Formation mechanism and surface property of exfoliated silica nano-plates

Nguyen Tran, Michael Wilson, Adriyan Milev, Gary Dennis, G S Kamali Kannangara

School of Natural Science, University of Western Sydney, Locked Bag 1797, Penrith South DC 1797, Australia

n.tran@uws.edu.au

Abstract. The silica nano-plates formed by exfoliation of the synthetic clay Lucentite in the poly(acrylic acid) aqueous solution has been examined using near edge X-ray adsorption fine structure (NEXAFS). Mg K - edge NEXAFS analysis shows that non surface (bulk) Mg ions were not chemically involved in the poly(acrylic acid)/clay intercalation, but were substantially involved in the exfoliation resulting in the silica nano-plates. During intercalation, O K - edge NEXAFS shows structural branches on the plate surfaces were formed. During exfoliation, these increased significantly. Si L3,2 - edge NEXAFS shows this occurred by migration of SiO4 groups within the exfoliated silica plates.

1. Introduction
Phyllosilicate clays consist of nano-plates of metal ions such as aluminium or magnesium in octahedral coordination with oxygen coordinated to one or more layers of tetrahedral silicate. The dimensions of height and length are approximately 1 and 100 nm or more which makes them nanomaterials. The preferential, face-to-face staking of these plates leads to formation of the regular van der Waals gaps or interlayer spaces with the average distance of 1 nm. The abilities to intercalate the spaces with nano-particles and polymers or delaminate (exfoliate) the stacked plates have opened up many opportunities in formation of nano-structured materials. Moreover further treatment to cause exfoliation produces silica nano-plates, which could be used as precursor for deposition of thin films via controllable, re-stacking process or as nano-fillers in nanocomposites [1,2].

Silica gel with usual pores can be formed via treatments of phyllosilicate clays with inorganic acids [3-7]. We have shown that an organic acid, namely poly(acrylic acid), can be used to form exfoliated silica nano-plates [8,9]. Here, we examine in more details the exfoliation mechanism and the surface property of the exfoliated plates.

2. Experimental
This work utilized Lucentite clay (Na0.33[Mg2.67Li0.33Si4O10(OH)2]), which consists of silicate nano-plates with the dimensions of height to length being approx. 1 : 300 nm. These silicate plates consist of the 2:1 structures in which, Mg ions remain within an octahedral layer, sandwiched between two layers of tetrahedral Si ions. Li may also replace some Mg ions in the octahedral framework, similar to that in Laponite clay [10]. Experiments leading to the poly(acrylic acid)/lucentite intercalation and
Lucentite exfoliation have previously been described [8]. The X-ray diffraction measurements have shown that reaction of the poly(acrylic acid) solution and clays at the temperatures of approx. 20, 30 and 60°C resulted in the intercalation, while reaction at 85°C resulted in the exfoliation or partial exfoliation. Products from these reactions are utilized here.

The NEXAFS measurements were carried out at the wide range beamline 24A (energy from approx. 10-1500 eV), NSRRC, Taiwan. Prior to the measurements, the samples were loaded into a UHV chamber (base pressure approx. 10^-9 mbar) using a conductive copper tape. The chamber was subsequently heated to approx. 200°C in order to minimize the adventitious surface contamination. The fluorescence yield absorption spectra were acquired at normal incident conditions. In particular, the sampling depth of the fluorescence yield L3,2-edge NEXAFS measurements of silica was estimated as 70 nm [11]. The resulting spectra were normalized using the standard spectrum recorded from a clean, gold grid reference.

