcc) Cu_3Pt type crystalline phase,[21] and the miller indices of these diffraction peaks are calculated to be (100), (110), (111), (200), (210), (211), (220), (300). The occurrence of diffraction peaks of (100), (110), (210), (211) and (300) superstructure reflection plane can be considered as the solid evidence of the formation of Cu_3Pt type crystalline phase with equilibrium ordered crystalline phase, meaning that the crystalline phase of the as-prepared Cu-Pt alloy can be controlled by this polymerized complex method. The atomic ratios of Ni: Pd, Ni: Pt, and Cu: Pt were determined approximately the same as the initial ratios according to the EDX analysis result (Fig. S1). Surface segregation may occur in the supported NPS. In this case, the atomic ratio of Ni:Pd in NiPd NPS is determined by atomic absorption spectrometer where the atomic ratio of Ni:Pd is 49.26: 50.74, also close to the initial elemental ratio of 50:50. The grain sizes of the Ni-Pt, Ni-Pd, Cu-Pt alloy NPS were determined to be in the range of 10-60 nm through transmission electron microscope (TEM) observations (Fig. S2–S4). These grains are supported by thin substrate, which is considered to be amorphous, as confirmed by the determination of C and O in EDX analysis results (Fig. S1). Figure 2 shows the XRD profiles of Ag, Pt, Pd, Cu and Ni particles prepared by this process using water soluble starch as bonding agent. In Fig. 2, the diffraction peaks of Ag, Pt, Cu, Ni can be observed. For Pd NPS (Fig. 2d), metastable PdC_x[22] phase coexists with equilibrium fcc Pd phase when the heating treatment temperatures are 623 and 673 K and the metastable PdC_x phase transforms into pure fcc Pd phase when the calcination temperature is increased to 773 K.

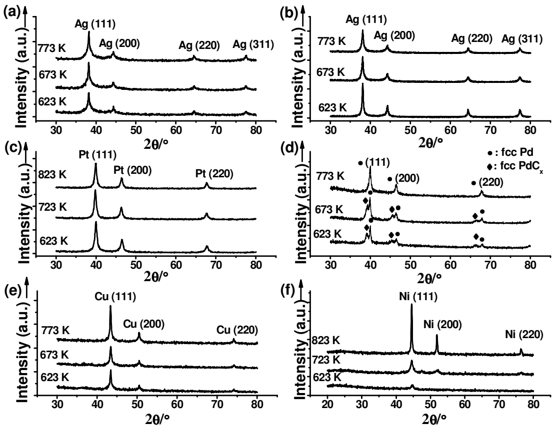

Figure 2. XRD profiles of Ag, Pt, Pd, Cu and Ni NPS being cailcined at different temperatures using starch as bonding agent and distilled water as solvent. a) using $AgNO_3$ as metallic source and polyvinylpyrrolidone (PVP, K-30) as surfactant. b) using $AgNO_3$ and without PVP. c) using $H_2PtCl_6·6H_2O$ and tween-80. d) using $Pd(NO_3)_2·2H_2O$, starch and tween 80. e) using $Cu(NO_3)_2·3H_2O$, starch, and PVP. f) using $Ni(NO_3)_2·6H_2O$,starch and PVP.

Figure 3 displays TEM images and SAED patterns of the Ag (a), Pt (b), Pd (c), Cu(d) NPS being calcined at different temperatures. All the particle sizes of Ag, Pt, Pd, Cu NPS are narrowly ranged between 5 and 15 nm. The crystalline phases of the as-prepared Ag, Pt, Pd,Cu NPS are fcc, as determined from the SAED patterns shown Figure S5-S8. In addition, starch is not the only agent that can be applied to prepare Ag, Pd, Pt, Cu and Ni NPS. Sucrose and $CO(NH_2)_2$ could also be used to prepare Ag NPS (Fig. S9). Lactic acid, sucrose and EDTA were used to prepare Pd NPS (Fig. S10). EDTA was applied to fabricate Pt NPS (Fig. S11). EDTA, lactose, and D-maltose, ethylenediamine were used to synthesis Cu NPS (Fig. S12). It should be pointed out that lactose and D-maltose have some reducing effect towards noble metals hence they are not suitable for preparation of Ag, Pt and Pd NPS by this polymerized complex method.

