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# Layer-by-Layer Thin Films and Coatings Containing Metal Nanoparticles in Catalysis

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Additional information is available at the end of the chapter

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## Abstract

The layer-by-layer (LbL) technique is one of the most promising ways of fabricating multilayer thin films and coatings with precisely controlled composition, thickness, and architecture on a nanometer scale. This chapter considers the multilayer thin films and coatings containing metal nanoparticles. The main attention was paid to LbL films containing metal nanoparticles assembled by convenient methods based on the different intermolecular interactions, such as hydrogen bonding, charge transfer interaction, molecular recognition, coordination interactions, as driving force for the multilayer buildup. Much attention has paid to the LbL films containing metal nanocomposites for multifunctional catalytic applications, in particular, photocatalysis, thermal catalysis, and electrocatalysis. The preparation protocol of LbL-assembled multilayer thin films containing metal nanoparticles (such as Au, Ag, Pd, Pt), metal oxides ( $\text{Fe}_3\text{O}_4$ ), and sulfides (CdS) that are supported on the various surfaces of nanotubes of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  membranes, graphene nanosheets, graphene oxide and further applications as catalysts with respect to photocatalytic, electrocatalytic performances is discussed. The systematization and analysis of literature data on synthesis, characterization, and application of multilayer thin films and coatings containing metal nanoparticles on the diverse supports may open new directions and perspectives in this unique and exciting subject.

**Keywords:** layer-by-layer assembling, thin films and coatings, polyelectrolytes, metal nanoparticles, immobilization, semiconductors, catalysts

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## 1. Introduction

One of the main purposes of nanotechnology is fabrication of highly functional low-dimensional materials and systems [1]. Most of such systems are produced by assembling of nano

objects in thin films or coatings [2]. The utilization of high functional materials is steadily growing and covers many areas of human activity such as fabrication of drug delivery systems [3], antibacterial coatings [4, 5], electronics [6], chemical sensors [7], and even in dentist applications. Some assembling procedures need to immobilize metal nanoparticles such as gold, silver, copper, palladium, and platinum to preserve them in origin state and to avoid the aggregation. Such immobilization can be proceeded by the incorporating of nanoclusters into polymer scaffold. The scaffold plays three main roles [8]:

