THIN FILMS OF LAYERED NANOCOMPOSITES

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One of the most significant challenges of chemistry of nanomaterials is their organization in the nanometer scale. One of the possible ways to produce the ordered structures and to study the effect of ordering on materials properties is to create stratified layered composites. They can be made by using the new deposition technique often termed as layer-by-layer assembly (LBL). This technique is quite simple and based on the sequential adsorption of alternating (mono)layers of oppositely charged inorganic colloids and polyelectrolytes and results in composite materials combining mechanical properties of polymers and unique physical characteristics of nanosized inorganic clusters. The nanoparticles are made prior to the assembly, and therefore, allow for the accurate control over their size and size distribution. In optimized LBL deposition the growth of the film is linear, *i.e.* the amount of the nanoparticles transferred in every deposition cycle is identical, which can be seen in the dependence of the UV-vis absorption density on the number of deposition cycles. Imbedding nanoparticles in polymer matrix makes them immobile, which eliminates phase separation even at the nanoscale. The latter significantly complicates the preparation of other composites based on nanoparticle/polymer mixtures spin-coated or painted on a substrate. As a result, in each *bilayer* LBL assemblies of nanoparticles have exceptional homogeneity. Analogous bilayers deposited one after another form stratum, which can be organized in any desirable way by building the multilayer system from different nanoscale building blocks. Sophisticated multilayer system with gradient properties and assemblies combining nanoparticles of different materials can be made. The functionality of each layer is determined by the properties of nanoparticles involved in the LBL process and can be alternated according to the predetermined order. Examples of multilayer stacks with magnetic, electrical and light-emitting properties determined by the sequence of the LBL layer will be demonstrated. Proper multilayer ordering affords the preparation of free-standing LBL films, which opens the way for the utilization of LBL films as a new class of nanostructured membranes and biomaterials.

Substantial advantages for film ordering were seen for the particles and macromolecular species with high shape anisotropy. Firstly, as compared to the predominantly round clusters, the anisotropic species provided greater area for intermolecular interactions with polyelectrolyte underlayer. The example of such system is adsorption of clay platelets on polyelectrolyte. Montmorillonite (natural anionic clay) sheets (100nm x 100nm x 1 nm) form LBL layers with a great degree of overlap between the sheets despite some mutual repulsion stemming from the like charge. The produced films had low density of gaps between the clay sheets and could serve as superb diffusion barriers. Secondly, anisotropic nanoscale building blocks such as semiconductor nanowires and carbon nanotubes can be organized in the lateral dimension taking advantage of sheer liquid force during the LBL assembly. We tested this approach for several systems such as CdTe nanowires and partially oxidized single wall carbon nanotubes. Lateral organization results in a substantial improvement of electrical and mechanichal characteristics of the produced anisotropic composites. Some of them exceed the analogs made by traditional techniques by 1-2 orders of magnitude.

Disordered nature of pure polyelectrolyte LBL films can also be utilized to obtain quite unique nanoscale assemblies. For instance, conjugated polymers possess a variety of interesting properties, however, their chemical synthesis can be complex. In particular, the introduction of specific reactive groups can be especially challenging. The interdigitation of two polyelectrolytes – one with desirable properties from bond conjugation and the other one with desirable functional groups -- affords the preparation of close-to-perfect molecular blends and coating that combine both requirements. This approach was demonstrated for a conjugated amplifying polymer blended with poly(allylamine hydrochloride). Subsequently, the luminescent CdTe nanoparticles were tethered to the amino groups via bifunctional poly(ethyleneglycole) linker. The efficiency of the excitation energy transfer between the conjugated polymer and the nanoparticle on the PEG rope can be regulated by the extension of the tether in different solvents that was demonstrated for water-alcohol mixtures. Thus, the disorder of the polyelectrolyte multilayers was utilized to design a molecular system with accurately controlled optical coupling.

Being stimulated by the simplicity and universality of the assembly procedure These and similar ordered multilayer systems from nanoparticles and related materials are being actively studied for a number of electronic and photonic applications. Some of them currently undergo the stage of commercial testing.

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