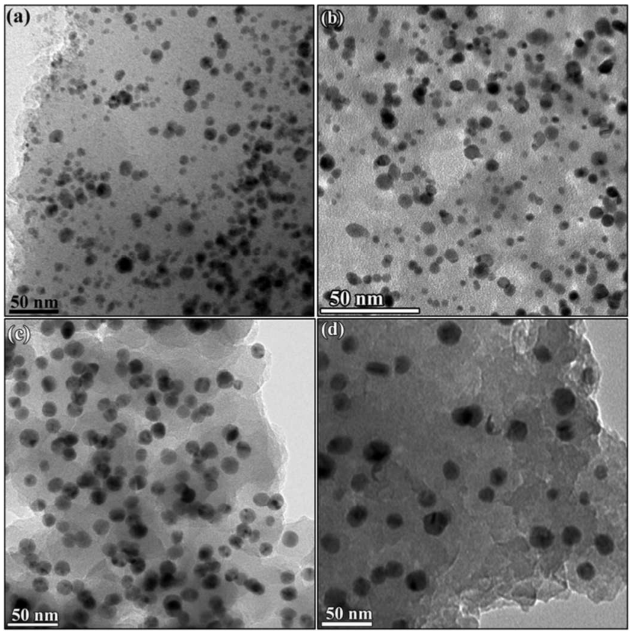

Figure 3. TEM images of Ag (a) NPS being calcined at 623 K by using $AgNO_3$, PVP and starch, Pt (b) NPS being calcined at 723 K by using $H_2PtCl_6·6H_2O$, starch and tween 80, Pd (c) NPS being calcined at 773 K by using $Pd(NO_3)_2·2H_2O$, starch and tween 80, Cu (d) NPS being calcined at 623 K by using $Cu(NO_3)_2·3H_2O$, starch and PVP. All the calcination procedure are performed under N_2 protecting atmosphere.

For preparation of nickel NPS, saccharides such as glucose, ribose, mannose, treharose, inulin, glactose, lactose, raffinose, xylose, cyclodextrin were suitable bonding agent (Fig. S13-S16). The nickel NPS calcined at 673 K showed superparamagnetic behavior while the nickel NPS calcined at 773 K showed a strong ferromagnetic behavior (Fig. S17) by using ribose as bonding agent. Acids such as gluconic acid, ascorbic acid, pyrogallol, glyoxylic acid, EDTA, pyruvic acid and malic acid could also be used as bonding agent to prepare Ni NPS (Fig. S18-S20). In addition to those described above, a number of other organic compounds were investigated for suitability as bonding agent in the formation of metallic Ni NPS. The suitable ones were gelatin and carboxymethyl cellulose (cmc) with high molecular weight (Fig. S21), amines (Fig. S22) including ethylenediamine, triethanolamine, formamide, DMF, and polyalcohols (Fig. S23 and S24) including ehtylene glycol, glycero, diglycol, 1,2-propanediol, maltitol, xylitol, pentaerythritol and insitol. Unexpectedly, m-dihydroxybenzene (Fig. S25 and S26) was also effective in forming Ni NPS by this polymerized complex method. Interestingly, when ehtylene glycol, glycero, diglycol, 1,2-propanediol were used, metastable hexagonal-closed-packed (hcp) nickel or Ni_3C phase was produced at 623 K, then the metastable phase transformed to stable fcc nickel phase at higher temperatures (Fig. S23). In the current method, polyalcohol serves as bonding agent rather than reducing agent when preparing Ni NPS, and the dosage of polyalcohol is less than 2 wt%. This is different from polyol method where polyalcohol acts both as solvent and reducing agent. When DMF and PVP were used, NiO first formed at 623 and 673 K, and then transformed to Ni at 773 K (Fig. S22d). When m-dihydroxybenzene was used as bonding agent without using PVP, NiO also formed at 623 K, then transformed completely to Ni at 773 K (Fig. S25).

Based on the experimental results, it is concluded that bimetallic Cu-Pt, Ni-Pd, Ni-Pt, and monometallic Pt, Pd, Ag, Cu, Ni NPS can be prepared by this method. Since various kinds of bonding agent can be applied to prepare these different kinds of metallic NPS with grain sizes in nanometer range and with equilibrium crystalline phase, the sizes and phases of these NPS is considered to be under control in this method. The mechanism is that, essentially, the metallic ions are associated with bonding agents through chemical bonding effect, resulting in the formation of ploymerized network structure during the evaporation of the solvent. Polymerization reaction occurs through functional groups of those bonding agents.[23,24] For instance, cross linking between hydroxyl, carboxyl, amine groups can take place, leading to the formation of polymerized network structure within which the metallic ions are distributed homogeneously.[21] It should be pointed out that certain bonding agents also have reducing ability, and then these agents are not suitable for preparing noble metallic NPS by this polymerized method. For instance, glucose is an effective bonding agent in forming polymerized network structure with Ni^{2+} ions, but it is not suitable for forming Ag NPS as it reduces Ag^+ into Ag before polymerization. Polyhydric alcohol also have reducing capacity, and Ag^+ are also readily reduced by these agents in aqueous solution. Therefore, the bonding agents with reducing ability should be avoided in preparing noble Pt, Pd and Ag NPS. At present, starch and sucrose are effective in the formation of stable polymerized complex with Pt^{4+}, Pd^{2+} and Ag^+ ions. EDTA is suitable for bonding with Pt^{4+}, Pd^{2+} Cu^{2+}, Ni^{2+}, but is not effective in bonding with Ag^+.