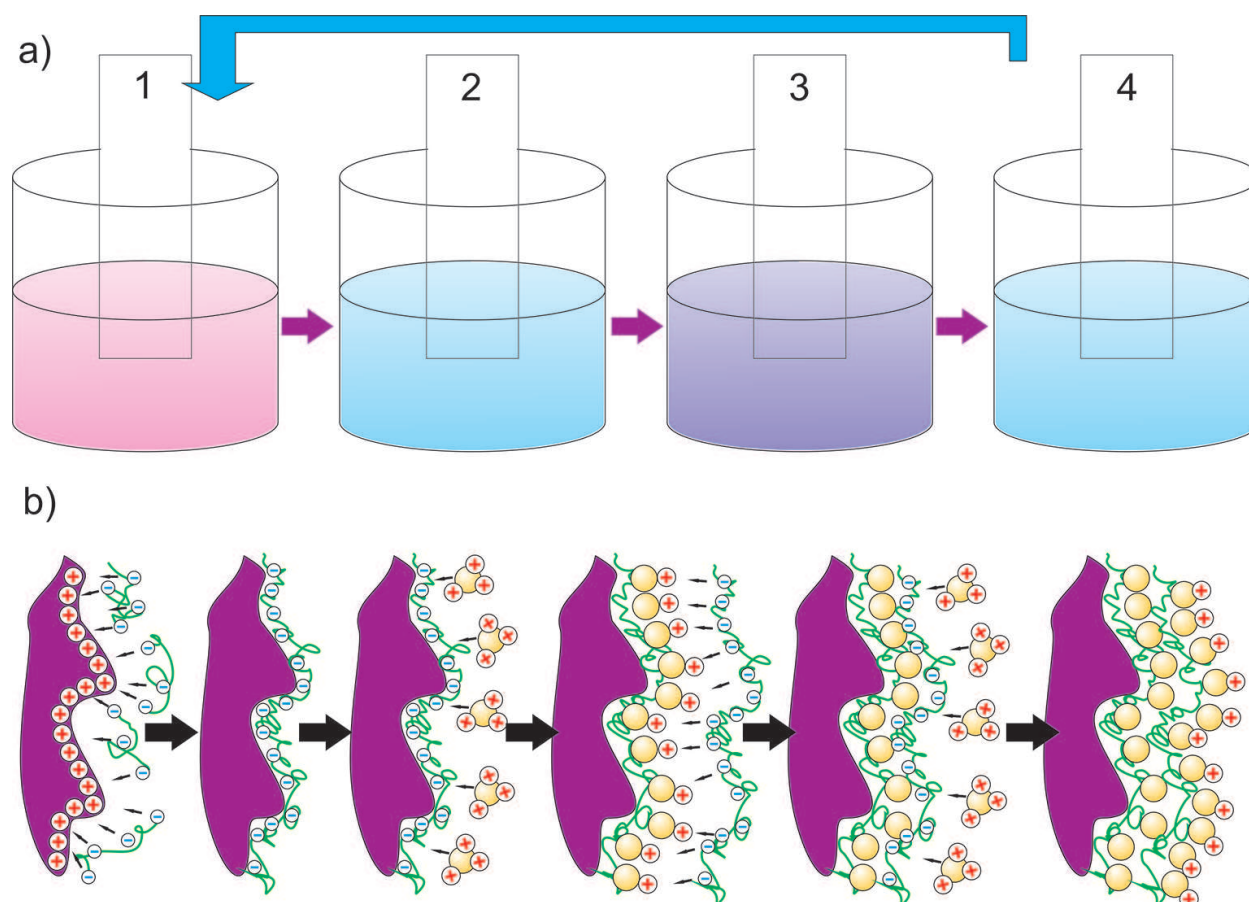
- (1) It provides assistance to particle assembling.
- (2) It ministers like a matrix for ordering and homogeneous orientation of systems.
- (3) Due to its some properties, such electronic properties, it acts as a functional element.

Polymer science and technology that spreads polymer-based biomaterials, catalysts bounded by polymer, nanofibers fabricated by polymer assisted electrospun and attracts tremendous attention [9]. The interlacing of polymer technology with nanoscience allows expanding both of them and solving the existing challenges in the fabrication on a nanoscale. Because of plenty of binding region in polymer, it can effectively immobilize the nanoparticles and at the same time act as a mediator between the substrate and nano objects [2]. Wide exploitation of polymers as supporting agents during formation of the coating is applied in the LbL assembling technique. The LbL assembling approach can be qualified as a good alternative approach to the well-known deposition methods, because it is versatile, inexpensive, and comfortable for use. Moreover, the large advantage of LbL method is that, in contrast to widespread strategies of fabrication of nanoscale structures on top of planar substrate such as chemical vapor deposition [10], atomic layer deposition [11], molecular beam epitaxy [12], hydrothermal deposition [13] and so forth, it is suitable for the formation of a uniform coating on curved surfaces [14]. The whole process of multilayer structures buildup by LbL assembling, whose driving force, despite hydrogen bonding, covalent bonding, etc., is mainly electrostatic interaction between the oppositely charged species [14, 15], usually consists of four steps [16] (**Figure 1a**):

- (1) Immersing of a cleaned, positively charged solid substrate into the solution of an anionic polyelectrolyte. Electrostatic force, collectively with adsorption, builds the first layer of multilayer construction.
- (2) Removal of the excess and weak adsorbed polyelectrolyte from the surface is carried out by substrate rinsing with deionized water.
- (3) Bilayer structure is achieved by immersing of the substrate into the solution of the cationic polyelectrolyte. This step restores the original surface charge.
- (4) Final rinsing removes the excess of cationic polyelectrolyte.

