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Preparation of highly dispersible metal oxide nanoparticles without hydrocarbon components using a superacid catalyst and their hybridization with organic polymers

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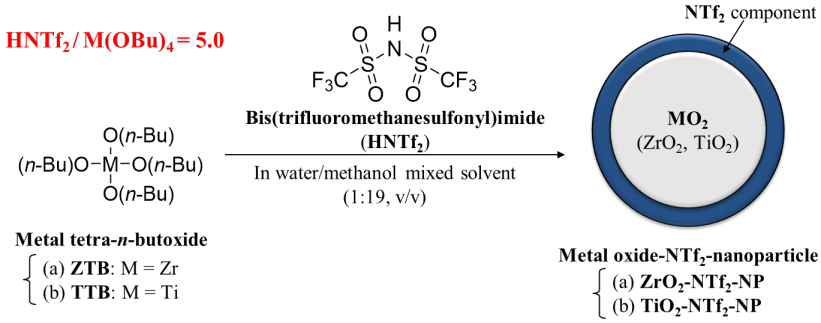
Abstract

The dispersion of metal oxide nanoparticles, such as zirconium oxide (ZrO_2) and titanium oxide (TiO_2) nanoparticles, is an important topic for their applications, particularly the formation of transparent organic-inorganic hybrid materials with high refractive indices. To prepare transparent hybrid materials composed of polymers and metal oxide nanoparticles, metal oxides are required to disperse well (nanoscale) in various media because interface scattering between organic and inorganic components are suppressed in hybrid materials. So far, as dispersants for these metal oxide nanoparticles, silane coupling agents,[1] surfactants,[2] and organic phosphonate[3] are often used. In addition, we have also reported the preparation of the highly water-dispersible ZrO_2/silsesquioxane and TiO_2/silsesquioxane hybrid nanoparticles by the two-stage sol-gel reactions.[4] However, dispersants for the metal oxide nanoparticles reported so far contain hydrocarbon components, which may cause problems in UV resistance.

In this study, we successfully prepared highly dispersible ZrO_2 nanoparticle (**ZrO_2-NTf_2-NP**) and TiO_2 nanoparticle (**TiO_2-NTf_2-NP**) without hydrocarbon components by the simple sol-gel reaction of zirconium tetra-*n*-butoxide (ZTB) and titanium tetra-*n*-butoxide (TTB), respectively, using water/methanol mixed solution of a superacid bis(trifluoromethanesulfonyl)imide ($HNTf_2$) (**Scheme 1**).[5] **ZrO_2-NTf_2-NP** was dispersed well in organic solvents, such as acetone, ethanol, methanol, DMF, and DMSO, as well as water, whereas **TiO_2-NTf_2-NP** was dispersed well in organic solvents, such as acetone, DMF, and DMSO, as well as water, which were confirmed by visual observations and UV-Vis measurements. The particle sizes of **ZrO_2-NTf_2-NP** and **TiO_2-NTf_2-NP** estimated by DLS measurements were *ca*. 3-4 nm and 5-6 nm, respectively. In addition, these metal oxide nanoparticles were possible to repeat precipitation of the solid product and dispersion in the solvents. Furthermore, hybrid films of PMMA and **ZrO_2-NTf_2-NP** were prepared by drying the diethylene glycol dimethyl ether/acetone mixed solution of the mixtures of these materials. The PMMA/**ZrO_2-NTf_2-NP** hybrid films with any compositional ratios were highly transparent.



Scheme 1. Superacid-catalyzed preparation of highly dispersible (a) zirconium oxide nanoparticle (**ZrO_2-NTf_2-NP**) and (b) titanium oxide nanoparticle (**TiO_2-NTf_2-NP**) without hydrocarbon components.

References

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