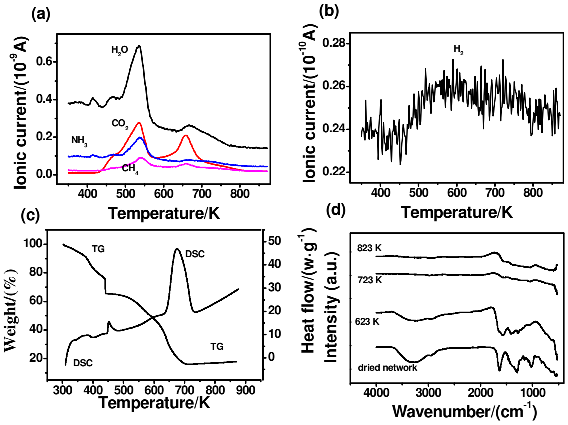

Figure 4. MS (a and b), TG and DSC (c) analysis result of the polymerized complex using glucose as bonding agent and distilled water as solvent, $Ni(NO_3)_2·6H_2O$ as metallic source and PVP as surfactant. The measurements were performed under N_2 protecting

atmosphere. FTIR measurement results (d) of the calcined products by employing $Ni(NO_3)_2{\cdot}6H_2O$, glucose, PVP and distilled water.

Figure 4 displays the mass spectroscopy (MS), thermogravimetric (TG), differential scanning calorimetry (DSC) ,and Fourier transform infrared spectroscopy (FTIR) analysis results for polymerized complex prepared with nickel nitrate, glucose and PVP where the measurements were carried out under N_2 atmosphere. In Fig. 4a and 4b, H_2, CH_4, H_2O, NH_3, CO_2 are identified during the heating process. This means that reducing gases of H_2 and CH_4 were released by the polymerized complex. The releases of CH_4, H_2O, NH_3 and CO_2 have two peaks at about 540 and 650 K. In Fig. 4c, two exothermic peaks centered at 445 and 650 K. In Fig. 4d, the FTIR measurement results of the dried network structure and the product being calcined at 623 K reveal peaks originate from vibration of O-H (3250 cm^{-1}), C-H (2970 cm^{-1}), C=O (1627 cm^{-1}), and C-O (1290, 1020 cm^{-1}) groups. However, the vibration peaks induced by O-H, C=O, C-O groups almost disappear when the heating temperature is enhanced up to 723 K and 823 K. This means that the dried precursor decomposes in the range of 623-723 K, resulting in the releasing of O-H, C=O, C-O groups and an exothermal peak at 650 K as determined from Fig. 4c. The vibration peak of C-H peak can also be detected. Therefore, the supporting agent of the as-obtained NPS is suggested to be mainly consisted of amorphous hydrocarbon when the heating temperature is 723 and 823 K while the amorphous agent contains C, H and O is suggested to be the supporting agent when the heating temperature is 623 K. The combined MS, FTIR and DSC results suggest that the formation of metallic NPS through a two-stage process. In the first stage, H_2, CH_4, H_2O, NH_3 and CO_2 were released from the polymerized complex in the range of 420-550 K. In the second stage of 600-700 K, the precursor continues to decompose through the elimination of C-O organic groups, resulting in the formation and growth of crystalline nuclei under the protecting effect of H_2 and CH_4 gases, and finally the metallic NPS come into being.

In summary, we have presented a novel and facile method in preparation of Cu-Pt, Ni-Pt, Ni-Pd, Pt, Pd, Ag, Cu, Ni metallic NPS. The basic principle of this method is bonding metallic ions with appropriate bonding agents, resulting in the formation of polymerized complex network structure. Heat treatment of the polymerized complex under N_2 yields metallic NPS with narrow size distribution. Starch and sucrose are effective in bonding with noble metallic ions as well as transitional metallic ions. Bonding agents with reducing ability can be applied to prepare transitional Ni and Cu metallic NPS. However, these bonding agents with reducing ability can't be operated to prepare noble Ag, Pt and Pd NPS. The study provides a novel and practical technique for producing single component metallic NPS as well as alloy NPS.

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