Assembly of nanometer-sized particles on various solid substrates has been the focus of intense interest in the development of new integrated functional materials. Layered double hydroxides (LDHs), known as anionic or hydrotalcite-like clays, have been investigated as a multifunctional inorganic material, for example, host materials[1] catalysts,[2] sorbents,[3] and bioinorganic[4] and polymer-inorganic composites.[5] To date in this area, most of the work performed has been on powder samples in colloidal solutions, where the bulk properties of the randomly assembled nanocrystals predominate over the contribution of the individual ones. LDH particles in the form of powders are considered one of the strongly correlated systems in the field of strong interparticle interactions[6] involving electrostatic forces as well as hydrogen bonding. These hydrophilic ensembles of LDH particles are expected to be less reactive toward incoming reactants, especially organic anions such as carboxylates. In this context, we recently introduced a novel method of controlling the face-to-face assembly of [Mg4Al2(OH)12]CO3·nH2O (MgAl-LDH) nanocrystals on Si substrates in closely packed arrays with a highly-ordered orientation, which can be used for solvothermal anion exchange to give a drastic anisotropic size change that can be observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM).[7] Multilayer LDH nanocrystals on solid substrates not only make chemical reactions much more reliable, but also open up a new platform of other useful chemical interfaces difficult to achieve in a bulk system. Motivated by the need to assemble functional nanomaterials based on hybrid thin films, we demonstrate in the present study that the LDH nanocrystal organization method can provide a tunable reactive inorganic interface, depending on the liquid media and the surface characteristics of the applied substrates. We were able to precisely modify the surface potentials of the LDH nanocrystals in colloid solutions by changing the solvents, leading to the well-oriented LDH monolayer films acting as a reactive inorganic interface for the fabrication of polymer–LDH hybrid films. The hydroxide groups of LDH provide a facile route to produce the additional surface modification required to develop nanoscale inorganic composite thin films, such as superhydrophobic[8] and polymer–inorganic hybrid films.[9] Among the existing synthetic approaches to the preparation of polymer–inorganic hybrid nanocomposites, surface-initiated polymerization (SIP) allows for the high affinity of the graft polymer by employing the surface modification of the initiator on the surface of layered inorganic compounds.[10] Graft polymers generated on clay surfaces by SIP have especially attracted considerable interest because of their practical applications involving improved mechanical, thermal, and barrier properties.[11] The density of the grafting surfaces could be adjusted by employing different initiators. However, in most systems based on silicate materials reported to date[12] it has been proved that the grafting polymer films have low polymer densities[9] because of the stepwise generation of the initiator molecules to form a monolayer, the difficulty in introducing initiators and monomers into the clay surfaces, and the occurrence of unnecessary side reactions. Herein, we present a precise control method to increase the grafting polymer density on hydroxyl-rich LDH surfaces by using self-assembled monolayers (SAMs) to create a uniform initiator monolayer, in which we were able to change the area coverage of the assembled LDH nanocrystals on the substrates. To the best of our knowledge, this is the first example of the graft density control of polymer films by adjusting the area coverage of an immobilized LDH monolayer with a highly oriented structure on oxide, metal, and polymer substrates. Specifically, the incorporation of poly(methyl methacrylate) (PMMA) on the immobilized LDH surface provides us with new polymer–LDH hybrid films as well as a nanoscale reaction platform, which is extremely difficult in bulk systems.

We investigated the orientation and area coverage of MgAl-LDH depending upon the applied substrates and solvents. Figure 1 shows that the tile-like LDH crystals were bound in parallel to the substrate planes on Si. Protic solvents gave a monolayer of MgAl-LDH with a high coverage of at least 50%, whereas nonprotic solvents such as toluene resulted in double and triple layers in some parts with a lower coverage of about 20%. Additional ultrasonic treatment in clean organic solvents for 30 min produced no distinguishable changes in the particle assembly, implying that the adhesion is strong enough to resist the ultrasound-induced vibration.

Figure 2a presents the surface coverage ratios, namely the percentage areas covered by the MgAl-LDH nanocrystals with respect to the whole Si surface, which are governed by the degree of attraction of MgAl-LDH to the substrates. Alcohols gave higher values of the lateral packing among the solvents. Most of the alcohols, denoted as Group I, gave ratios of around 70% to 90%.
The Group II alcohols showed medium values in the range of about 50–60%. Group III gave values of 40–50% and Group IV gave values below 30%. The surface coverage ratios in protic solvents were correlated with the zeta potentials ($\zeta$) in the colloidal solutions. We suggest that the high zeta potentials and particle size analyses (see Supporting Information, Figs. S1 and S2) reflect the larger surface coverage ratios and more laterally compact array of MgAl-LDH on Si than those in the branched alcohols.

