



Quantitative determination of isomorphous substitutions on clay mineral surfaces through AFM imaging: A case of mica



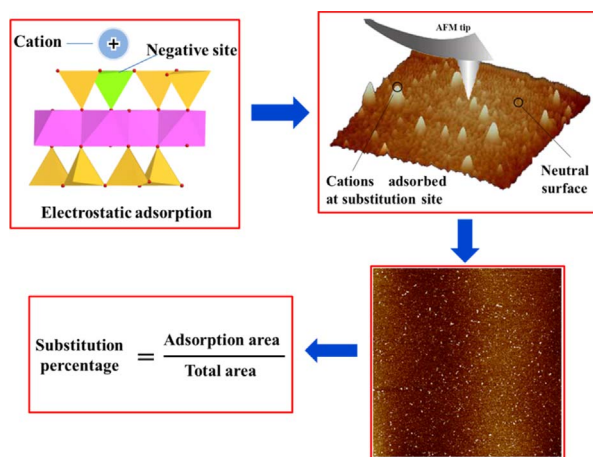
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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a method for the quantitative determination of isomorphous substitutions on clay mineral or nanosheet surfaces has been presented in order to provide accurate, reliable and quantitative information for the isomorphous substitutions on clay mineral surfaces. It was based on the selective adsorption of a specific organic ion (benzyltrimethylammonium ions, BTMA⁺) on the substitution sites on clay mineral surfaces, and the atomic force microscopy (AFM) imaging of the adsorption. The adsorption behaviors of BTMA⁺ at the substitution sites were verified by molecular dynamic simulations. By means of an image processing software, the AFM images could be analyzed and the areas as well as area percentages of the substitution sites on the clay mineral surfaces could be determined. The case of mica, one kind of clay minerals, was showed for example in this study.

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1. Introduction

Since graphene was first prepared by Novoselov and Gein et al. [1] through mechanical exfoliation of highly oriented pyrolytic graphite (HOPG), significant interests have been attracted to prepare two-dimensional (2D) or nanosheet materials from layered minerals, such as graphite, molybdenum disulfide and clay minerals. Graphene exfoliated from graphite was supposed to be the most promising 2D material for its extraordinary properties such as supreme mechanical stiffness [2], large specific surface area [3], and high electrical as well as thermal conductivity [4,5]. Monolayer or few-layer MoS₂ has also shown good potential applications in nanoelectronics, optoelectronics, spintronic and valleytronic devices [6], it has also been proved to be an efficient adsorbent for heavy metal removal recently [7]. As for clay minerals, increasing attention is drawn to the newly developed 2D materials since clay nanosheets are more and more widely applied in composite materials [8]. For example, in the field of flame retardant materials, layered silicates have been added to polymeric materials for flame retarding purpose, the nanocomposite structure was collapsed at high temperature, and then the clay platelets become free to migrate thus to form a thermal insulation and low permeability superficial clay-rich char which significantly reduces the heat release rate and slowed spread of fire [9–11]. In terms of electrode materials, the use of exfoliated 2D clay nanosheets in electrode materials shows a huge discharge capacity and excellent rate characteristics [12]. As for the biomedical fields, the ion exchange nature and biocompatibility of clays make them versatile carriers for many vital drugs. Therefore, clay nanocomposites as drug delivery systems have been developed to improve the temporal and spatial presentation of drugs in the body, to protect drugs from physiological degradation or elimination, to improve patient compliance, and to enhance quality control in the manufacturing of drug products [13].

By this token, clay minerals are playing an increasingly important role in nanocomposites for the remarkable property improvements in comparison with the normal microscopic counterparts, such as nanometer thickness, extraordinary high surface area and ease by which they can be hybridized by polymers or ions to form new composites [14]. However, in the aspect of mineralogy, lattice defects such as isomorphous substitution present in the clay or nanosheet surface are known to significantly affect clay property [15]. Generally, clay minerals are composed of silica tetrahedron (T) and alumina or magnesia octahedral sheet (O) and form the TOT layer structure (or 2:1 layer) or the TO layer structure (or 1:1 layer) [15], Shown in Fig. 1. The resulting structure surfaces can be either electrically neutral or negatively charged. The neutral siloxane surfaces, where no isomorphous substitution occurred (e.g., talc, pyrophyllite and the Si-tetrahedral side of 1:1 kaolin), are the least reactive surface found on clay minerals [16]. When Al substitutes for Si, negative charge, polar and hydrophilic sites are introduced onto the siloxane surface. Since it determines the surface electrical property, surface polarity, surface free energy, wetting behaviours and so on, the isomorphous substitution will affect the interactions between nanosheet of clay and polymer while prepare clay/

