Preparation of Coordination Polymer Glasses Encapsulating Metal Complex Catalysts

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Coordination polymers (CPs) are crystalline compounds composed of metal ions and bridging ligands. Recent reports indicate that several CPs transform to a glassy state by a melt-quench process[1]. A typical example is a coordination polymer composed of zinc (II) ions, (di)hydrogen phosphate ions, and imidazolium ($[Zn^{II}(HPO_4)(H_2PO_4)_2](ImH_2)_2$ (ZnPIm, Im = imidazolate) (Fig.1-a). The amorphous nature of ZnPIm glass resulted in the enhancement of proton (H^+) conductivity than ZnPIm in the crystalline state due to the highly flexible nature of imidazole and (di)hydrogen phosphate ions[2].

In addition, crystal-glass transformation of CPs via melt-quenching offers diverse accessibility to unique processing abilities and properties by using immobilized guest molecules. Such an immobilization technique can be applied to the heterogenization of metal complex catalysts. The interaction between metal complex catalysts and organic ligands liberated in the vitrification process results in facile immobilization of the catalysts in CP glasses, resulting in the heterogenization of the catalysts with high durability.

Herein, we prepared a film of ZnPIm glass containing iron(III) 5,10,15,20-tetraphenyl-21H,23H-porphyrin (Fe^{III}(TPP)) ion via a melt-quenching process. The films supported on slide plates have a smooth surface and thickness of 3-9 μm (Fig. 1-b). Fe^{III}(TPP) was stably immobilized in the ZnPIm glass by the coordination of imidazolate liberated from ZnPIm frameworks during the melt-quench process. The films exhibited catalytic activity for the carbon dioxide reduction under the visible-light irradiation by taking advantage of electron-donation to the active Fe^{III} site by imidazolate. The ZnPIm glass film with a thickness of 9 μm exhibited three-times higher activity than those of 3 μm, indicating that CO_2 molecules efficiently access Fe^{III}(TPP) immobilized in the subsurface of ZnPIm glass film.

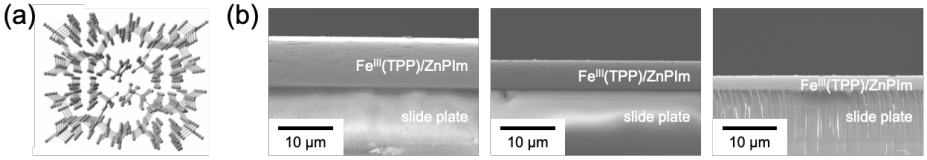

Fig. 1 (a) Crystal structure of ZnPIm and (b) scanning electron microscope (SEM) images from the side of ZnPIm glass containing Fe^{III}(TPP) with thickness of 9 μm (left), 7 μm (middle), and 3 μm (right).

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