We applied MgAl-LDH particle deposition to other selected substrates, such as oxide, metal, and polymer substrates in 1-propanol, which gave the highest surface coverage on Si, as shown in Figure 2b. Surprisingly, gold substrates showed a large coverage value, even though the inert noble metal surface would be expected to have small electrostatic charges. The strong binding property between the MgAl-LDH particles and the selected substrates was mainly ascribed to electrostatic forces. The positively charged MgAl-LDH particles are attracted to negatively charged substrates such as SiO$_2$, Au, O-poly(dimethylsiloxane) (PDMS), and O-polystyrene (PS). In contrast, positively charged substrates such as Ti and TiO$_2$ may involve very weak forces so as to give small coverage ratios. This argument is supported by the fact that the coverage on a PS substrate was strongly enhanced from 10% to 50% by O$_2$-plasma treatment.

Grafting polymerization (Scheme 1) was successfully applied to the monolayer assembled MgAl-LDH surfaces by grafting polymers with a spherical nanostructure. 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) was functionalized on the MgAl-LDH surface by immersing the samples in an ethanolic solution of 1% v/v TMSPMA and was activated to produce in situ formation of polysiloxane connected with the hydroxyl groups of the MgAl-LDH surface. The SEM images in Figure 3 clearly show that PMMA was polymerized faster on the MgAl-LDH particles than on the Si surface, which also reveals the introduction of regular nanostructures of PMMA with a diameter of between 30 and 100 nm that increases as the initial amount of methyl methacrylate (MMA) monomer increases. A low MMA concentration produced small granules, giving MgAl-LDH particles with rough surfaces, whereas they were originally very smooth. At a high concentration of MMA, the polymer films formed bulky beads on the MgAl-LDH crystals and the exposed Si surface, giving dense and thick polymer layers. In addition, two layers of PMMA particles were formed on the MgAl-LDH crystals, and the diameter of the particles in the second layer was larger than that in the first one, demonstrating that new PMMA particles were generated on the former layer by a secondary growth mechanism.

We applied the polymerization to a MgAl-LDH/Si substrate coated with a 3-sulfopropyl methacrylate potassium salt (SPMP) as the polymerization initiator immobilized on MgAl-LDH surfaces through anion-exchange and electrostatic adsorption. The SEM images in Figure 3 demonstrate that PMMA was deposited exclusively on the SPMP modified MgAl-LDH surfaces and not on the exposed Si surface. The surface selectivity of the polymerization reactions was observed in low and high MMA concentrations, ascribed to the electrostatic adsorption of sulfate anions of SPMP only onto the positively charged LDH surfaces. The SEM images (see Supporting Information, Fig. S5) reveal partial grafting and incorporation of SPMP initiators on side faces of the LDH crystals. In contrast to the case of TMSPMA, the morphology of the PMMA film formed on the SPMP-modified LDH surface was smooth and continuous, which is ascribed to the different packing density of SPMP and TMSPMA on MgAl-LDH surfaces.

In particular, we applied this method to MgAl-LDH/Au systems, producing a strong interface between gold and polymer, which...
usually exhibit weak binding affinity when they are in direct contact with each other. Figure 3e shows the SEM images of the PMMA nanostructures on TMSPMA/LDH/Au, where the PMMA is generated only on the surface of the TMSPMA/LDH particles. The requirement for TMSPMA as a molecular linker was confirmed by the IR spectra supporting the polymerization of PMMA on the TMSPMA/LDH/Si substrates. The polymerization does not occur on the bare gold surface under the same experimental conditions.

The glass substrates allowed for the optical microscopic characterization of multi- or monolayer assembled MgAl-LDH (Fig. 4). While the as-prepared MgAl-LDH coated samples have random stains due to the multilayered MgAl-LDH, the washed samples were transparent and tinged with blue. For the monolayer of MgAl-LDH on glass in Figure 4c, the transmittance of visible light decreases as the wavelength increases, as compared with the untreated glasses. For instance, the transmittance is 98% at 600 nm and 87% at 400 nm. The UV-vis spectra for the PMMA-coated MgAl-LDH films show that the transmittance significantly decreased in the wavelength range below 350 nm, and that the films provided complete shielding to wavelengths below 300 nm, which are the principal cause of sunburn reaction, even though they showed similar transparency to the LDH/glass in the visible range. This result strongly demonstrates that the PMMA/LDH hybrid thin film with a well-organized LDH nanocrystal monolayer has an excellent UV blocking effect, even though it is an extremely thin hybrid film. The high transparency in the visible range is also attributed to the one monolayer thick LDH film of about 50 nm and the thin polymer layer. Thanks to the excellent optical properties of PMMA and improved optical, thermal, and mechanical properties of the hybrid nanocomposites, this PMMA/LDH system would be a good candidate for developing optical coatings and fibers.

