

## Fabrication of the Sponge-like Layered Silver(I)-alkylamine Complexes and Their in situ Reduction

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A series of layer-structured silver(I)-alkylamine complexes with sponge-like morphology and abundant macroporosity were self-assembled in the alcohol/water system. After in situ reduction, the layered silver(0)-alkylamine composites were obtained.

The layered organic-inorganic materials have found many applications in chemistry, biotechnology and materials science<sup>1,2</sup> for their unique organic-inorganic hybrid structures.<sup>3</sup> Recently, the studies on layered silver compounds have attracted considerable interests due to their unique optical, electrical and catalytic behaviors. Dance and co-workers<sup>4</sup> successfully assembled layered silver thiolates in the acetonitrile solvent on the base of the coordination effect between silver(I) and alkanethiols. Later, the orientation determination of their alkyl chain, thermal stability, application fields and structure transformation dynamics of such materials have also been studied.<sup>5-12</sup> More recently, a series of the long chain silver carboxylates with layered structure were synthesized which were suggested as the precursors of the silver nanoparticles.<sup>13</sup>

The primary alkylamine is another important ligand for the noble metal ions.<sup>14</sup> Gomez et al.<sup>15</sup> have successfully fabricated fibrous gold (I) alkylamine complexes by the reaction of AuCl (tetrahydrothiophene) with long chain alkylamines in toluene. Albeniz et al.<sup>16</sup> have prepared a layered ionic silver amino complex in acetonitrile system and suggested a bilayer structure which was different from the corresponding thiolates.<sup>12</sup> On the other hand, long chain alkylamines have also been widely applied as the templates to synthesize the mesoporous materials in the alcohol/water solution because they could self-assembled into the micelle or liquid crystal structure in this system.<sup>17</sup> In our group, using both the micelle formation tendency of long chain alkylamines in water/alcohol system and their coordination effects, a series of the silver(I)-alkylamine complexes with uniformly layered structure were successfully synthesized and after reduction, the layered silver(0)-alkylamine hybrid composites were also obtained. Both materials might have the potential applications as catalysts, optical and electrical devices. In addition, unlike the case of the previous preparation process in organic solution, the handling in water/alcohol system was more environmental friendly, facile and cheaper.

The synthesis procedure of the samples are described as follows: a silver nitrate aqueous solution was poured into the mixture of alkylamine, isopropyl alcohol and ethanol in the molar ratio of H<sub>2</sub>O : EtOH : *i*-PrOH : amine : AgNO<sub>3</sub> = 120 : 24 : 6 : 2 : 1 under vigorous stirring. The reaction mixture immediately concreted and formed a white hydrogel with much larger volume than the sum of the volume of the original reaction solution. Then

the hydrogel was aged for 30 min and washed with a large quantity of 50 wt% ethanol solution. Finally, the product was centrifugated and dried under room temperature in dark for 24 h. The samples obtained were denoted as LSA-*n* (*n* means the carbon atom number in the alkylamine). For comparison, an analogue of LSA-14 was also prepared in acetonitrile systems according to the literature method<sup>16</sup> and the sample was named as LSA-14-O. To further study the reduction behavior of the samples, a 0.4 wt% KBH<sub>4</sub> solution was added drop-wisely to the reaction mixture before the washing process. The molecular ratio of Ag<sup>+</sup> and BH<sub>4</sub><sup>-</sup> was 4 : 1. The reduced samples were named as LSA-*n*-R.

The powder XRD patterns of the LSA-*n* samples (Figure 1) showed that these products were layer-structured and the *d*-spacing values of the synthesized samples varied with the alkyl chain length of the ligands. However, when the carbon numbers of the alkylamines were eight or less, none of the layered structure formed. This phenomenon was similar to that occurred in the synthesis of mesoporous materials where no mesostructure was obtained for the amine with short alkyl chain because the micelle could not form. For the samples with *n*-hexadecylamine and *n*-tetradecylamine, the *d*-spacing value of these materials were a little larger than those of corresponding thiolate,<sup>12</sup> probably because the coordination structures of the alkylamines were different from those of the thiolates. On the contrary, the *d*-spacing value of the sample with *n*-dodecylamine was lower than the silver *n*-dodecanethiolate. This could be explained by the relative larger solubility of *n*-dodecylamine in ethanol/water systems which might lead to the decrease of the interlayer alkylamine density during washing process, resulting in the increase of the tilt degree of the alkyl chain. Additionally, the LSA-*n*s have the similar *d*-spacing values with their analogues prepared in acetonitrile (e.g., LSA-14-O in Figure 1), probably indicating that our samples possessed the same configuration as previously reported.<sup>16</sup> It is also found that the *d*-spacing values of all LSA-*n*s were larger than those of the