polymer nanocomposite [11]. A high degree of isomorphous substitution means a more hydrophilic and stronger electronegative surface, thus the clay sheet and polymer are connected mainly by electrostatic interaction. A low degree of substitution implies the hydrophobic surface and the hydrophobic interaction plays the dominant role. As a result, a comprehensive understanding of the distribution and degree of substitution sites on clay nanosheet surface reveal the distribution of reactive sites and the quantity of polymers which will interact with those reactive sites. Namely, the information of substitution sites can be used as predictors of the polymer/clay interactions. However, little studies have been reported to study the quantitative determination of the isomorphous substitutions on clay mineral surfaces in our knowledge scope.

Considering that the substitution sites are negatively charged while the siloxane surfaces are neutral charged, cations may adsorb at these sites by electrostatic adsorption selectively. Therefore, the adsorption sites can be used as an indicator of the isomorphous substitution sites. Meanwhile, Atomic force microscopy (AFM) has become a powerful tool for the study of surface morphology in nanoscales. Accordingly, the adsorption of ions on clay nanosheet surfaces might be directly observed through AFM imaging, allowing the marking of the region of the substitutions areas. The marked regions in the AFM images could be analyzed by using an image processing software [17], thus to obtain the exact area of the substitutions areas. As the total area of the nanosheet surfaces can also be obtained from the AFM image processing, the percentage of substitutions areas can be easily determined. In other words, the quantitative determination of isomorphous substitutions on clay nanosheet surfaces might be realized through the selective adsorption of one special cation ion on the surfaces, AFM imaging and image processing. Fig. 2 shows the schematic diagram of this method for determining the isomorphous substitutions.

In this work, an attempt was made to verify the hypothesis mentioned above, in which benzyltrimethylammonium ions (BTMA⁺) was used as the cation ion for the adsorbate. The objective of this work was to put forward a method for the quantitative determination of isomorphous substitutions on clay or clay nanosheet surfaces, which are of great significance for fully understanding clay mineral and preparing the clay/polymer nanocomposites.

2. Experiments

2.1. Materials

The mica sample used in this work was from China, Fig. 3 displays the X-ray diffraction (XRD) pattern of the sample, it shows that mica materials are composed of muscovite and polyolithionite, both belong to mica family, indicating that the sample is high-purity mica.

Benzyltrimethylammonium bromide [$C_6H_5CH_2N^+(CH_3)_3Br^-$] referred to as BTMA⁺, was obtained from Sinopharm Chemical Reagent Co., Ltd, China and of analytical pure grade.

All the water used in this work was ultrapure water distilled and deionized by Millipore Super Q system (Millipore, America) with the

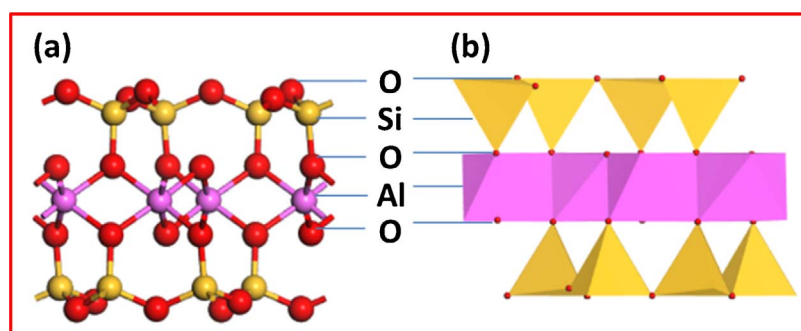


Fig. 1. TOT layer (or 2:1 layer) structure.

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