By repetition of these cycles [17], a desired number of layers can be achieved on curved planes, as shown in **Figure 1b**, therefore the whole thickness of multilayer is easy controlled. Generally, to create a difference in surface charges, using the LbL procedure,

various polyelectrolytes are employed. The mostly applied positively charged polyelectrolytes are: poly(allylamine hydrochloride) (PAH), polyethyleneimine (PEI), or poly(diallyldimethylammonium chloride) (PDDA) and negatively charged polyelectrolytes are: poly(vinyl sulfate) (PVS), poly(acrylic acid) (PAA), or poly(styrene sulfonate) (PSS). It should be also mentioned that the LbL method expands the possibilities of obtaining organic/inorganic films with high accuracy just by changing the number of multilayers, concentration and pH of the solution. The application area of nanosystems obtained by LbL assembly is very wide. It includes fabrication of layers with magnetic, fluorescent, catalytic and various electronic properties. For example, the magnetic multilayers can be used in medicine as well as other technical applications. Fluorescent properties are widely benefited in optical devices. LbL-assembled catalysts can be applied for hydrogenation, oxidation of various substrates and water splitting. Nobel metal particles incorporated into the multilayer structures are adopted as coatings for light absorption enhancing by the surface plasmonic effect. In the following subsection we consider the LbL thin films and coatings containing metal nanoparticles, metal oxides, and sulfides together with their application of in catalysis.



**Figure 1.** Schematic illustration of the LbL assembling process by alternately dipping of a positively charged substrate into the solutions of a oppositely charged polyelectrolyte (a) and formation of shell structure on curved planes (b).