In conclusion, we demonstrated a novel method of optimizing the coverage of monolayer MgAl-LDH nanocrystals on solid substrates with maximum face-to-face contact by changing the solvent systems at room temperature without using any additional molecular linker. The LDH nanocrystals could be readily assembled on polymer and gold substrates by simple ultrasonification. PMMA nanostructures with a high-graft density were successfully generated on an immobilized LDH monolayer by employing UV-induced polymerization, which makes it possible not only to control the reaction kinetics, but also the grafting polymer density by adjusting the coverage values of the MgAl-LDH monolayer. This experimental strategy opens up a new route to the facile preparation of polymer–inorganic interfaces. The utilization of MgAl-LDH nanocrystals as an inorganic cross-linker has several advantages, such as structural and thermal stability, and this strategy is readily applicable to various solid surfaces with a tunable coverage. Thanks to the reactive hydroxide groups of the LDH nanocrystals, a layer of polymer chains with various functional groups can be partly planted on the surface of inorganic materials according to the specific requirements for applications. Therefore, the present technique can be of great interest in the optical, chemical, biological, and environmental research fields, since the area control of the hydroxyl-rich surface of LDH nanocrystals provides a new way to
produce additional surface modification in nanoscale polymer–
inorganic composite thin films.

**Experimental**

**Materials and substrates:** The hydrotalcite-like compound MgAl-LDH was synthesized according to the previously reported procedure [23]. MMA, potassium persulfate (K2S2O8), SPMP and all of the solvents were of analytical grade and purchased from Aldrich. TMSPOA was obtained from Fluka. The silicon (100) wafer and micro slide glass substrates were cleaned using piranha solution. Indium tin oxide (ITO), SrTiO3 (STO) (100), LaAlO3 (LAO) (100), Au/Si, Ag/Si, Ti/Si, TiO2/Si, and PS were used as-received or after polishing by diamond paste. The flat PDMS substrates were made using Sylgard 184 (Dow Corning) using Si as a template.

**Immobilization of MgAl-LDH:** About 10 mg of the MgAl-LDH nanocrystals were suspended in 20 mL of each solvent in a covered laboratory glass flask, and then the flask was immersed in an ultrasonic bath (95 W, 28 kHz) at room temperature in the ambient atmosphere. The substrates were cleaned with an O2-plasma cleaner (Harrick, 30 W), dipped in a colloidal suspension (100 mg/mL) of MgAl-LDH, and treated by ultrasound for 2 min. The MgAl-LDH coated substrates were placed in the solvents without MgAl-LDH, followed by sonication for 1 min to rinse them off and then dried at 70°C in air.

**Grafting Polymerization of MMA:** Prior to the polymerization, all samples of monolayer MgAl-LDH on substrates were prepared in 1-butanol. The surface functionalization on MgAl-LDH/Si was carried out in 1% (v/v) ethanol solutions of TMSPMA for 3 h. The MgAl-LDH/Si was also functionalized by 10 mg/mL SPMP aqueous solution for 3 h. The TMSPOA/MgAl-LDH/Si and SPMP/MgAl-LDH/Si samples were washed with deionized water and dried at 120°C in a dark room. The surface modified MgAl-LDH/Si was treated with 20 mL of K2S2O8 solution for 30 min at room temperature. Under vigorous stirring, MMA was then added and the mixture was irradiated under UV light using a 600 W high-pressure mercury lamp for 30 min at room temperature, and the samples were then washed with deionized water and dried in air.

**Measurement:** The SEM images were obtained on a Philips XL30. A thorough inspection using SEM for the monolayer MgAl-LDH/Si revealed that each sample shows a variation of its surface coverage ratio of less than 3% on average. The particle size measurements in colloidal suspensions were performed with a Malvern Instruments laser-beam particle size analyzer, model 1000HSA. The zeta potentials were measured using a DT-300 instrument, Dispersion Technology, Inc., at 25°C. The ζ value of the LDHs in water was 98 mV at pH 9.3, which is higher than that in ethanol (59 mV at pH 8.7). The zeta potentials in primary alcohols (1-propanol: 173 mV at pH 8.5, 1-butanol: 112 mV at pH 8.2) are higher than those in a secondary alcohol (2-propanol: 40 mV at pH 8.3) or a tertiary alcohol (2-methyl-2-propanol: 23 mV at pH 8.0). The UV-vis absorption measurements were carried out in a Varian spectrophotometer, model Cary 5000. The FTIR spectra were obtained with a vacuum optics available spectrometer, model IFS 66 v/s (Bruker), which has a resolution of 4 cm⁻¹ and a photovoltaic liquid cooled MCT detector.

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[19] The characteristic IR peaks of carbonate groups in MgAl-LDH appear at 680 cm⁻¹ and 900 cm⁻¹, and the peaks corresponding to PMMA film appear at 1730 cm⁻¹ (C=O stretching) and 1150 cm⁻¹ (C–O–C stretching) (see Supporting Information, Fig. S3).