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Spectra study and size control of cobalt nanoparticles passivated with oleic acid and triphenylphosphine

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ABSTRACT

This paper compares the performance of two surfactants—triphenylphosphine (TPP) and oleic acid (OA) as a pair of capping agents in the synthesis of magnetic Co nanoparticles (NPs). Magnetic colloids of cobalt NPs are prepared by reducing solute cobalt chloride in the presence of stabilizing agents at a high temperature and characterized by TEM. Infrared spectra reveal that a chemical bond can be formed between O of C═O band and Co atoms while a coordinate bond forms between P and Co atoms around the NPs on the surface. OA binds strongly to the particle surface during synthesis that hinders the particle from growing; the TPP reversibly coordinates neutral metal surface sites that favor rapid growth. We studied the influence of changing the TPP/OA concentration ratio on the particle size distribution and crystallinity of Co NPs. Our results indicate the presence of TPP/OA is able to control particle growth, stabilize the colloidal suspension and prevent the final product from oxidation by air.

1. Introduction

Magnetic NPs exhibit strong size-dependent properties that may provide insight into the scale limits of magnetic storage and microelectronics, which are crucial to information technology [1,2]. The desire to identify and understand the size-dependent properties of materials at the nanometer scale has motivated the preparation of size-tunable monodisperse NPs with controllable internal structures [3,4]. To prepare stable magnetic colloids, a surfactant has to be added as a capping agent in order to control the particle growth and limit oxidation. To this end, Sun and Murray have demonstrated the synthesis of Co NPs in the presence of a pair of organic surfactant, such as OA and trioctylphosphonic [4]. We also employ a combination of surfactant in the presence of stabilizing ligands OA and TPP to control the particle growth and stabilizing the particles [5]. The purpose of using the TPP, instead of the tributylphosphine or trioctylphosphine, is that the phenyl can provide greater steric hindrance than that of the straight chain alkyl. It can be controlled to synthesize cobalt NPs with small size. However, the difference of bonding condition between these capping agents at a NPs surface and the influence of these capping agents on the particle size distribution are studied less [6].

Herein we synthesis cobalt NPs by reduction of cobalt chloride with lithium triethyl boronhydride (superhydride) in the presence of TPP and OA. We specifically investigate the bonding condition of OA and TPP at NPs surface by Infrared spectra and find that organic molecules form a relatively close-packed layer around NPs surface and a chemical bond can be formed between O of C═O band and Co atoms while a coordinate bond forms between P and Co atoms. As long as there are OA and TPP in the reaction solution, different molar ratios of TPP/OA can be employed to control the particle growth and limit oxidation.

2. Experimental

2.1. Materials

The experiment of synthesis was carried out under nitrogen purge. All reagents were purchased from ACROS. Diphenylether solution of superhydride ($LiBEt_3H$) was prepared by first mixing the tetrahydrofuran (THF) superhydride solution with diphenylether and then evaporating THF.

2.2. Nanocrystal synthesis and size-selection

Cobalt nanocrystals were prepared by high temperature solution phase reducing method [7]. 0.13 g cobalt chloride (anhydrous), 0.32 ml OA and diphenylether (30 ml) were mixed together under nitrogen and then heated nearly to 100 °C. Then

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0.79 g TPP was added and heated to 210 °C. The Co NPs began to emerge with the injection of diphenylether superhydride (2 ml) during vigorously stirring solution. The color gradually changed from blue to black during the first minute as the Co NPs nucleated and began to grow. The reaction was held at 200 °C for 30 min. Then the dispersion Co NPs was cooled down to room temperature, and a black precipitate appeared by adding ethanol to the dispersion. The black precipitate was collected by centrifugation and washed with ethanol several times to remove excessive surfactant. The black magnetic precipitate was in turn redispersed in heptane and precipitated partially by slow titration of ethanol. Centrifuging the suspension isolated a precipitate enriched in the large NPs (30 wt%) and leaved small NPs (70 wt%) in the supernatant. Additional ethanol was added to the supernatant to isolate a second fraction of small NPs. Cobalt NPs was obtained by the gentle destabilization/redispersion procedure with a size distribution of $\sigma \sim 5\%$ [8].

2.3. Characterization of samples

The composition of the organic molecules-passivated cobalt NPs was measured on the ESCA LAB5 X-ray photoelectron spectrometer (XPS) with monochromated Mg X-ray at 10 kV. The structure of Co nanocrystals was investigated by a Rigaku D/MAX-200 X-ray diffractometer (XRD) with Cu K*a* radiation (λ = 1.5406 Å). Infrared (IR) spectra of the samples were recorded using a Bruker EQUINOX55 at room temperature by dropping the colloid solution on a KBr tablet. The graphs of transmission electron microscopy (TEM) were obtained from JEM 200CX operating at 200 kV.

