Electronic Supplementary Material for PCCP

Electronic Supplementary Information

Preparation of Langmuir-Blodgett Films of Aligned Sepiolite Fibers and Orientation of Methylene Blue Molecules Adsorbed on the Film

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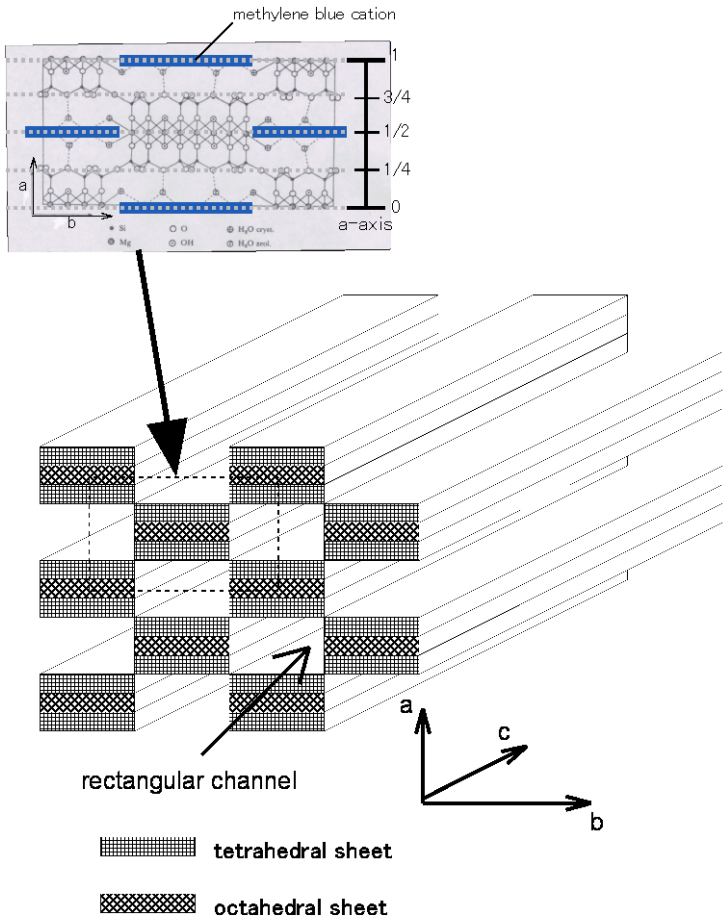
[A] In order to demonstrate that methylene blue (MB^+) cation can enter the channel of sepiolite, the powder XRD pattern of the MB^+-adsorbed sepiolite was measured. The basic idea is that, if MB^+ is present in the channel of the sepiolite in regular order, the relative peak intensities in the diffraction pattern will be changed from those in the pattern of sepiolite (without MB^+). On the contrary, if the cationic dye is adsorbed on the external surface of sepiolite, the pattern will be unchanged. For comparison, the XRD patterns of the rhodamine 6G cation ($R6G^+$)-adsorbed sepiolite and polycrystalline methylene blue (chloride) were measured. The cationic dye of $R6G^+$ can not enter the channel of sepiolite because of its large size.

The dye (MB^+ or $R6G^+$)-adsorbed sepiolite samples were prepared as follows. Sepiolite (0.2 g) was suspended in the aqueous solution of each dye at $1x10^{-3}$ mol dm^{-3} (100 ml), and the suspension was ultrasonicated for 60 min. The suspensions were left standing for 4 days. Then, each of the dye-adsorbed sepiolite was separated from the supernatant by suction. After being washed with a little amount of water, the samples were dried under the ambient condition.

The XRD patterns of sepiolite, MB^+/sepiolite, and $R6G^+$/sepiolite are given in the main text as Figure 10, together with the interpretation of the XRD data. These XRD results clearly show that MB^+ cation is able to be present in the channel of sepiolite in regular order. On the other hand, $R6G^+$ cation, the size of which is larger than the size of the channel, is not present in the channel but adsorbed on the external surface of sepiolite.

In our opinion so far, the reason for the enhancement of the (400) peak in the XRD pattern of the MB^+-adsorbed sepiolite is that the MB^+ cations would occupy the channel as the long-axis of MB^+ is parallel to the c-direction (channel direction) and the molecular plane is parallel to the b-c-plane. As a result, the diffraction intensity of the (400) peak would be enhanced as illustrated in the following figure.



[B] It is necessary to show that electronic spectra of MB^+ adsorbed on a randomly aligned sepiolite film should not be dependent on the polarization direction of the incident light. We prepared a cast film of sepiolite; some drops of the sepiolite dispersion were put on a glass substrate and dried under the ambient atmosphere. Needless to say, the fiber alignment in the film was completely random. After being dried, MB^+ was adsorbed onto the film by immersing the film in the aqueous dye solution for a few days. Then, the film surface was rinsed with water slightly. The polarized spectra of the film were given below. The measurements were carried out in the same way as that applied to the film samples in this work (Fig. 11); after one measurement (spectrum (a) in the figure below), the sample was rotated by 90 degrees, and then the other spectrum (spectrum (b) in the figure below) was recorded. A little difference is observed between the spectra (a) and (b), which would be caused by the irregularity in the cast film (upon the rotation, the measured point differed from the first measured point). In comparison with the polarized spectra shown in Fig. 12 in the main text, the spectra of the cast film indicate the random orientation of MB^+. In other words, the spectra of the cast film are independent of the polarization direction.

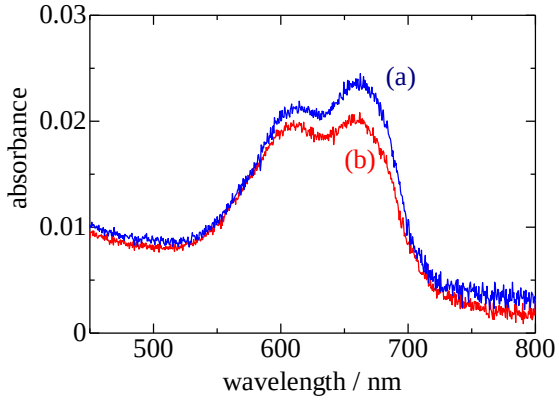


Fig. Polarized electronic spectra of MB^+ adsorbed on a cast film of sepiolite (before and after 90°-rotation).