Shape-controlled synthesis of Ni particles via polyol reduction

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\textbf{Abstract}

Metallic Ni powders with different morphologies including icosahedra, microspheres, and flowerlike clusters composed of nanoflakes were successfully fabricated via polyol process. Alkalinity played the key role in the formation of these novel structures. The as-prepared products were characterized by X-ray diffractometry (XRD), field scanning electron microscopy (FESEM), transmission electron microscope (TEM), and selected area electron diffraction (SAED). A layer-by-layer growing process was demonstrated based on the experimental results. Magnetism investigation revealed that icosahedra and clusters exhibited much enhanced coercivity.

\section{1. Introduction}

Metal particles in both nano and microsize range have attracted much attention for use in catalysis, optoelectronics, Raman scattering, biological, and chemical sensing due to their unique physical and chemical properties [1–11]. It was demonstrated that the size, morphology, and crystallinity of the metal particles were critical for their properties and applications [12–17]. Therefore, shape-controlled synthesis of metallic structures has been a subject of intensive research in recent years. In this regard, noble metal such as Pd, Au, and Ag crystals with various morphologies, including cuboctahedra, cubes, bars, rods, nanowires, decahedra, icosahedra, right bipyramids, triangular or hexagonal thin plates, and nanoboxes, have been successfully fabricated [18–25]. Unlike noble metals, synthesis of base metal such as Ni nano/microstructure with well-controlled shape remains a challenging task. Most of the reported Ni morphologies were clusters and spheres, and only a few Ni single crystals have been fabricated [26–34]. For example, Li et al. synthesized single crystal triangular and hexagonal Ni nanoplates with the help of iron species. [35] Qian et al. reported a complex-surfactant-assisted hydrothermal reduction method to synthesize single crystal Ni nanobelts [36]. Amiens et al. reported the synthesis of nickel nanorods outside a template [37]. However, none of these methods could act as a generic approach to a series of Ni structures and there are limited reports on the synthesis of Ni polyhedra up to now [38].

Polyol process was originally developed by Fievet et al. and then adopted by Xia et al. as a general methodology for shape control in metallic structures [18,39,40]. In this process, polyol acts as both solvent and reducing agent. Noble metals such as Pd, Au, and Ag can be obtained via polyol process under neutral or even acidic conditions. However, enough alkalinity is necessary for the Ni [II] reduction due to its lower oxidation potential. That might be one of the reasons why regular Ni nanostructures are difficult to obtain via polyol process because the pH value could play an important role in the formation of different morphologies [41].

In the present work, Ni powders with different morphologies including icosahedra, microspheres, and flowerlike clusters composed of nanoflakes were successfully fabricated via polyol process. A layer-by-layer growth mechanism was proposed according to the experimental results and Bravais’ rule. The magnetism of the nickel powders with different morphologies was also investigated.
2. Experimental procedure

All analytical chemical reagents were obtained from Beijing Chemical Reagents Co. and used without further purification. In a typical experimental procedure for the synthesis of Ni icosahedra and clusters, 1.2 g NiCl2·6H2O was dissolved into 60 mL of polyol glycol to get homogeneous solution. Then an appropriate amount of NaOH was added into the NiCl2·6H2O solution and stirred until NaOH was dissolved completely. The mixture was sealed in a Teflon-lined autoclave of 100 mL capacity and heated at 200 °C for 8 h. After cooled to room temperature naturally, the precipitates were filtered off and washed with distilled water and anhydrous ethanol in sequence and then dried at 60 °C overnight. Ni microspheres were synthesized in the mixture solvent of polyol glycol and distilled water instead of pure polyol glycol. The pH value of the solution was examined using a pH meter.

The crystalline phase of the as-prepared samples was characterized by X-ray diffractionmetry (XRD, X’pert PRO, Panalytical) at a range from 10° to 110°. Their size and morphology were inspected with field scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, H-800) with selected area electron diffraction (SAED). The magnetic properties were recorded using a vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature with an applied field up to 10kOe.