3. Results and discussion

3.1. XPS characterization

XPS is used for particle surface element analysis. In XPS analysis, the penetration depth of the XPS beam used is between 3.0 and 5.0 nm while the chain length of the OA and the TPP is about 2.0 nm. So the depth probed from the surface of the cobalt NPs to the core of the cobalt NPs is between 1.0 and 3.0 nm, which ensures that the surface valence of the molecule-coated cobalt NPs can be obtained. Fig. 1(a) is the XPS spectrum of the freshly prepared cobalt NPs. Characteristic peaks of cobalt, carbon and phosphorus are observed, all the residual surfactant are removed by washing the precipitate with ethanol several times, the characteristic peaks of carbon and phosphorus are introduced from the TPP and OA coated surface of cobalt NPs. According to the results, OA and TPP should react or coordinate with the surface atoms of the Co NPs to prevent the oxidation or aggregation of Co NPs.

Fig. 1(b) is the XPS spectrum showing the Co $2p_{3/2}$ and Co $2p1_{/2}$ peaks of cobalt NPs from a dispersion kept under air for 30 days. The Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks of the cobalt NPs kept under air for 30 days are present at 778.5 and 793.6 eV, respectively. The difference between two peaks is 15.1 eV, which is consistent with the standard spectra of the element cobalt, indicating that the Co NPs in heptane are fairly stable against further oxidation.

3.2. IR characterization

To understand the observed difference between OA and TPP in serving as the capping agent, we analyze the samples with IR spectroscopy. The IR spectra of the free TPP, OA, and the OA and TPP capped-Co nanocrystals (the free OA and TPP have been removed through excessive washing of the samples with ethanol) are shown in curves a, b, and c of Fig. 2(A), respectively. These results provide additional information about the local molecular environment of the OA, TPP ligand on the nanocrystals surface. As shown in spectrum c of Fig. 2(A), there are characteristic absorption peaks of the TPP and OA, which also appear in curve a and b of Fig. 2(A), indicating that the organic molecules are indeed absorbed on the nanocrystals. As shown in Fig. 2, the peaks corresponding to C=O stretching at 1710 and 1285 cm^{-1}, P–Φ stretching at 1711 cm^{-1}, the rocking and bending mode of the methylene group $\omega(CH_2)$ at 1270 cm^{-1}, the bending mode of the phenyl group $\gamma(=CH)$ at 742 cm^{-1} and δ (benzene ring) = 697 cm^{-1} can be clearly seen. The only difference among these characteristic peaks is either the peak intensity or slight shift of the peak position. For example, the peak position of the longitudinal modes of the OA and TPP shifts to lower wave numbers after TPP/OA are adsorbed on the surface of the cobalt NPs, appearing in the region of 2925–2923 cm^{-1} for Va (CH_2), 2854–2852 cm^{-1} for Vs (CH_2) and 2958–2955 cm^{-1} for Vs (CH_3,ip). This is believed to be due to the organic molecules forming a relatively close-packed layer, constraining their own mobility on the surface of the NPs [6,9]. Thus, this steric constraint affects the transverse modes (rocking mode, wagging mode, etc.) more than that on the longitudinal modes (stretching mode, etc.). A dense coverage by the organic surfactant is crucial to prevent the particles from being oxidized by air. However, the peaks corresponding to the C=O stretching mode $\nu(C=O)$ at 1710 and 1285 cm^{-1} disappear in curve C but the P–Φ stretching mode

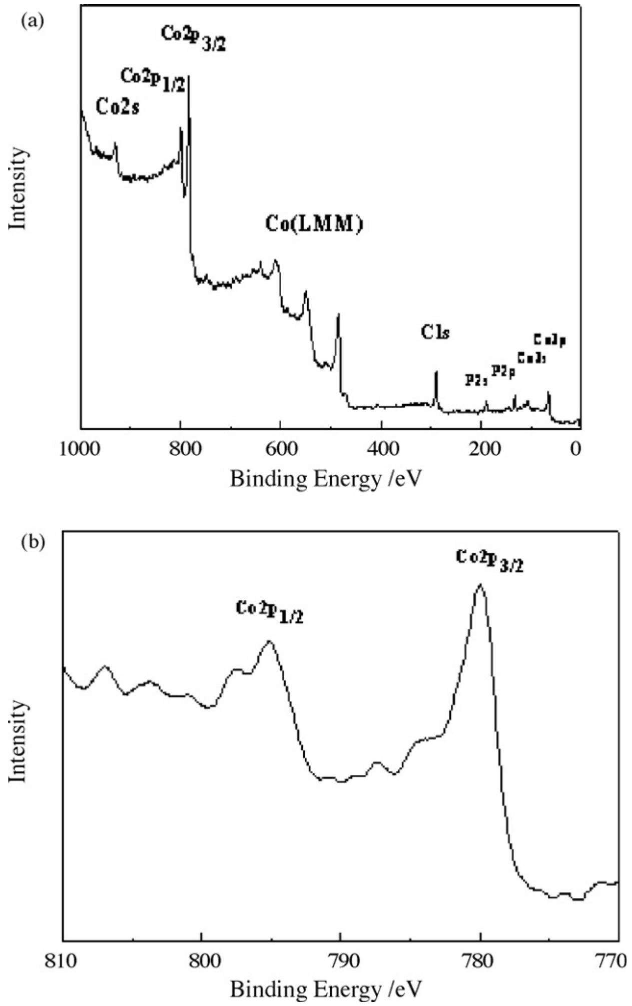

Fig. 1. XPS spectra of (a) molecule-coated cobalt NPs and (b) Co 2p of cobalt NPs kept for 30 days.