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Atomically thin, large area aluminosilicate nanosheets fabricated from layered clay minerals

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HIGHLIGHTS

- Aluminosilicate nanosheets were fabricated by monolayer exfoliation of mica clay.
- Ultra high aspect ratio nanosheets with μm-scale lateral sizes were achieved.
- Exfoliated nanosheet showed significantly reduced band gap energy. ($E_g = 4.13$ eV).

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ABSTRACT

Two-dimensional (2-D) nanosheets, which have dimensions of atomically thin thickness with extremely high aspect ratio, have gathered great attentions due to their interesting properties and potential applications. Especially, some ceramic nanosheets including borides, carbides and sulfides became epitomes of novel functional nanomaterials since they exhibited unique electrical and surface properties distinguished from their bulk forms. In this study, atomically thin nanosheets of aluminosilicate oxides were fabricated via exfoliation of layered clay mineral, mica (muscovite; $KAl_3Si_3O_{10}(OH)_2$). To overcome the difficulties in exfoliations of large area nanosheets from mica, which has relatively strong interlayer bonding originated from layer charge, polymer assisted wet chemical method were applied. Amphiphilic polymer molecules were successfully intercalated into the ion exchanged muscovite particles to separate each layer. The resulting product possesses nanosheets with micrometer scale lateral sizes. The measured thicknesses of the nanosheets were mainly fell in two groups (1.2–1.7 nm and 2.2–2.7 nm) which correspond to the mono- and di-layer thichnesses of the muscovite with polymer adsorbates, respectively. The FT-IR and Raman results indicated that the adsorption of polymer molecules on the both surfaces of the aluminosilicate nanosheets significantly weaken or even break the interlayer bonding. Contrary to the highly insulating nature of bulk muscovites, the exfoliated nanosheets showed reduced bandgap energy which corresponds to semiconductor regime. The measured optical bandgap of the aluminosilicate ceramic nanosheets was 4.13 eV, which makes this ceramic nanosheet material a potential candidate for various electronic and electro-optic applications including wide bandgap semiconductors and photocatalysts.

1. Introduction

Two-dimensional (2-D) layers with atomic or molecular thickness have led to a surge of interest in a wide range of applications from electronics to electrochemistry [1,2]. The 2-D nanosheets could normally be obtained by either top-down or bottom-up approaches which are exfoliation of the layered crystals and monolayer growth utilizing precise deposition methods (CVD, ALD, etc), respectively. The top-down approach was quite successful when the layered crystals were formed by weak interlayer bonding while strong covalent bonding is associated between the atoms in each layer [3–9]. However, it has been challenging to mechanically exfoliate monolayer oxide sheets from the layered clay minerals due to the relatively strong electrostatic bonding force which is originated from the nature of layer charge [10,11].

Muscovite; $KAl_3Si_3O_{10}(OH)_2$ is a representative form of mica, a layered clay mineral comprised with negatively charged

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aluminosilicate layers and potassium interlayer cations. As a consequence of isomorphic substitutions of Si^{4+} ions by Al^{3+} ions in the muscovite, each aluminosilicate layer has negative layer charge of $2e^-$ in the half unit cell. For that reason, the potassium cations are tightly locked in the muscovite interlayers by the strong electrostatic forces between them [12,13]. Several works have been reported concerning the cation exchange to remove the potassium cations. White reported that potassium cations could be partially removed by molten salt reaction with lithium nitrate [14]. Zhao et al. found that the interlayer spacing of the muscovite could be expanded by the cation exchange process [12]. Ion exchange with large-chain cations also showed possibility to pillar the interlayer and significantly increase the spacing [15]. Yu et al. reported that the alkylammonium cations were uniformly anchored on the surface of aluminosilicate layers thereby further increase in the interlayer spacing was achieved [16–18]. Jia et al. also found that octadecyl trimethyl ammonium chloride (OTAC) also could be intercalated into the interlayer of muscovite and thereby yielded muscovite monolayers [19,20]. But the resulting exfoliated nanosheets were still in the level of tiny fragments. Lateral sizes of them were mostly smaller than 100 nm. Recently, Harvey et al. have reported that surfactants could successfully promote the exfoliation of layered silicates without chemical pretreatment through a liquid phase exfoliation (LPE) process (sonication in a surfactant solution followed by centrifugation). The average thickness of the nanosheets was 2.37 nm, which corresponds to the thickness of a few layers of the layered silicate. However, the size of the exfoliated nanosheets were still quite small with lateral sizes in sub micrometers [21]. For the practical applications of ceramic nanosheets, it is anticipated to develop more effective way to exfoliate large area 2-D nanosheets from layered oxides.

Here, we attempted to investigate the possibility to exfoliate muscovite by using amphiphilic polymer (Poly (vinylpyrrolidone); PVP), not using ionic polymers. The PVP molecules contain strong hydrophilic components (the pyrrolidone moiety) and a considerably hydrophobic group (the alkyl group). Generally, PVP has been commonly used as a dispersant for colloidal solutions that could prevent the aggregation of colloidal nanoparticles through steric hindrance effect [22]. For the muscovite exfoliation, this amphipathic PVP polymer was introduced for two roles. One is the exfoliation through bonding between carbonyl groups on the pyrrolidone moiety in PVP molecules and hydroxyl groups on the surface of the muscovite. The other is to prevent self-aggregation of exfoliated nanosheets through the repulsive forces stemming from hydrophobic polyvinyl chains that stretch towards solvents. In this work, we demonstrate that muscovite can be exfoliated in aqueous solutions through the presence of amphiphilic polymer without repetitive ion exchange. Also, aluminosilicate nanosheets with relatively large-scale can be obtained from this amphiphilic polymer without agglomeration.

