

## Embedded High Density Metal Nanoparticles with Extraordinary Thermal Stability Derived from Guest–Host Mediated Layered Double Hydroxides

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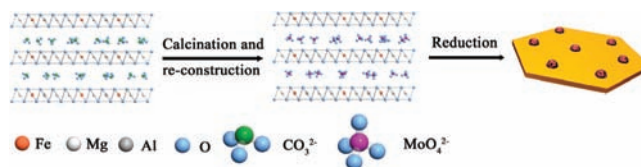
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**Abstract:** A chemical precursor mediated process was used to form catalyst nanoparticles (NPs) with an extremely high density ( $10^{14}$  to  $10^{16}$  m<sup>-2</sup>), controllable size distribution (3–20 nm), and good thermal stability at high temperature (900 °C). This used metal cations deposited in layered double hydroxides (LDHs) to give metal catalyst NPs by reduction. The key was that the LDHs had their intercalated anions selected and exchanged by guest–host chemistry to prevent sintering of the metal NPs, and there was minimal sintering even at 900 °C. Metal NPs on MoO<sub>4</sub><sup>2-</sup> intercalated Fe/Mg/Al LDH flakes were successfully used as the catalyst for the double helix growth of single-walled carbon nanotube arrays. The process provides a general method to fabricate thermally stable metal NPs catalysts with the desired size and density for catalysis and materials science.

Metal nanoparticles (NPs) exhibiting high activity and selectivity play a key role in heterogeneous catalysis and materials science.<sup>1</sup> Various catalytic processes based on metal NPs have been developed, e.g., carbon monoxide oxidation over Au NPs<sup>2</sup> and carbon nanotube (CNT) growth on Fe NPs.<sup>3,4</sup> Most metal NPs are loaded onto supports by impregnation, but it is difficult to obtain well dispersed metal NPs with uniform size and good thermal stability, especially at high loadings.

Metal NPs with tunable particle size, shape, and composition are produced in solution.<sup>5</sup> When they are used for catalytic reaction and nanomaterial (e.g., CNT) synthesis at high temperature, the NPs tend to aggregate into large particles. Thus, physical barriers, e.g., surfactants,<sup>6</sup> ligands,<sup>7</sup> dendrimers,<sup>8</sup> an open shell of support,<sup>9</sup> or a meso/nanoporous oxide shell,<sup>10–12</sup> have to be introduced to separate the metal NPs from each other to prevent sintering. The encapsulating of metal NPs in hollow shells of inorganic materials into ‘yolk–shell’ type nanoreactors by layer-by-layer deposition,<sup>13</sup> templating,<sup>12</sup> or surface protected etching<sup>11</sup> has also been developed. In addition, several chemical approaches that rely on the formation of alloy<sup>14</sup> or substrate effects<sup>15</sup> have been explored to stabilize metal NPs. Up to now, it is still difficult to obtain flake catalysts that comprise high density (over  $10^{14}$  m<sup>-2</sup>) metal NPs with uniform size that exhibit good thermal stability at high temperature (such as 900 °C) by these physical and chemical approaches. A flake catalyst is highly desirable for heterogeneous catalysis and materials science, e.g., controllable synthesis of aligned single-walled CNTs (SWNTs), which requires a high density of metal NPs stable at high temperatures above 750 °C.<sup>4,16</sup>

In this Communication, we explored the idea of chemical precursor mediated formation of high density metal NPs (from  $10^{14}$  to  $10^{16}$  m<sup>-2</sup>) with good thermal stability on the flakes of layered double hydroxides (LDHs). LDH is a class of synthetic two-dimensional (2D) nanostructured anionic clays consisting of positively charged layers with charge-balancing anions between them.<sup>17</sup> In the procedure used, the metal cations were dispersed in the LDHs.<sup>17</sup> The other component in the LDHs were controlled by anion exchange<sup>18</sup> or the destruction–reconstruction route.<sup>19</sup> The homogeneously distributed cations were reduced to form well dispersed NPs with the control of their size and improvement of their thermal stability achieved through a pinning effect on the metal NPs by intercalating suitable anions in the LDHs. Both Fe and Co NPs have been produced successfully. These catalysts have a high density of metal NPs and were extraordinary catalysts for SWNT-array double helix synthesis.



**Figure 1.** Schematic illustration to show the formation of high density metal NPs by the incorporation of MoO<sub>4</sub><sup>2-</sup> in Fe/Mg/Al LDH.

