In-situ observation of Cu-Pt core-shell nanoparticles in the atomic scale by XAFS

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Abstract: Bimetallic nanoparticles play an important role in potential industrial applications, such as catalysis, optoelectronics, information storage and biological labeling. Herein, homogeneous Cu-Pt core-shell nanoparticles with the averaged size of 8 nm have been synthesized by chemical methods. Cu atoms diffusion process, which motivated by heating, was observed in-situ by using temperature-dependent x-ray absorption fine-structure (XAFS) spectroscopy. Results show that Cu diffuse gradually from Cu core to Pt shell in these nanoparticles with increasing temperature. We also found the surface ligand (O) bonded Pt at the room temperature and were removed gradually by heating the sample. The analysis of the diffusion process in bimetallic nanoparticles will provide important guideline for their designing and tuning.

Introduction

It is well known that bimetallic nanoparticles exhibit perfect physical and chemical properties that differ from corresponding bulk materials because the addition of a second atomic species not only changes the structure of nanoclusters but also controls their electronic structure. Bimetallic nanoparticle has spawned an enormous research effort aimed at application in catalysis\textsuperscript{1,2}, optoelectronics\textsuperscript{3,4}, information storage\textsuperscript{5,6}, biological labeling\textsuperscript{7,8}. Recently, controlling the external morphologies (e.g., shape, size and uniformity) has become focus of many studies in order to exploit the relationship between the structure and properties, which is necessary to apply nano-materials in nanotechnology\textsuperscript{9}. However, internal structure of nanoparticles which influencing the physical property directly are very important to be paid attention as well\textsuperscript{10,11}. Although synthesis and characterization of bimetallic clusters have motivated numerous experimental and theoretical studies, the atomic distribution, structural dynamic and thermodynamic behavior of bimetallic nanoparticles, which directly affects their properties, still remain less explored.

It is common sense that bimetallic clusters exhibit high performance usually by annealing process. It may be due to that the surfactants were removed by high temperature and the internal structure of
bimetallic nanoparticles formed prior coordination. A few researches reported experimental evidence of temperature effects on the bimetallic internal structure\textsuperscript{12,13}. For instance, the process of thermodynamic behavior of Pt-Cu nanoparticles aggregating in various temperatures was investigated by XRD to exhibit the diffusion and nucleation process. However, XRD technique only provided long-range order but not short-range order\textsuperscript{14,15}. Pt-Cu metallic nanoalloys were usually studied at room temperature in order to avoid removal of stable ligand and increasing of the size of nanoparticles. Herein, we focus on the structure and the diffusion of Cu-Pt nanoparticles in different temperatures by in-situ XAFS technique.

**Experimental methods**

Core-shell Cu-Pt nanoparticles were synthesized with a similar scheme employed in the Fe-Pt synthesis, washed by ethanol and segregated by centrifuging. Then 22 mg dried core-shell Cu-Pt nanoparticles were dissolved with 100 mg graphite powder as well as plenty of hexane. The solution was mixed homogeneously by Ultrasonic. Finally the mixed solution was dried in vacuum drying oven and pressed into a pellet in a stainless steel holder and used to collect the XAFS data.

The same apparatus for temperature-dependant in-situ XAFS study on atomic kinetics across the MIT in crystalline VO\textsubscript{2}\textsuperscript{16} was employed to probe the thermodynamic process of core-shell nanoparticles, which can preserve the precision of XAFS data enough to explain the real process. Powder X-ray diffraction (XRD) data were collected at U7B stations of the National Synchrotron Radiation Laboratory (NSRL, Hefei). Energy-dispersive spectroscopy (EDS) analysis and high-resolution transmission electron microscopy (TEM) image were obtained by a JEM-2010 TEM.

**Results and discussion**

Fig.1a shows TEM image of the as-prepared Cu-Pt core-shell nanoparticles, exhibiting a homogenous core-shell shape with the averaged size of 8 nm. And the corresponding size distribution, which will benefit extraction of precise structure parameter, was presented in the inset of Fig.1a. In order to check if the nanoparticles were core-shell structure, we performed the Cu K-edge and Pt L\textsubscript{3} edge XAFS measurements at room temperature. Fig.1b shows the Fourier transforms (FTs), looking at the data in the R-space (real space), of EXAFS spectra at Pt L\textsubscript{3}-edge. Two intense peaks emerge in the region 1.5-3.1 Å for the as-made sample (green solid line), consisting of a lower-R peak (1.5-1.8 Å) and a higher-R peak (2.5-2.2 Å), much different from the signal of the Pt foil (red solid line). It can be easily found out that these two peaks correspond to the Pt-ligand bond and the Pt-Pt bond, respectively. In contrast, Cu K-edge FT-EXAFS spectra shown in the Fig.1c was similar to the Cu foil except for the amplitude. The missing of the signals of Cu-O and Cu-Pt peak indicates that the Cu cluster in our sample presents in the form of elemental crystal. It was well-known that Cu clusters were extremely oxidized to form CuO or CuO\textsubscript{2} if they were exposed to air\textsuperscript{17}. Therefore, Cu clusters in the as-made sample should be protected by Pt shells to avoid oxidizing. Based on all above analyses, we can get a simple and clear view about the structure of the as-prepare Pt-Cu nanoparticles: Pt coordinated with ligand of PVP in the shell and protected Cu core from oxidization, and Cu formed core in the nanoparticles without oxidization and alloying.