3. Results
The Mg K-edge NEXAFS spectrum of Lucentite is in agreement with those previously reported for the clays, formed by alternating layers of tetrahedra and octahedra (Figure 1) [13]. According to the dipole selection rule, these spectra can simply be interpreted as due to the transitions of the Mg 1s electrons to the unoccupied 3p orbitals [14]. The Mg K-edge spectra of Lucentite and the intercalated product recovered after mixing an aqueous solution of poly(acrylic acid) and Lucentite at approx. 20°C are essentially identical, suggesting that the co-ordinated structures of Mg ions in the bulk remain virtually unchanged. The Mg K-edge spectrum of the exfoliated product recovered after mixing poly(acrylic acid) solution and Lucentite at approx. 85°C is not well-defined. These results support our previous FTIR data in which, the Mg ions within the bulk were not chemically involved in the intercalation, as they were substantially involved in the exfoliation.

Figure 1. Normalised Mg K-edge NEXAFS spectra of (A) Lucentite; (B) intercalated product and (C) exfoliated product. (Note that spectrum A and B overlap)

The O K-edge NEXAFS spectrum of the silica reference is interpreted as due to the electronic transitions from 1s to 2p orbitals [15-18] and the pre-edge peak at approx. 530-533 eV is interpreted as due to the surface branches (Figure 2) [19]. Thus, further analyses of the O K-edge NEXAFS allow some estimate of the differences in concentration of branch introduced between the intercalated and exfoliated structure. The degree of branching can be seen to increase from Lucentite to intercalated structures to exfoliated silica plates.

This is also supported by the Si L3,2-edge NEXAFS. Figure 3 shows the Si L3,2-edge NEXAFS spectra of the silica powder reference, Lucentite, the intercalated and exfoliated structures. The Si L3,2-edge spectrum of silica is in agreement with those previously reported [15-18, 20-23]. According to the density-of-state calculations, peaks A and B in the Si L3,2-edge spectrum is primarily due to the transitions of Si 2p electrons into the 4s empty orbitals, while peak C is due to the transition into the 4s and into the 3d empty orbitals [16-18]. In particular, peaks A and B in the Si L3,2-edge NEXAFS spectrum of the exfoliated silica plates are well-defined. This is interpreted as due to an increase in the
average crystallite size of the silica plates, as a result of the coupling of the individual tetrahedral layers during the plate formation [23].

Figure 2. O K - edge NEXAFS spectra of (A) Lucentite; (B) intercalated product and; (C) exfoliated product (note that A and B overlap). The spectrum of the silica reference is shown on the right.

Figure 3. Si L_{3,2} - edge near NEXAFS spectra of (A) Lucentite; (B) intercalated product and; (C) exfoliated product and (D) silica reference

Figure 4 summarizes the mechanism for the intercalation and exfoliation of Lucentite in poly(acrylic acid) into the tetrahedral structures of silica plates. First, branch concentration on the plate surfaces occurs (Fig 4B) followed by removal of the octahedral layers, then coupling of the remaining tetrahedral layers with reorganization of the SiO_4 groups to generate additional branches (Fig 4C).

Figure 4. (A) schematic showing the 2:1 tetrahedral/octahedral structures of silicate nano-plates within Lucentite. The triangular arrays represent the tetrahedral layers. The grey rectangular shapes between these arrays represent the octahedral layers formed by Mg/Li ions; (B) intercalation of the polymer fully extended chains within the interlayer spaces and formation of branches. The triangles not within the triangular arrays represent the branches; (C) exfoliation and increase of branch concentration on the surface of the exfoliated silica plates.

It has been suggested during treatments of clays with strong inorganic acids, the cations (eg Al^{3+}, Mg^{2+} etc) from the central octahedral layers are replaced by protons and sliding or rotation of the SiO_4...
units resulted in porous silica gel [3, 4]. The mechanism for the weak acid described here must be different since the nature and the surface property of the silica produced is clearly different.

4. Summary
The Mg K - edge NEXAFS spectra showed that the Mg ions within the octahedral layers are not chemically involved in the polymer/clay intercalation until exfoliation occurs. The O K - edge and Si L3,2 - edge NEXAFS spectra showed that the branch concentration occurred on the surface after intercalation but this become more significantly during exfoliation as coupling of the tetrahedral layers and reorganization of the SiO4 groups occurred.

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