immersing the solid support in a (second) admixed polymer ion-functional molecule solution having a net electric charge opposite to that of the (second) polymer ion solution, and repeating such immersing steps of the solid support in the admixed polymer ion solution and the admixed polymer ion-functional molecule solution to form a desired multi-layered thin film.

In another aspect of the present invention, it provides a functional thin film which comprises multiple layers of non-flexible functional molecules and multiple layers of polymer ions fixed on a solid support. Such thin films have not hitherto been producible in any way.

DESCRIPTION OF THE DRAWINGS

FIG. **1** shows QCM frequency changes observed in the alternate layer-by-layer assembling of Examples 1 to 4.

FIG. **2** shows QCM frequency changes observed in the alternate layer-by-layer assembling of Examples 3 and 4.

FIG. **3** shows UV spectra observed in Examples 8 to 10.

FIG. **4** shows QCM frequency changes observed in the alternate layer-by-layer assembling of Examples 35 and 36.

FIG. **5** shows an increase in UV absorbance at 665 nm observed in Example 37.

FIG. **6** shows QCM frequency changes observed in the alternate layer-by-layer assembling of Examples 38 and 39.

FIG. **7** shows UV spectra observed in Examples 40 and 41.

FIG. **8** shows QCM frequency changes observed in the alternate layer-by-layer assembling of Example 42.

DESCRIPTION OF THE INVENTION

According to the present invention there is provided an ulitrathin film having a thickness of a molecular level, from a variety of molecules, ranging from low molecular weight to high molecular weight molecules, by layering such molecules in the desired number and in the desired order.

The conventional alternate layer-by-layer method is based on the foresaid principle. In the present invention, the adoption of the admixed polymer ion-functional molecule solution, instead of a simple polymer ion solution, makes it possible to layer non-flexible or rigid functional molecules in any desired number and in any desired order of the layers to form an ultrathin film of a molecular level, while such molecules have been difficult to layer in the conventional methods as they are susceptible to association with each other, particularly in the case of proteins.

As can be seen from the above-mentioned principle, according to the present invention the admixed polymer ion-functional molecule solutions can be utilized directly in the preparation of films and hence the decomposition or denaturation of such functional molecules is avoided. Thus, the method for fixing functional molecules according to the present invention provides a remarkable technique for constructing novel functional materials, in marked contrast to the methods hitherto proposed for fixing functional molecules in which chemical modifications of the molecules are needed or denaturation of the molecules occurs and impairs the intrinsic functions of such molecules.

The method of the present invention can be applied to a wide variety of functional molecules since the molecules have only to be mixed with polymer ions to form admixed solutions and need not be modified with specific functional group to develop specific properties for the layering. For example, even materials which are generally difficult to isolate can be easily layered simply by mixing with polymer ions in solutions. In addition, rare materials generally occurring in an extremely small amount can be utilized in the form of admixed solution with polymer ions.

The present invention is also advantageous in that different types of functional molecules can be used in combination and fixed in any desired order so as to construct highly useful composite materials with multiple functions.

In the present invention there are generally employed flexible organic polymer ions as matrices for fixation and thus mass diffusion throughout the thin films is facilitated as compared with the case in which rigid components such as lipids are used as the matrices. It should however be noted that rigid organic or inorganic polymer ions can also be utilized as the fixation matrices in the present invention.

The method of the present invention for preparing thin films can be practiced in an extremely easy manner in a short period of time by simply immersing solid supports into admixed polymer ion-functional molecule solutions, without need of any sophisticated devices. Thus, any types of solid materials can be selected as supports to produce systems imparted with additional functions due to the supports.

The invention will now be described more specifically.

Polymer ions to be used in the present invention can be defined as organic polymers having functional groups with an electric charge on their molecular skeletons or branches, or inorganic polymers with an electric charge. Usable polyanions (anionic polymer ions) are generally ones having such functional groups as sulfonic acid, sulfuric acid and carboxylic acid, which are negatively chargable, and include poly(styrenesulfonate) (PSS), poly(vinylsulfate) (PVS), dextransulfate, chondroitin sulfate, poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), poly(maleic acid), poly(fumalic acid), and montmorillonite (Mont). Polycations (cationic polymer ions) usable are ones having such functional groups as quaternary ammonium group and amino group, which are positively chargable, and include poly(ethyleneimine) (PEI), poly(allylamine hydrochloride) (PAH), poly(diallyl-dimethyl-ammonium chloride) (PPDDA), poly(vinylpyridine) (PVP) and poly(lysine). These polymer ions are all soluble in water or in a water-organic solvent mixture. Also usable are electrocouductive polymers, functional polymer ions such as those from poly (aniline-N-propane-sulfonic acid) (PAN), and biopolymers such as deoxyribonucleic acid (RNA) and polysaccharide with an electric charge (e.g. pectin). Rigid organic polymer ions such as those deirived from polythiophene, polyaniline and poly(phenylene vinylene) can also be used in the present invention.

All types of functional molecules are applicable in the present invention, so long as such molecules are soluble in a solution together with polymer ions as exemplified above.

Applicable in the present invention are not only such functional molecules as conventionally employed in the alternate layer-by-layer method, but also various types of non-flexible functional molecules which have been hitherto impossible to layer, thereby enabling the construction of a variety of novel functional thin films.

Examples of suitable functional molecules include proteins such as glucose oxydase (GOD; molecular weight 18600, isoelectric point 4.2), peroxydase (POD; molecular weight 42000, isoelectric point 7.2), glucoamylase (GA; molecular weight 100000, isoelectric point 4.2), alcohol dehydrogenase (ADH; molecular weight 100000, isoelectric point 9), diaphorase (DA; molecular weight 700000, iso-