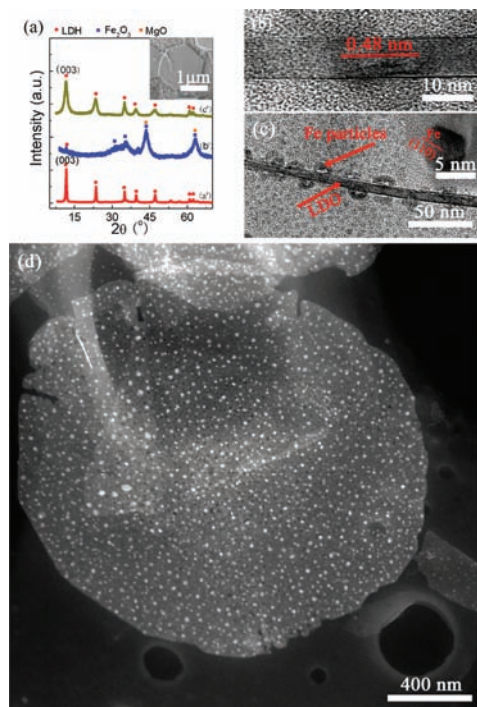
This strategy which invoked anion modulation in the LDH flake by guest–host chemistry and controllable reduction for the formation of metal NPs is illustrated in Figure 1. Fe/Mg/Al-CO<sub>3</sub><sup>2-</sup> LDH flakes were synthesized by a facile coprecipitation method. The prepared LDHs had a diameter of several micrometers and a thickness of tens of nanometers (Figures 2a and S1). Powder X-ray diffraction data, presented in Figure 2a, showed the Fe/Mg/Al-CO<sub>3</sub><sup>2-</sup> LDH had good crystallinity and the lattice parameters were  $a = 0.304$  and  $c = 2.247$  nm. After calcination at 450 °C for 1 h, metal oxides were left as the main components (Figure 2a). The calcined material was then put into a Na<sub>2</sub>MoO<sub>4</sub> solution for 24 h to reconstruct its hydroxalcalite-like structure with MoO<sub>4</sub><sup>2-</sup> intercalated as the charge-balancing anions. The obtained Fe/Mg/Al-MoO<sub>4</sub><sup>2-</sup> LDH has the same lattice parameter  $a$  but a larger  $c$  (2.326 nm) due to the intercalation of MoO<sub>4</sub><sup>2-</sup>. Thus, plate-like Fe/Mg/Al-CO<sub>3</sub><sup>2-</sup> and Fe/Mg/Al-MoO<sub>4</sub><sup>2-</sup> LDH flakes were obtained (Figures S1 and S2).

The layered double oxides (LDO), which were the calcined products of the LDH, maintained the plate-like morphology and layered structure after the removal of CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup>, and the Fe was still well dispersed in the calcined flakes (Figure 2b). With the introduction of H<sub>2</sub>, neighboring Fe atoms rapidly formed Fe

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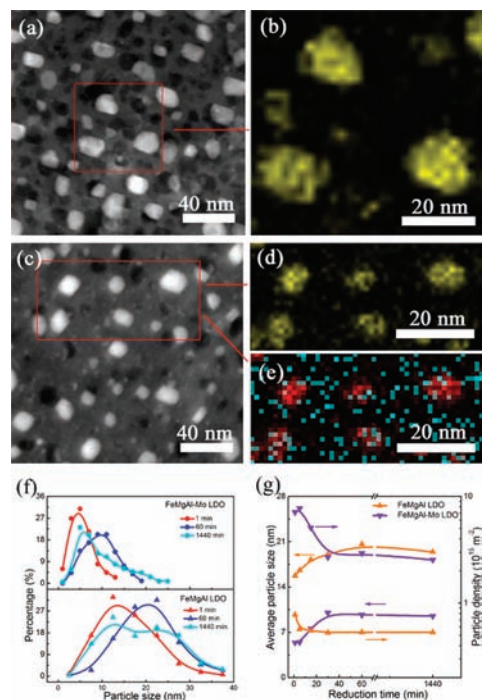
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NPs. Sintering was prevented because Fe atoms in different layers would have to migrate over the interlayer spaces to sinter. Figure 2c and d show the well dispersed Fe NPs produced on both sides of an Fe/Mg/Al LDO flake after a 5-min reduction. These had sizes of 1–40 nm (mean = 16.6 nm) and a density of  $5.7 \times 10^{14} \text{ m}^{-2}$ . When the  $\text{CO}_3^{2-}$  anions were replaced with  $\text{MoO}_4^{2-}$  anions by guest–host chemistry, well dispersed Fe NPs of much smaller sizes (1–14 nm, mean size = 5.5 nm) and higher density ( $7.1 \times 10^{15} \text{ m}^{-2}$ ) were obtained on the Fe/Mg/Al-Mo LDO with the same reduction time.



**Figure 2.** (a) XRD patterns of the Fe/Mg/Al- $\text{CO}_3^{2-}$  LDH (a') and its calcined form (b'), calcined at 450 °C for 1 h, and the Fe/Mg/Al- $\text{MoO}_4^{2-}$  LDH (c') obtained by the destruction–reconstruction procedure, with inset scanning electron microscopy (SEM) image of the morphology of the LDH flake. (b) Cross section of layered LDO showing an interlayer spacing of 0.48 nm. (c) Transmission electron microscopy (TEM) and inset high resolution TEM images of the cross section showing the morphology of the Fe NPs embedded in the Fe/Mg/Al LDO flake. (d) Scanning transmission electron microscopy (STEM) image of the Fe NPs distributed on the reduced Fe/Mg/Al LDO flake.

