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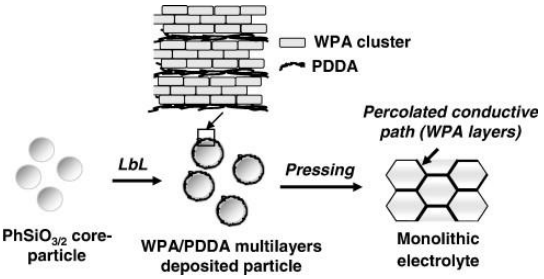
Research keywords: Organic-inorganic hybrid materials, Sol-gel method, Hydrothermal process, Supramolecular assembly, Layer-by-layer assembly, Bioinspired materials, Structurally colored materials, Nanoparticles, Theranostic materials, Photocatalysts, Mixed-anion compounds, Metal oxynitrides, etc.

Heteropolyacid-based composites for proton conductors



Thermally and chemically stable phenylsilsesquioxane ($PhSiO_{3/2}$) particles were prepared by sol–gel process, and ultra-thin layers of oppositely charged poly(diallyldimethylammonium chloride) (PDDA) and dodecatungstophosphoric acid (WPA) were alternately deposited on the negative-charged $PhSiO_{3/2}$ particles via layer-by-layer (LbL) assembly technique. Hygroscopic property of WPA was remarkably reduced owing to the formation of PDDA/WPA complex. The amount of WPA adsorbed on $PhSiO_{3/2}$ particles was estimated to be ~ 0.03 (g/g $PhSiO_{3/2}$). Transparent and monolithic pellet can be obtained from the resultant core–shell particles by pressing. Proton conductivity of WPA-deposited samples increased about 4 orders of magnitude compared with unmodified samples, and reached to about 10^{-4} S/cm at 80 °C and 80% relative humidity [1].

Next, cesium salts of Cs_2SO_4, Cs_2CO_3 and $CsHSO_4$ and WPA were mechanically milled to synthesize chemically durable WPA composites. The X-ray diffraction patterns of composites suggested the formation of partially substituted $Cs_xH_{3-x}PW_{12}O_{40}$ composites after milling at 720 rpm for 10 min. Proton conductivities under both humidified and dry conditions of the resultant composites markedly improved. The proton conductivities strongly depended on the type of cesium salt. The hydrogen bonding distance *L* in the frame structures of the composites was estimated from the ^{1}H-isotropic chemical shift. The proton conductivities in dry conditions of $WPA{\cdot}6H_2O$ and the composites were strongly represented to *L* [2].

[1] Y. Daiko, K. Katagiri, K. Shimoike, M. Sakai, A. Matsuda, *Solid State Ionics*, **178**, 621 (2007).

[2] Y. Daiko, H. Takagi, K. Katagiri, H. Muto, M. Sakai, A. Matsuda, *Solid State Ionics*, **179**, 1174 (2008).