LAYER-BY-LAYER ASSEMBLY OF {NANOCLAY-(SOL-GEL OXIDE)}$_N$ AND {NANOCLAY-(OXIDE NANOPARTICLE)}$_N$ MULTILAYERS

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Introduction

Decher and co-workers developed a layer-by-layer (LbL) assembly method to synthesize polyelectrolyte multilayers in 1990s.[1] This method forms multilayers through alternative adsorption of positively and negatively charged species from solutions. Since then, a wide variety of multilayers have been synthesized with this LbL technique using various building units, where polyelectrolytes or polymers are usually used to "glue" the structures. In particular, nanoclay-polymer multilayers with excellent mechanical properties have been made.[2,3] Before this study, only several all-inorganic multilayers had been made via LbL assembly of oppositely charged nanoparticles (NP).[4] In this study, we synthesized, for the first time, two new classes of all-inorganic multilayers: {nanoclay-(sol-gel oxide)}$_n$ and {nanoclay-(oxide NP)}$_n$.

Experimental, Results and Discussion

Small pieces of Si/SiO_2 wafers were cleaned and used as substrates. To make {nanoclay-(sol-gel oxide)}$_n$ multilayers, a sodium montmorillonite (MMT) clay and a zirconium (IV) acetate hydroxide powder were purchased to make exfoliated MMT suspension and sol-gel ZrO_2 precursor, respectively. The sodium MMT suspensions (nominally 0.5 wt. % MMT) were first vigorously stirred for a week and then settled for 24 hours before supernatants were collected.[3] Aqueous sol-gel ZrO_2 precursors were prepared by dissolving zirconium acetate hydroxide into deionized water and mixing by 20 minutes ultrasonication. A computer-controlled programmable dip coater (Nima Technology Ltd.) was used to perform the LbL deposition. The synthesis protocol for making {MMT_x-(sol-gel ZrO_2)}$_n$ multilayers consists of four dipping steps: a substrate was dipped into a precursor solution, a MMT suspension, and then deionized water twice. These four steps make up one deposition cycle. Most specimens were prepared with 30 deposition cycles, resulting in {MMT-(sol-gel ZrO_2)}$_{30}$ multilayers. The substrate dipping and withdrawing speeds were kept at a fixed value of 20 mm per minute. The substrate was allowed to hold in air stagnatically between two adjacent dips. Holding was also used in the precursor solution, MMT suspension, and deionized water. Typical holding durations of 45 seconds and 1 minute in the MMT suspension and water, respectively, were adopted. After completing the desired deposition cycles, all specimens were air dried and then characterized. Selected specimens were further annealed isothermally to dehydrate and remove residue acetate groups. Typical as-deposited multilayers are shown in Fig. 1, and further details about the synthesis methods and multilayer character have been reported elsewhere.[5,6]

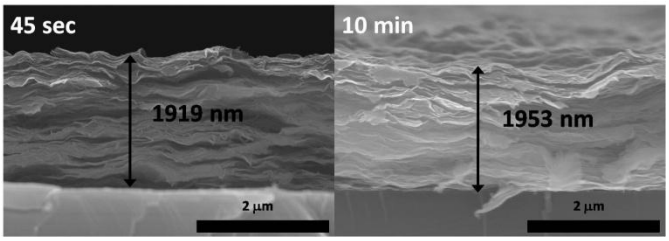

Fig. 1. Representative cross-sectional SEM images of {MMT-(sol-gel ZrO_2)}$_{30}$ multilayer synthesized (Holding time in air are labeled). See Ref. 5 for more details.

In the next step, we further made three variants of multilayer "plate-ball" nanostructures, which represent increasing complexity; schematics of these three targeted structures, along with representative SEM images of the actual multilayers made in this study, are shown in Fig. 2. To make these structures, CeO_2 (< 25 nm) and anatase TiO_2 (< 25 nm) NP were used. Approximately 0.0225 g NP were dispersed into 75 ml deionized water to prepare a 0.03 wt. % NP suspension. The suspension was stirred for 20 minutes with a magnet, and ultrasonicated for 20 minutes. NaOH or HCl was added into the suspension to change the pH. The suspension was further ultrasonicated for 20 minutes before usage. These NP suspensions are used together with the sol-gel ZrO_2 precursor and the exfoliated MMT suspension for LbL electrostatic assembly of the three variants of multilayers, as shown in Fig. 2.

Variant I, a {MMT_x-(CeO_2 NP)}$_n$ multilayer, was prepared by repeating the following four steps periodically: (1) A substrate was dipped into a CeO_2 suspension (pH = ~ 2.38 so that CeO_2 NP are positively

charged; point of zero charge or PZC of CeO_2 = 8.1) and held for 10 minutes; (2) the substrate was rinsed in deionized water for three times (in three beakers) for 2, 1, and 1 minute, respectively; (3) the substrate was dipped into a MMT suspension (with negatively charged MMT) and held for 45 seconds; and (4) the substrate was rinsed twice in deionized water (in two beakers; 1 minute each). A representative SEM image is shown in Fig. 2(I).