## 2. LbL thin films and coatings containing metal nanoparticles, metal oxides, and sulfides

### 2.1. LbL thin film and coatings containing gold (AuNPs) and silver (AgNPs) nanoparticles

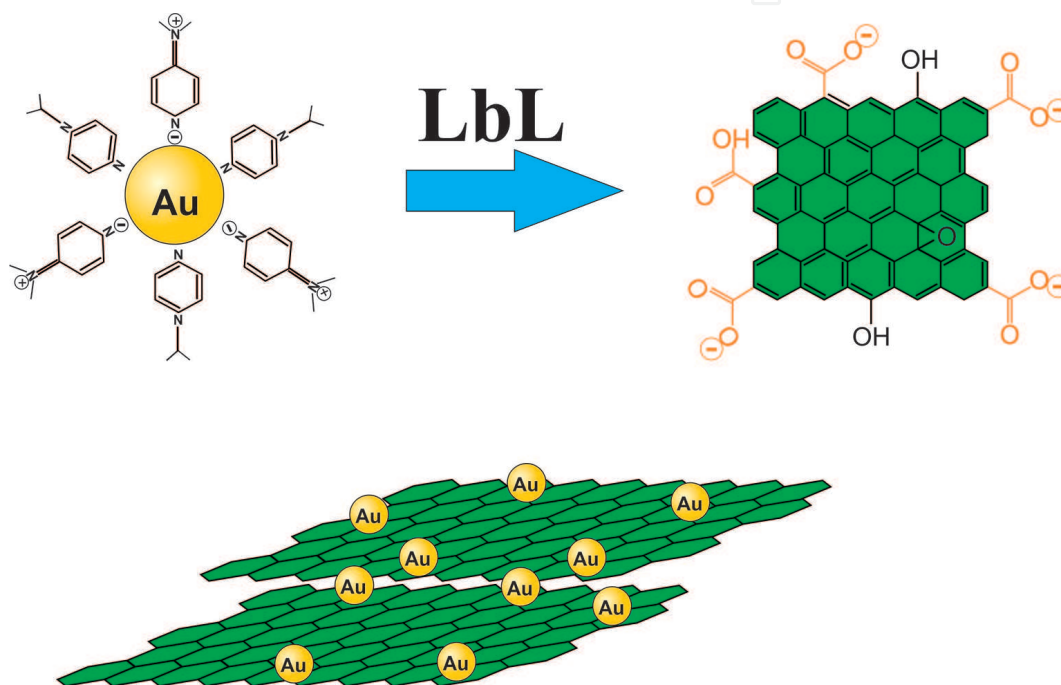
The metal nanoparticles with attractive optical, electronic, and catalytic properties are used in a broad range of applications ranging from physics to medicine [18]. For assembling such nanoscaled particles with controlled parameters, it is necessary for scientists to develop new methods which can allow to obtain constructions with required properties [19]. The charge transfer properties of metal particles incorporated in a thin layer depend on particle size and distance between them in vertical and space distributions [20]. At the same time, the dependence between the particle size reflects to a high reactivity/selectivity for the hydrogenation of unsaturated alcohols [21, 22]. Recently, noticeable research works were conducted with respect to immobilization of mono- and bimetallic nanoparticles into the matrices of ultrathin films to obtain the effective nanocatalysts [23]. Such, LbL-assembled layers of gold nanoparticles within interpolyelectrolyte complexes can be formed either by interaction of poly(ethyleneimine)-gold nanoparticles (PEI-AuNPs) with poly(acrylic acid) (PAA) or by interaction of poly(acrylic acid)-gold nanoparticles (PAA-AuNPs) with PEI [24]. It is also well known that the noble metal nanoparticles, in particular Au, Ag, and Pt possess strongly marked plasmonic properties, which can be controlled by changing fabrication parameters. Thus, changing of volume, dipolar coupling, or a type of solvent alters the wavelength of plasmonic resonance. For instance, dipolar coupling of Au can be controlled by changing the distance between the particles, such distance among the particles is easily adjusted by modification of dendrimers, highly branched monodisperse molecules. The dendrimers have the series of chemical modifications and cavities which act as templates for nanoparticle growth. For example, polyamidoamine (PAMAM) or carboxyl-terminated PAMAM [25] dendrimers are utilized as a matrix with effective nanoparticle stabilization [26]; therefore, Au, Cu, Pt, and Pd nanoparticles can be formed and stabilized therein [27]. The wavelength of surface plasmonic resonance of nanoscaled gold nano objects incorporated within PAMAM depends on the number of the layers. Increasing of the number of LbL-assembled PAMAM enlarges the distance between the Au nano objects, which leads to an ultraviolet shifting of plasmonic glow. Besides the tuning of plasmonic properties, it is also possible to adjust the fluorescent properties of gold nano objects only by magnification the thickness of multilayer or by the increasing the number of LbL cycles. For example, fluorescence of Au, covered in a core-shell manner by organic multilayers, can be easily tuned by varying the number of nonfluorescent layers [28].

Silver/gold coatings formed onto a commercial anion exchange resin via LbL [5] are very appropriate bimetallic composition for catalytic reduction of nitroaromatic compounds. Such core-shell heterostructures can be prepared by using of electrostatic force of the charged resin beads. Such resin beads support immobilization of anionic metal precursors of silver/gold nanoparticles onto the solid resin matrix and reduce 2-nitrobenzoic acid to obtain the corresponding amines through the effective catalysts.