In order to obtain quantitative information of the local structure, FT-EXAFS of the first shell (0.17-0.33 nm) were fitted (see circle lines in Fig1b and c) using theoretical phase-shift and amplitude
generated by FEFF 8 program. The coordination number $N$ of Pt can give some useful information to prove core-shell structure. In Table 1, $N_{\text{Pt-Pt}} + N_{\text{Pt-Cu}}$ is 12 in total, indicating that the NP surface is covered entirely with Pt atoms, in agreement with the report by Zhang\textsuperscript{18}. It can also be concluded that the Cu-Pt nanoparticles present the core-shell structure.

![Fig. 1](image)

**Fig.1** (a) TEM images of Cu-Pt core-shell nanoparticles; (b) and (c) the FT-EXAFS spectra of Cu-Pt core-shell nanoparticles at Pt L\textsubscript{3}-edge and Cu K-edge.

Pt L\textsubscript{3}-edge XAFS spectra of diffusion process in the temperature range 25-600°C were shown in Fig 2. The extended XAFS (EXAFS) functions $\chi(k)$ (Fig. 2a) and the corresponding FTs (Fig. 2b) exhibit remarkable and systematic temperature evolution. As the temperature increases, it was found that the EXAFS oscillations of the Cu-Pt nanoparticle changed significantly. This change is originated from the fact that, as the diffusion occurs between Cu and Pt atoms, the average number of Cu neighbor atoms surrounding the Pt absorbers increases, resulting in the formation of the Cu-Pt alloy. This observation can be also indentified with the Fourier transform profiles in the real space. The FT curve at room temperature shows a intense peak in the range of 1.5-2 Å, which was typical characterization of the Pt-ligand (O). It was interesting to find that the intensity of the peak of Pt-ligand about 1.5 Å decreased and disappeared at 230°C, suggesting that the surface ligand can protect Cu-Pt nanoparticles surface at high temperature.

![Fig. 2](image)

**Fig. 2** (a) $k^2\chi(k)$ of Cu-Pt nanoparticles at Pt L\textsubscript{3}-edge and (b) Corresponding FTs vs. temperature.

According to the parameters from the EXAFS fits in the table 1, the coordination number of the Pt-
ligand, exactly the Pt-O bond, drops from 3.1 at room temperature to 1.6 at 130 ℃ and disappear at 230 ℃. With temperature increasing, the peak shifts to lower R and gradually becomes more intense. This may arise from the formation of the Pt-Cu alloy when Cu atoms gradually diffuse to the Pt shell. The structure parameters in the table 1 can perfectly explain the change. At the interface of the core-shell at room temperature, only a small amount of Pt-Cu bonds existed. When heating the sample, the coordination number of the Pt-Cu bond increased from 1 at room temperature to 4 at 600 ℃, suggesting the diffusion was finished. Meanwhile, that of the Pt-Pt bond decreased gradually from 6.2 to 0, suggesting the total Cu-Pt alloy formed at the temperature of 600 ℃. Therefore, from the change of the coordination number of Pt-Pt and Pt-Cu, it can be estimated that the percentage of Cu-Pt alloy at the interface was 2%, 10%, 30%, 60% and 100% at 25℃, 130℃, 230℃, 400℃ and 600℃, respectively.

Table 1 Structural parameters of bond distance R, coordination number N, and Debye factor from EXAFS fits of the as-prepared Cu-Pt nanoparticle at different temperature.

| Sample | Bond     | R (Å)     | N    | Φ (10^-3 Å²) |
|--------|----------|-----------|------|--------------|
| Pt-Pt  | Pt-O     | 2.00 ± 0.01 | 3.1 ± 0.3 | 8.0 ± 0.8  |
| Pt-Pt  | Pt-Cu    | 2.64 ± 0.01 | 1.0 ± 0.8 | 6.0 ± 0.8  |
| 130-Pt | Pt-O     | 2.03 ± 0.01 | 1.6 ± 0.8 | 12.0 ± 0.8 |
| 130-Pt | Pt-Cu    | 2.65 ± 0.01 | 1.8 ± 0.8 | 16.1 ± 0.8 |
| 130-Pt | Pt-Pt    | 2.35 ± 0.01 | 5.3 ± 0.8 | 4.7 ± 0.8  |
| 230-Pt | Pt-O     | 2.66 ± 0.01 | 1.4 ± 0.8 | 6.0 ± 0.8  |
| 230-Pt | Pt-Cu    | 2.34 ± 0.01 | 1.3 ± 0.8 | 13.6 ± 0.8 |
| 230-Pt | Pt-Pt    | 2.83 ± 0.01 | 3.3 ± 0.8 | 3.0 ± 0.8  |
| 400-Pt | Pt-Cu    | 2.68 ± 0.04 | 2.3 ± 0.8 | 7.2 ± 0.8  |
| 400-Pt | Pt-Pt    | 2.80 ± 0.05 | 2.8 ± 0.8 | 3.5 ± 0.8  |
| 600-Pt | Pt-Cu    | 2.65 ± 0.03 | 4 ± 0.8  | 8.1 ± 1.2  |

Conclusions

In summary, we prepared homogeneous Cu-Pt core-shell nanoparticles with average size of 8 nm by chemical methods. By performing temperature-dependent x-ray absorption fine structure measurements, we studied in situ the local structures of core-shell nanoparticles at different temperatures. The result shows the surface ligands bonded Pt at the room temperature and were removed gradually by heating the sample. The temperature evolution of the coordination number of the Pt-Cu and Pt-Pt bonds also provides insight into the extent of the alloying at the interface between the Pt shell and the Cu core of the Cu-Pt nanoparticles. This detailed information about the diffusion process should be useful for designing and controlling bimetallic nanoparticles for high implication.

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