Variant II, a $\{MMT_x\text{-}(CeO_2\text{-}TiO_2)_2\text{-}CeO_2$ NP$)\}_n$ multilayer, was made via LbL assembly of five "layers" of NP ($CeO_2^{(+)}$-$TiO_2^{(-)}$-$CeO_2^{(+)}$-$TiO_2^{(-)}$-$CeO_2^{(+)}$) with alternating charges between two MMT layers in each repeating unit of the multilayer. This is achieved by five dips in positively charged CeO_2 or negatively charged TiO_2 suspensions in a sequence. We controlled the pH of both NP suspensions to be ~ 7 so that CeO_2 (PZC = 8.1) NP are positively charged but TiO_2 (PZC = 5.9) NP are negatively charged. A representative SEM image is shown in Fig. 2(II), the total thickness of five NP layers is about 80 nm, which agrees well with the targeted structure.

Finally, we made the Variant III by replacing the MMT_x layers in Variant II with thicker and stiffer $\{MMT_x$-(sol-gel $ZrO_2)\}_n$ multilayers. A representative SEM image is shown in Fig. 2(III). While Variants I & II have good in-layer and normal-to-layer permeability, Variants III has limited normal-to-layer permeability but good in-layer permeability, enabling potentially applications as multi-channeled sensors. Variants III are also likely stronger and stiffer than the other two variants.

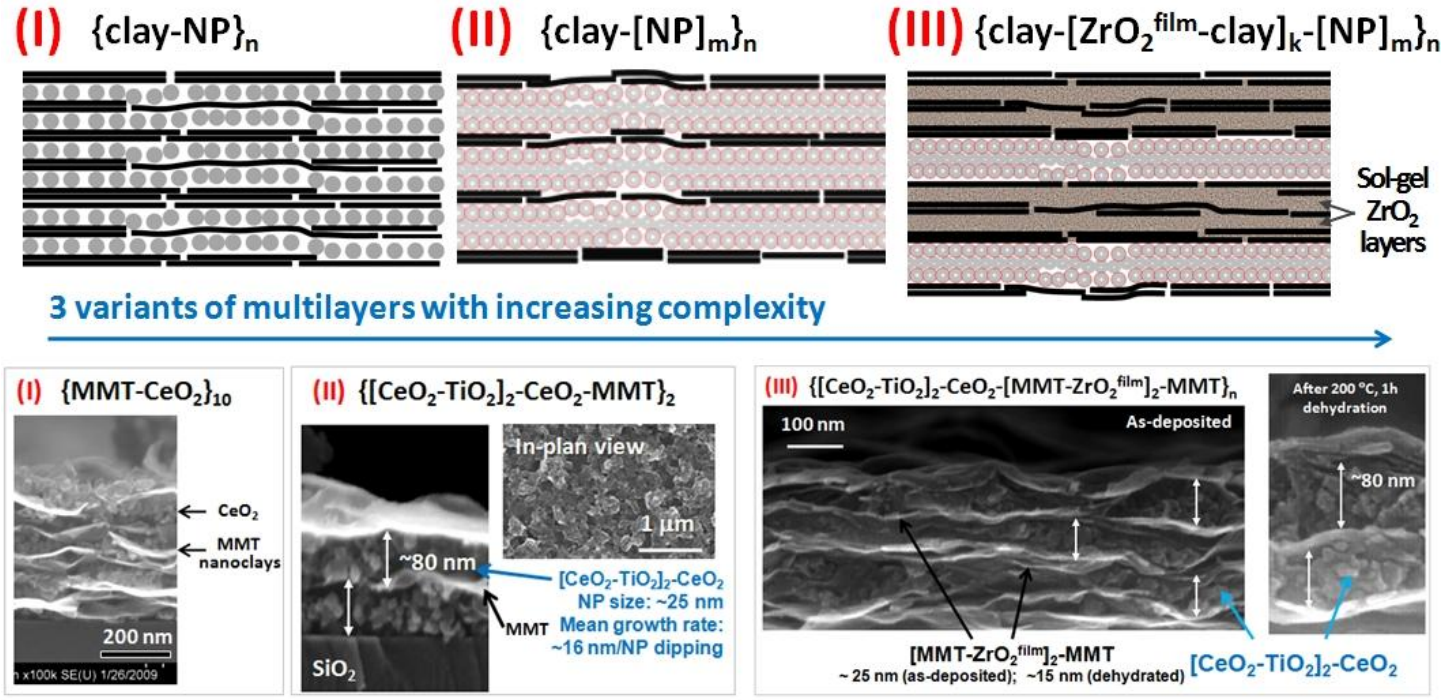

Fig. 2: Three variants of the targeted multilayers and representative SEM images.

Conclusions

Two new classes of all-inorganic nanostructured multilayers, $\{MMT_x$-(sol-gel oxide$)\}_n$ and $\{MMT_x$-(oxide NP$)\}_n$, as well as their variants, have been successfully synthesized. The synthesis of $\{MMT_x$-(sol-gel $ZrO_2)\}_n$ multilayers demonstrates the feasibility of making sol-gel oxide "glued" multilayers, thereby introducing an innovative nanoscale fabrication concept. Further details of the synthesis procedure and multilayer growth mechanisms were reported elsewhere.[5] The synthesis of $\{MMT_x$-(oxide NP$)\}_n$ multilayers and several variants further illustrates the versatility of this LbL assembly technique by achieving yet another new type of all-inorganic multilayers with a novel "plate-ball" architecture. Potential applications in high-temperature filtering membranes and several types of sensors can be envisioned.

References:

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