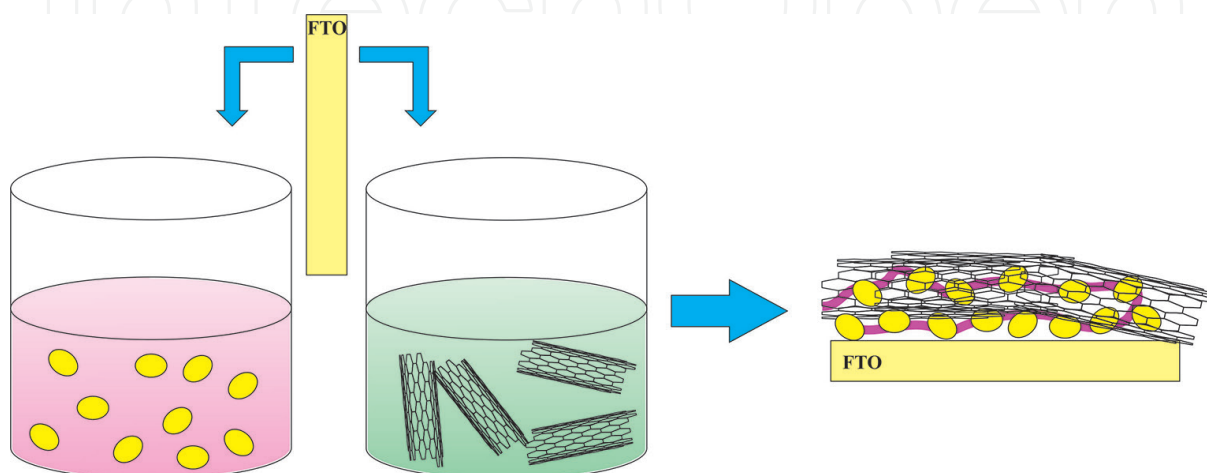
**Figure 2** demonstrates a simple method of integrating the electroactive gold nanoparticles (AuNPs) with graphene oxide (GO) nanosheets. Such LbL structures composed of three-dimensional electrocatalytic thin films are active toward methanol oxidation [9]. This approach



involves the electrostatic interaction of negatively charged graphene oxide nanosheet with positively charged AuNPs. The distribution of gold nanoparticles on the surface of GO can be controlled using the LbL method, the latter enhances the stability keeping from aggregation during the electrocatalytic cycles. Due to high versatile and tunable properties of LbL-assembled thin films, a hybrid electrocatalyst can be easily designed for direct methanol fuel cell (DMFC). Such LbL assembly allows for the fabrication of the nanoparticle/graphene hybrid multilayer structure, which exhibits a wide range of functionalities. **Figure 3** shows a schematic representation of the LbL film made of poly-N-vinylpyrrolidone-stabilized AuNPs (PVP-AuNPs) and single-walled CNTs deposited on a fluorine-doped tin oxide (FTO) glass. Such structures may be used in the field of catalysis, fuel cells, and sensing.



