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Theoretical study on mechanism of mesoporous TiO₂ synthesis by multi-scale computational methods

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【Introduction】

Surfactant-template synthesis has gathered a considerable attention because this method has been used to form a variety of mesoporous materials, which could find applications in catalysis, membrane and separation technology, and molecular engineering.

Ionic surfactants self-assemble into micelles, and organize inorganic materials into a variety of mesoporous forms through the mediation of electrostatic, hydrogen-bonding, covalent and van der Waals interactions. This process is composed of both physical and chemical interactions, which is not possible to be simulated only using traditional classic molecular dynamics (MD) simulation, and also because of its large scale, the systems can not be studied using *ab initio* quantum chemical methods. In this study, multi-scale computational approaches, which are developed in our laboratory, were successfully used to simulate the formation of Cetylmethylammonium Bromide (CTAB) cylindrical micelle and organization of TiO₂ on the micelle surface.

【Method】

“New-Ryudo” program, a molecular dynamics simulator developed in our laboratory, was used to simulate the formation of cylindrical micelle structure of CTAB molecules and organization of TiO₂ on the micelle surface. We introduced a new function to stochastically deal with chemical reaction within the scheme of classical molecular dynamics. Equilibration and MD simulation of systems were performed using CVFF force field. For detailed reaction mechanism study, we employed our original tight-binding quantum chemical molecular dynamics program “New-Colors”.

【Results and discussion】

Under the experimental conditions, our “New-Ryudo” program was successfully performed on the study of organization of TiO₂ on the CTAB micelle surface. Initial structure composed by micelle surface of 9 CTAB molecules, 64 water molecules, 8 TiO²⁺ and 8 SO₄²⁻ ions to represent ionic state TiSO₄ in water solvent. After 12.5 ps MD simulation, the system was equilibrated, as shown in Fig. 1A. The next 2.5 ps simulation was performed to simulate the reaction process in forming TiO₂ solid phase. The final structure is shown in Fig. 1B. The results clearly showed the formation of hydrated Ti(IV) oxide coordination complexes and oxygen bridge formed between these complexes. The simulation is in good agreement with the reaction mechanism obtained from previous experiments, indicating that our program is certified to simulate chemical reaction in large scale systems. Meanwhile, a smaller system including TiO²⁺, SO₄²⁻ and water molecules was truncated from the equilibrated system, a quantum chemical molecular dynamics simulation was performed on the system to study the formation reaction mechanism of TiO₂ solid state. We observed also a structure of the hydrated Ti(IV) oxide coordination complex; bond population analysis provided a strong evidence for the coordinate covalent bond formation between Ti and water molecules. The details of these studies will be presented in the conference.

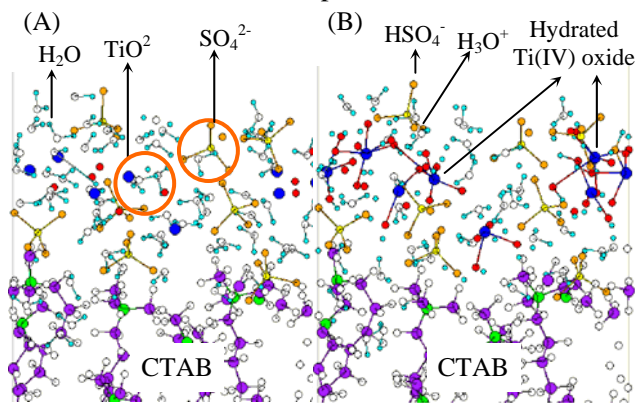


Fig. 1 MD simulation of TiO₂ organization on CTAB micelle surface: (A) equilibrated system after 12.5 ps MD simulation and (B) final structure after 15.0 ps MD reaction simulation.