Synthesis and characterization of stable Ag^+ ion clusters

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1. Introduction

Silver has a great advantage over other metals when it comes to adsorbing radioactive iodine species, but in previously conducted studies, silver ion clusters (AICs) could not be thoroughly investigated theoretically and spectroscopically. Several studies have reported the UV-vis absorption of these clusters to be in the 250-350 nm region, but the results of these studies have not been consistent since the absorption depends on the surrounding chemical environment and the number of Ag atoms forming the Ag ion cluster. Furthermore, in most of these studies, the experiments and spectroscopic analyses are conducted in the liquid state (de-ionized water and organic solvents). The most common method for the synthesis of AICs or silver nanoparticles (Ag NPs) requires a reducing agent as $NaBH_4$ or radioactive ray irradiation (gamma-ray or electron beam).

2. Experiment details

3-(ethylenediamino)propyl-functionalized silica gel (EDS gel) was purchased to adsorb the AIC. The EDS gel was placed into two different Ag^+ solutions obtained from two different Ag^+ precursors: $AgNO_3$, Ag_2SO_4. Furthermore, two Ag NP suspensions were prepared according to a previously reported protocol. First, gallic acid and ammonia were put into $AgNO_3$ solution. As a result, Ag NP suspension was synthesized and called GA. As for the other suspension, $NaBH_4$ and sodium dodecyl sulfate (SDS) were put into $AgNO_3$ solution and called NB. EDS gel was placed into each prepared solution and filtered, washed and dried for the preservation of ethylenediamine. To further assess the role of the EDS gel in the formation of the AICS, 3-mercaptopropyl-funcionalized silica gel (MS gel) was prepared and used as a control.

3. Results and discussion

X-ray photoelectron spectroscopy (XPS) results revealed that the Ag in the silica gels existed in the ion cluster state. The XPS spectra of the Ag 3d peak [Fig. 1] revealed a positive oxidation state for the binding energy of Ag impregnated in EDS. An AIC was not formed during impregnation with other silica gels. The binding energy of the Ag^+ ion included in the EDS gel was different from its binging energy in $AgNO_3$ impregnated into MS gel. In the $AgNO_3$ impregnated into MS gel, Ag is considered to exist as Ag^+ ion state. Thus, in the case of $AgNO_3$ impregnated into MS gel, the Ag^+ ions formed an AIC and interacted with the amine (from ethylenediamine). Regardless of the precursor, the peak appeared upon the interaction of the EDS silica gel with the Ag^+ ion. However, this peak was not observed with other silica gels.

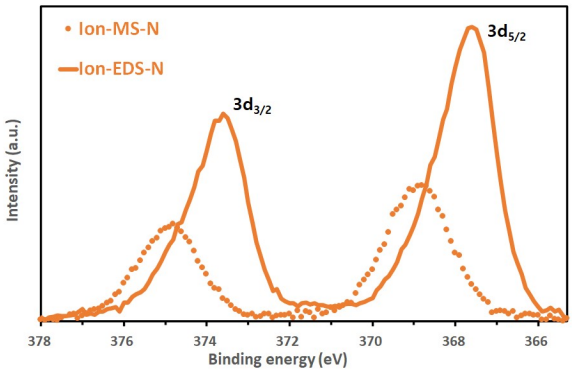

Figure 1: Ag 3d XPS spectrum of Ag^+ ion of $AgNO_3$ impregnated EDS gel (Ion-EDS-N) and Ag^+ ion of $AgNO_3$ impregnated MS gel (Ion-MS-N).

Furthermore, an increase in the absorption peak in the 360 nm region was attributed to the AICs. The obtained peak of AICs was also compared to that obtained in other studies and to a control group (mercaptopropyl functionalized silica gels, Ag^0, Ag^+ ion). In addition, Raman spectroscopy detected the effect of additives. The obtained AICs were stable even in the presence of oxygen owing to their interaction with ethylenediamines.

4. Summary

In this study, Ag^+ ion clusters (AICs) were obtained without the need of a reducing agent; ethylenediamine acted as a weak reducing agent, and Ag exhibited a high standard reduction potential. The obtained AICs remained stable upon their interaction with the amine and were characterized by various spectroscopic techniques.

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