**Figure 2.** LbL integration of gold nanoparticles (AuNPs) with graphene oxide (GO) nanosheet.



**Figure 3.** LbL films of PVP-AuNPs and single-walled CNTs supported on a fluorine-doped tin oxide (FTO) glass.

## 2.2. Immobilization of Pd and Pt nanoparticles into the LbL matrix

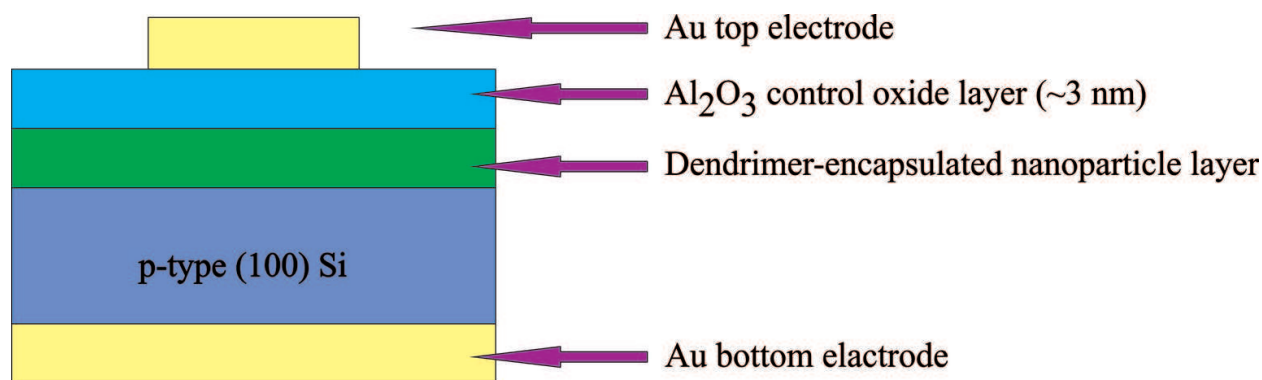
One of the main important catalytic properties of Pt and Pd containing films is electrocatalytic oxidation of methanol [12, 29, 30]. Immobilization of Pd nanoparticles (PdNPs) usually proceeds on solid supports, such as carbon, graphene, metal oxides, and zeolites [26]. Assembling of PdNPs onto carbon allows for obtaining a nanocomposite possessing chemosensitive properties. The electrocatalytically active graphene-palladium composites can be utilized as hydrogen detectors [31]. The PdNPs are stabilized by capping with ligands, ranging from small organic molecules to large polymers [22]. Immobilization of PdNPs in the form of spherical aggregates takes place by using of dendritic molecules such as amine-terminated PAMAM dendrimers (G1.0 PAMAM) or POSS-NH<sub>3</sub><sup>+</sup> [32]. The process of self-organization of spherical templates is carried out in solution at room temperature, which allows for obtaining the dendrimers with an average size of about 70 nm.

The PdNPs synthesized by the reduction of Pd(II) to Pd(0) by using NaBH<sub>4</sub> can be incorporated onto magnetic nanoparticles (MNPs). Such incorporation is carried out by the LbL technique, which is suitable to poly(acrylic acid)-poly(ethyleneimine)/Pd(II) multilayers formation in a core-shell manner [33]. Such hybrid structures are considered to employ for the hydrogenation of various olefin alcohols. Besides using MNP as a substrate, it is also possible to assemble nanosized Pd-polyelectrolyte multilayer onto aluminum powder [34]. Diversity of PdNPs diameters, within multilayers onto aluminum powder, can be regulated by changing the ratio between poly(acrylic acid) and Pd(II). Such changing allows to obtain the ranging of particles with diameters from 2.2 to 3.4 nm. Consequently, by this way, it is easy to tune the catalytic selectivity of such a hybrid system.

The Pt nanoparticles (PtNPs) with good optical and catalytic properties can also be incorporated within PAMAM dendrimers. The simple way of PAMAM dendrimers with incorporated Pt nanoclusters deposition is LbL assembling them onto the solid substrates [28]. For instance, the Pt-PAMAM structures are obtained through the chemical reduction of H<sub>2</sub>PtCl<sub>6</sub>, in the presence of PAMAM, using formic acid as a reducing agent. Then, by alternating immersions of the substrate into the polyelectrolyte solutions consisting of poly(vinylsulfonic acid) and PAMAM dendrimers the multilayer structures are produced. Time duration for each layer formation is about 5 min [35].

Using PAMAM dendrimers/PtNPs allows to obtain the nonvolatile memory (NVM) devices [36]. However, the process of NVM assembling is slightly differ from the above-described process and involves the formation of PtNPs within a ultrathin film matrix, formed by covalent LbL assembly of pyromellitic dianhydride (PMDA) and second generation of PAMAM dendrimer in supercritical carbon dioxide (SCCO<sub>2</sub>). To design such a structure, nanoparticles' precursor is sequestered within a dendrimer matrix by using SCCO<sub>2</sub> as a processing medium. This technique of preparation nanostructured films, with assistance of SCCO<sub>2</sub>, at room temperature is a comparable clean process.

Aside from NVM, the metal-insulator semiconducting (MIS) devices can be formed using dendrimer-encapsulated nanoparticles. MIS installation proceeds by the covalent molecular assembly of dendrimers with incorporated agents. The MIS device configuration is shown in **Figure 4**.