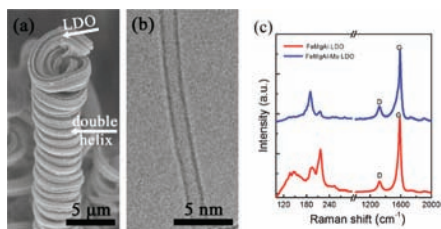
The NPs were embedded in the LDO flake and exhibited strong interaction with the support, which effectively prevented sintering (Figures 2d, 3a–e, and S3). It can be noted that the Fe NPs on Fe/Mg/Al-Mo LDO were much smaller, and the EDS mapping results revealed that Mo existed around the Fe NPs, which indicated that Mo can be pinned between the Fe NPs to prevent further sintering (Figure 3c–e). Thus, even when the catalysts were calcined for 1440 min in a  $\text{H}_2$  atmosphere at 900 °C, the mean diameters of the Fe NPs only increased from 15.7 to 20.6 nm on Fe/Mg/Al LDO and from 5.4 to 9.5 nm on Fe/Mg/Al-Mo LDO (Figure 3f and g). In addition, only a slight decrease in particle density was observed after the long reduction time, which revealed the metal catalyst NPs exhibited good thermal stability (Figures 3f and g, S4, and S5). Furthermore, when Fe was replaced by Co, Co NPs of much smaller sizes (3–9 nm, mean size = 4.9 nm) and at a higher density ( $4.53 \times 10^{15} \text{ m}^{-2}$ ) were obtained by the modulation of  $\text{MoO}_4^{2-}$  intercalation (Figure S6).



**Figure 3.** High-angle annular dark-field (HAADF)-STEM image (a) and Fe map (b) of the NPs formed on the Fe/Mg/Al LDO flakes reduced at 900 °C for 5 min. The HAADF-STEM image (c) and Fe map (d) of the NPs formed on the Fe/Mg/Al-Mo LDO flakes reduced at 900 °C for 5 min. (e) The element mapping showing the distribution of Fe (red) and Mo (turquoise) on the reduced Fe/Mg/Al-Mo LDO flakes. (f) The size distribution of Fe NPs on Fe/Mg/Al and Fe/Mg/Al-Mo LDO flakes reduced at 900 °C. (g) The average particles size and density of Fe NPs formed on the reduced Fe/Mg/Al and Fe/Mg/Al-Mo LDO flakes after different reduction times.

After the introduction of a carbon source for CVD growth of CNTs, randomly entangled SWNTs and some carbon encapsulated NPs were presented on the Fe/Mg/Al LDO (Figure S7). Surprisingly, SWNT-array double helices were synthesized on the Fe/Mg/Al-Mo LDO (Figures 4a and b and S8). This may be because SWNTs can be assembled into an array form on both sides of the ultralight flake ( $\sim 0.2 \text{ ng}$ ) due to the high density of the small catalyst particles. The SWNT arrays on the LDO flakes were free to grow in the way that minimizes the stresses associated with the growth. When the SWNT array tips meet spatial resistance, they continued growing out from the LDH flake by coiling onto themselves in an SWNT-array double helix.<sup>20</sup> As compared with the production of double-walled or multi-walled CNT-array helices,<sup>20</sup> here, the catalyst NPs with a much smaller size and higher density were obtained on the Fe/Mg/Al-Mo LDO through the guest–host chemistry. The specific surface area of the SWNTs that existed as double helices was 680  $\text{m}^2/\text{g}$ . Strong radial breathing mode peaks and a low  $I_D/I_G$  ratio from Raman spectra were illustrated in Figure 4c, which indicated SWNTs were obtained on both Fe/Mg/Al and Fe/Mg/Al-Mo LDO flakes.

In summary, well dispersed embedded metal NPs with a high density (ranging from  $10^{14}$  to  $10^{16} \text{ m}^{-2}$ ) and good thermal stability were obtained by the chemical precursor mediated formation of the metal NPs on LDH flakes. This used a pinning effect of Mo around the Fe NPs to obtain a high density of small Fe NPs (over  $10^{15} \text{ m}^{-2}$ ) formed on  $\text{MoO}_4^{2-}$  intercalated LDHs. These Fe NPs were active for the formation of SWNT-array double helices. Since Fe, Co, Ni, Cu, and some noble metals can be dispersed in the lamellar LDH flake, the presented guest–host mediated procedure



**Figure 4.** (a) SEM image of SWNT-array double helices grown on Fe/Mg/Al-Mo LDO flake. (b) High resolution TEM images of the SWNTs on Fe/Mg/Al-Mo LDO. (c) Raman spectra of the synthesized SWNTs on Fe/Mg/Al and Fe/Mg/Al-Mo LDO.

is promising for the fabrication of metal NPs with a small size, high density, and good thermal stability for catalysis and materials science.

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**Supporting Information Available:** Detailed experimental details; SEM and TEM images, metal NP size distribution, and as-grown CNT products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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