3. Results and discussion

3.1. Effect of alkalinity

The reduction mechanism of the polyol process can be formulated as below [39]:

\[
\text{CH}_2\text{OH} – \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{M}^{2+} + 2\text{CH}_3\text{CHO} + 2\text{OH}^- \rightarrow \text{M} + \text{CH}_3\text{CO} – \text{COCH}_3 + 2\text{H}_2\text{O} \quad (2)
\]

It can be seen that alkali condition is necessary for the Ni [II] reduction. As a matter of fact, alkalinity has great effect on both purity and morphology of the resulting Ni powders. We have examined the variation of the concentration of NaOH while keeping other experimental condition constant. Results showed that when the concentration of NaOH was below 0.3 M, pure metallic Ni could not be obtained. When the concentration of NaOH was above 0.6 M, the obtained samples were flower-like clusters composed of nanoflakes. When the concentration of NaOH was precisely controlled between 0.4 and 0.5 M, the products were dominated by well-dispersed Ni polyhedra. An increase in the concentration of NaOH would result in a corresponding increase in alkalinity. We have demonstrated that an increased alkalinity could also be obtained by introducing some water into the polyol solution. The effect of the volume ratio of H2O/(H2O+EG) on the pH value of the solution is shown in Fig. 1. Both NaOH solution with and without NiCl2·6H2O were examined. The concentration of NaOH was 0.25 M and the concentration of NiCl2·6H2O was 0.05 M. It can be seen that the pH value increases as a result of the increase of water content. Therefore, pure Ni powders were accomplished in the mixture solution within less time and at relatively lower concentration of NaOH as well as using less polyol. We believe this is a significant progress for the conventional polyol method. It should be pointed out that Ni polyhedra and clusters could also be obtained in the mixture solvent at high concentration of NaOH. This result further confirmed that it was alkalinity that influenced the morphology of the resulting particles.

3.2. Characteristics of the products

XRD patterns of the products obtained with the concentration of NaOH above 0.4 M and the products obtained in the mixture solution with the molar ratio of OH⁻/Ni²⁺ higher than 2.5 can be well assigned to face-centered cubic (fcc) Ni. Fig. 2 shows XRD pattern of the products obtained with the concentration of NaOH at 0.5 M. The five diffraction peaks of (111), (2 0 0), (2 2 0), (311), and (2 2 2) of fcc Ni can be easily observed. No peaks of nickel oxide or hydroxide are detected, indicating the high purity of the products.

Fig. 3a shows the FESEM images of the sample obtained with the concentration of NaOH at 0.3 M.
When we moved the electron beam along the edges of the hexagon during the TEM examination, it was found that the diffraction spot patterns exhibited similar quasi-hexagonal shape (underside). Distances and angles measured in the patterns reveal that all the faces of the icosahedra have a preferential growth direction along \{111\} planes. Surface energies associated with different crystallographic planes are usually different, and the \{111\} planes have the lowest surface energy for fcc crystal structure. So the polyhedra enclosed by the \{111\} planes are the most stable structure\[24\]. However, when we set the electron beam upon the corners of the hexagon, there existed a much different and complex diffraction pattern (upside), indicating the polyhedra were not single crystals. According to geochemical crystallography and the experimental results in the literature, it can be concluded that the Ni icosahedra are multiple twinned particles (MTPs). The simple form of fcc Ni crystal is octahedron instead of icosahedron \[24,38,42\]. The synthesis of single crystals was also achieved and the results will be reported somewhere else.

The samples obtained with the concentration of NaOH above 0.5 M were flowerlike clusters composed of nanoflakes. Fig. 4a and b shows the FESEM images of the sample obtained with the concentration of NaOH at 1.2 M. The nanoflakes are several nanometers thick and hundreds of nanometers in width. The inset SAED pattern is similar with that taken from the faces of the icosahedra, indicating that the flakes also have a preferential growth direction along \{111\} planes.

Fig. 5 shows the FESEM images of the sample obtained in the mixture solution with the volume ratio of H\(_2\)O/EG (polyol glycol) at 1:4 and the concentration of NaOH at 0.25 M. The particles are well-dispersed quasi-spheres with an average size of 1 \(\mu\)m. It should be pointed that the content of water in the mixture solvent must be limited to a small extent because the reducibility of polyol would be influenced by the addition of water\[43\].

3.3. Growth process

Many of the previous reports addressed the formation mechanism on the basis of time-dependent experimental results.
As to the formation of polyhedra, it was commonly accepted that the origin of the symmetry might be related to the nature that metal particles tend to grow with the structure of one of the platonic solids with all faces made of the same regular polygon and the same number of polygons meeting at each corner. The growth process was usually attributed to the Ostwald ripening. However, rare work concerned about the exact growing step of the structures.