2. Experimental

2.1. Materials and methods

The muscovite powder (IMERYS, USA, average particle size: 30 μm) was heat-treated at 750 °C for 5 h in a muffle furnace (C-14, Hantech Co., Ltd.). The heat-treated muscovite powder was subjected to molten salt reaction with $LiNO_3$ (Sigma-Aldrich Prod. No. 227986) at 300 °C for 48 h. The resulting products were washed with deionized water and isolated by centrifugation in a Labogene 1248 centrifuge with a fixed-angle rotor (GRF-G-85-6) for 15 min at 7870.72 × g. The washing and centrifugation steps were repeated for the residue of Li-species to be sufficiently removed. The samples collected after the Li-ion exchange process were named Li-the number of process cycle-M (muscovite). Polymer intercalation and exfoliation steps for the Li-substituted muscovite powders were done in the PVP aqueous solution (0.8×10^{-3} M, MW: 40000; PVP40 Sigma-Aldrich) by vigorous stirring for 24 h. The exfoliated nanosheets were obtained from the sediments in centrifugal tube after the centrifugation. Washing and this centrifugation process were repeated 5 times to eliminate the excessive polymers. The exfoliated nanosheet samples were named as PVP-the number of Li exchange cycle-M sheets.

2.2. Measurements

Langmuir-Blodgett (LB) deposition method (KSV NIMA L & LB Troughs) was employed to transfer the exfoliated nanosheets on quartz substrates to form muscovite monolayer film with uniform distribution. The surface pressure at the air-water interface confirmed by the π-area isotherm was $10\,mN\,m^{-1}$ for the stable monolayer formation of the nanosheets on the surface treated quartz substrate.

Powder X-ray diffraction system (Rigaku Ultama IV XRD) with Cu Kα radiation (λ = 0.15405 nm) over the 2θ range of 3-60° was used to characterize the crystal structure and a degree of swelling of Li ion exchanged muscovite. Field Emission Scanning Electron Microscope (SEM, JSM-7100F (JEOL)) with Energy Dispersive Spectroscopy (EDS) was employed for microstructure and element analyses for the samples. Raman spectroscopy data were collected using Lab Ram ARAMIS (Horiba), with an excitation laser wavelength of 532 nm (ND: Yag laser) and operating power of 5 mW. Middle-infrared ($4000 - 650\,cm^{-1}$) transmission spectra were collected with a Cary 670 (Agilent) FT-IR spectrometer with ATR accessory (ZnSe, Ze crystal). Precise measurements for the nanometer scale thickness of the exfoliated aluminosilicate nanosheets were done by atomic force microscopy (AFM) in the non-contact mode using a XE-100 (Park systems). The UV–vis transmittance spectra were measured on Ultraviolet visible spectrophotometer (UV-3600 Shimadzu) at room temperature under ambient conditions. From the obtained transmittance measurement, the absorption edge was determined using Tauc plot [23]. The optical absorption coefficient is defined as;

$$\alpha(h\nu) = A(h\nu - E_g)^n \tag{1}$$

where $h\nu$ is the incident photon energy, A is a constant, E_g is the optical band gap of the material and n is either 2 for indirect band transitions or 1/2 for direct band transitions. The absorption coefficient can also be determined by the following relation:

$$\alpha = \{1/t\}ln\{T/(1 - R)^2\} \tag{2}$$

where T is the transmittance, R is the reflectance and t is the thickness of the film.

For the XRD, SEM-EDS, FTIR and Raman analyses, powder samples were dried in the oven at 120 °C for 24 h. Thin film samples for AFM, SEM and UV–vis analyses were prepared by Langmuir-Blodgett method on silicon and glass substrates.

3. Results and discussion

The overall exfoliation procedure of the 2-D aluminosilicate nanosheets is schematically illustrated in Fig. 1. Pristine muscovite was heat-treated to remove inherent hydroxyl crosslinking between aluminosilicate layers and potassium cations in the layered muscovite structure. The heat-treated muscovite was subjected to a molten salt reaction with $LiNO_3$. It is known that small Li cations are able to occupy octahedral sites in the muscovite layers by this molten salt reaction [14]. The Li cations are believed to compensate the negative layer charge, consequently reduce the strong electrostatic forces between layers. The interlayer space expansion by this molten salt reaction could be confirmed by XRD analysis.

Fig. 2(a) shows the XRD patterns of pristine and Li doped muscovite by the repeated $LiNO_3$ molten salt reaction cycles. XRD spectrum of pristine muscovite was identified as the monoclinic potassium aluminum silicate hydroxide phase with lattice constants of a = 0.52 nm, b = 0.9021 nm, c = 2.007 nm and $\beta = 95.7°$ and with the space group ($C2/c$) (JCPDS no. 84–1302). Muscovite is alternately composed of