**Figure 4.** MIS device configuration consisting of Au bottom electrode, dendrimer-encapsulated nanoparticle layer,  $\text{Al}_2\text{O}_3$  layer, and Au top electrode.

### 2.3. Assembling of LbL films and coatings containing $\text{Fe}_3\text{O}_4$ and CdS

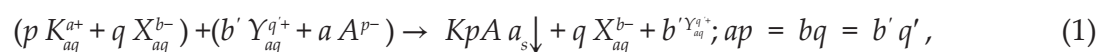
In this section, we describe LbL immobilized  $\text{Fe}_3\text{O}_4$  and CdS nanoparticles that possess magnetic, semiconducting, optic, and other properties. Since metal oxides are widely used in gas sensing application [38], electrochemical capacitors [39], lithium-ion batteries [40], photocatalytic materials [41]; it is important to develop their installation direct on the electrodes. Therefore, the process of immobilization of metal oxides such as  $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$ , and ZnO by using the LbL method, where the general assembling of metal oxides proceeds with assistance of polyelectrolytes [42], has been tremendously studied [43]. In the past two decades, a great attention has been paid to the synthesis of  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles due to their cheapness, nontoxicity and readily producing. Direct deposition of  $\text{Fe}_3\text{O}_4$  onto an electron conductive material, such as indium tin oxide (ITO)-coated glass, allows using it in electrochemical capacitor application [44] and biomedicine. Combination of various fabrication methods of these particles with the LbL deposition technique allows to obtain high quality core-shell architectures. The  $\text{Fe}_3\text{O}_4$  preparation method in general involves the dissolution of the mixture of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  in aqueous solution (chemical coprecipitation). The obtained particles of  $\text{Fe}_3\text{O}_4$ , modified by polymers, can be coated onto quantum dots (Qds), such as CdTe, in a core-shell manner via the LbL technique. Such strategy allows to fabricate the magnetic luminescence  $\text{Fe}_3\text{O}_4$  nanocomposites [44]. The medical application of magnetic structures, incorporated via LbL has also been developed. In particular, the  $\text{Fe}_3\text{O}_4$  and Pt nanoparticles, incorporated into hemoglobin, improves the biosensitivity of the protein [45]. Employment of  $\text{Fe}_3\text{O}_4$  for magnetic separations of protein is possible by coating it onto  $\text{SiO}_2$  particles [46]. Another good example of  $\text{Fe}_3\text{O}_4$  particles involved in the high functional core-shell formation is  $\text{Fe}_3\text{O}_4/\text{Au}$  structure. Such composition is widely applied in biomedical and technological fields due to their unique optical, magnetic, and catalytic properties [47].

Since the  $\text{Fe}_3\text{O}_4$  particles possess magnetic properties, it is possible to assemble them with the help of magnetic field. Combination of the LbL technique and magnetic field leads to compaction of particle packing without increasing the total thickness of the obtained film [48].

CdS is one of the most interesting semiconducting materials due to its band structure, luminescent aptitude, etc. Nanoscaled CdS particles with a size range up to 10 nm can be considered as



Qds and currently attract a large number of researchers due to their unique optical and electrical properties [49]. There are several CdS Qds preparation methods, but among them the LbL derivation, also known as successive ionic layer adsorption SILAR [50] deposition, is a very promising approach due to its versatility and simplicity to obtain high controlled objects. The method is as follows: in separate beakers, the dissolved ions of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  are deposited onto a substrate, forming CdS structure. It is obvious that the structure-building force is Columbic attraction. This technique proceeds without participation of polymers, consequently it is not necessary to remove organics by the calcination of structure for increasing the attaching surface between the CdS layer and the active materials. The theoretical description of SILAR (LbL derivation) [50] can be described as following, the sequential immersion of the substrate into oppositely charged liquid solution results the reaction between the substrate and dissolved species. Heterogeneity of layer structure enriches by rinsing in water after each dipping into electrolyte solution. The principle of film growing can be explained by the following equation:



where,

K is cation ( $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{+}$ , etc.)