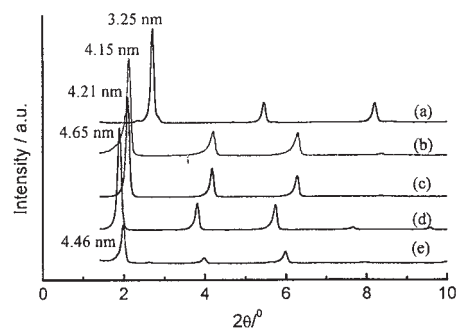


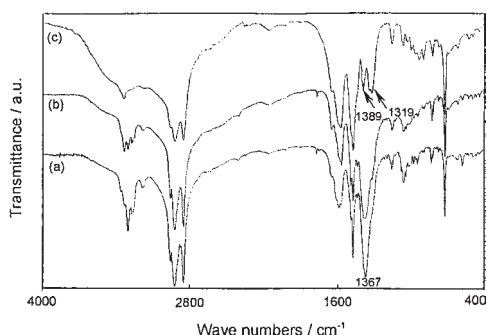
Figure 1. XRD patterns of LSA-12 (a), LSA-14-O (b), LSA-14 (c), LSA-16 (d) and LSA-16-R (e).

corresponding alkylamines, meaning that the silver ions had participated into the formation of the layered structure.

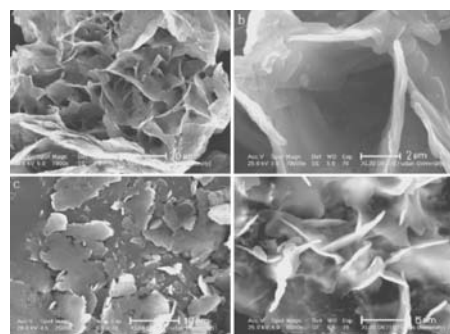
The FTIR spectrum of LSA-16 (Figure 2a) showed that the peaks of the N-H stretching bands obviously appeared in the region between 3100 and 3400  $\text{cm}^{-1}$ , while in the FTIR spectrum of hexadecylamine (Figure 2c), only a broadened peak caused by the strong intermolecular hydrogen bond appeared. The fact proved that the existence of silver ions hindered the formation of the hydrogen bond between amine molecules. Another obvious difference between the LSA-n's and the corresponding alkylamines could be found in the region between 1420 and 1250  $\text{cm}^{-1}$ . The characteristic double peak at 1389 and 1319  $\text{cm}^{-1}$  for hexadecylamine transformed into a strong single peak at 1367  $\text{cm}^{-1}$  on the IR spectrum of LSA-16. Furthermore, the photosensitivity of the LSA-n samples were greatly weakened compared with those of the silver(I) salts without using amines as the ligands. The color change of the former was obviously slower than those of the latter, further indicating the existence of the interaction between amines and silver.

Figure 3a and 3b are the SEM images of LSA-16. It is clear that the sample possess a lamellar structure and aggregated into a sponge-like morphology with abundant macroporosity. From the image at high magnification (Figure 3b), the thickness of each lamella was estimated ca. 400 nm. The EDX was used to analysis the composition of the LSA-16 and the result showed the existence of Ag, N, C and O in the lamella.

After reduction, the color of the hydrogel turned from white to black, implying that the Ag(I) in the sample had been reduced. The oxidation state change of silver was also confirmed by XAES. The bonding energy of the unreduced samples was about 1.3 eV higher than that of the reduced ones, indicating the reduction of the silver.<sup>18</sup> The FTIR spectrum of LSA-16-R (Figure 2b) was similar to that of the sample before reduction except the change of the relative intensities and ratios of N-H stretching bands. The facts probably indicated that the molecular configuration of the amines between the layers was almost the same as that before reduction but the interaction between silver and amines altered. This change could also be observed from the XRD patterns and SEM images. Although the layered structure was still retained after reduction, the *d*-spacing shrank (e.g., Figure 1e), which maybe caused by dissolving away of the interlayer amines a little during the washing step for the relative weaker interaction of amine and Ag(0), or the escaping of the interlayer  $\text{NO}_3^-$ , the counter-ions, after reduction. The lamellar morphology of LSA-16-R was still observed from its SEM image



**Figure 2.** FTIR spectra of silver-hexadecylamine complex before reduction (a), after reduction (b) and hexadecylamine (c).



**Figure 3.** SEM images of LSA-16 (a) and (b), LSA-16-R (c) and (d).

but some edge-dilapidation happened for the weaker interaction of amine-Ag(0) (Figure 3c and 3d).

In conclusion, a series of the layered silver(I)-alkylamine complexes with sponge-like morphology have been successfully prepared through the self-assembly method in the alcohol/water mixture system and the silver(0)-alkylamine composites with layered structure were also obtained by the in situ reduction. These materials might have the potential applications in some important fields, such as catalysts, optical and electrical devices for their special structures.

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