It is worthy to note that some of the icosahedra have one or more caps on the vertices as shown in Fig. 3. The size of the caps ranges from a dot to that can almost enclose the whole body of the icosahedron. These traces reveal that the growing process of the icosahedra was layer-by-layer.

Bravais’ rule is of wide validity for crystals, which states that “the largest faces have the densest packing of atoms”. It is usually interpreted as meaning that the face with denser packing of atoms has slower rate of growth. The faces corresponding to the slow growth rate become steadily larger, while those corresponding to the rapid growth rate disappear entirely. Accordingly, the faces orthogonal to the fivefold rotational axe of the icosahedral crystal grow most rapidly and exist as vertices. Therefore, when a regular icosahedral crystal starts to grow again, vertices would break-through first and act as sidestep for further growth. Scheme 1 illustrates the growing process of the icosahedra. The sketch map is given along with the corresponding FESEM images of the samples. The growing points were marked in circles. All the present FESEM images were taken from the same sample. Because the particles were not growing synchronously, it is reasonable to choose several particles at different growing stages from a certain sample to illustrate the growing process. One of the vertices breaks through in step 1 and grows into a pentacle along the five faces as shown in step 2. Finally, the whole icosahedron would be enclosed by the new layer as shown in step 3.

The breakthrough point might be more than one vertex of the icosahedron. Therefore, there are two ways for the new layers to wrap the icosahedron. This was also confirmed under FESEM. The results were shown in Scheme 2. When the angle of the pentacle reaches the edge of the icosahedron as shown, it would climb over it and continue to grow (path 1) or meet with another layer originating from other vertices. Then the two layers would join and grow together (path 2).

The formation of the clusters composed of nanoflakes also follows this two-dimensional growing process. The difference might rest with the initial stage of the crystallization. Ni [II] was easier to be reduced when the concentration of NaOH was high. Quick reduction led to disordered aggregation instead of platonic polyhedra at the early stage of the reaction, and the disordered aggregates further grew into flower-like clusters through the two-dimensional growing process. The formation of quasi-spherical clusters in the mixture solution must result from an even quicker aggregation during both nucleating and growing stage.
3.4. Magnetic investigation

The magnetic properties of the samples with different morphologies were recorded using a VSM and the hysteresis loops at room temperature are shown in Fig. 6. The typical coercivity (Hc), saturation magnetization (Ms), and remanent magnetization (Mr) are listed in Table 1. The Hc values of icosahedra and clusters were much enhanced compared to that of microspheres. The Hc value of icosahedra was a bit higher than that of clusters. The microspheres were aggregations composed of

![Scheme 2. Illustration of different growing process of the new layer.](image)

![Fig. 6. Hysteresis loops of the samples with different morphologies: (a) icosahedra; (b) clusters composed of nanoplates; (c) microspheres; and (d) the overlapped hysteresis curves of them.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coercivity (G)</th>
<th>Magnetization (emu/g)</th>
<th>Retentivity (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Icosahedra</td>
<td>176.80</td>
<td>48.030</td>
<td>7.752</td>
</tr>
<tr>
<td>Flowerlike clusters</td>
<td>171.43</td>
<td>51.695</td>
<td>14.361</td>
</tr>
<tr>
<td>Microspheres</td>
<td>134.20</td>
<td>53.294</td>
<td>8.381</td>
</tr>
</tbody>
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numerous small nanoparticles which have strong interaction between them. On the contrary, clusters and icosahedra have much less primary particles. It was reported that the interaction between particles would decrease the coercivity\cite{41,44}. That is reason why icosahedra and clusters exhibit much enhanced coercivity. In order to eliminate the size effect, we have also examined the magnetic properties of the spherical nickel powders we synthesized before. The particle size is about 300 nm and the coercivity is 155.19 G, which is still lower that that of icosahedra (176.80 G). The Mr value of flowerlike clusters was much higher than that of icosahedra and spheres. That might be attributed to the effect of surface or shape anisotropy.

4. Conclusion

In summary, Ni powders with different morphologies including icosahedra, microspheres and flowerlike clusters composed of nanoflakes were successfully fabricated via polyol process. The concentration of NaOH played the key role in the formation of the novel structure. A layer-by-layer growth mechanism was proposed according to the experimental results and Bravais’ rule. Furthermore, the magnetism of the nickel powders with different morphologies was also investigated and results revealed that icosahedra and flowerlike clusters exhibited much enhanced coercivity.

Acknowledgment

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References