A represents the anions (O, S, or Se)

p is the number of cations

a is the numerical value of charge on cation

Y is the ion which is attached to chalcogen ion

X represents an ion in cationic precursors

q represents the number of ions

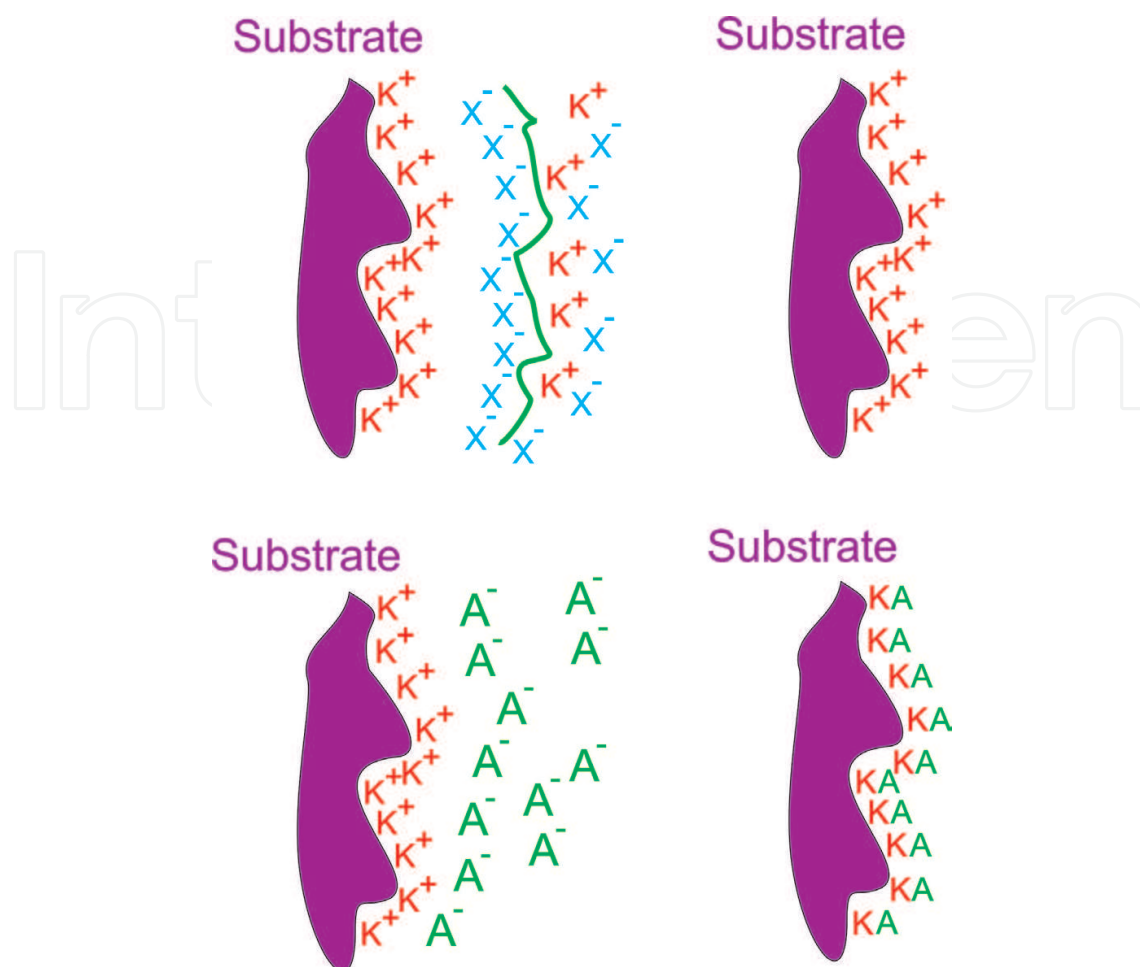
b represents the charge value of ions

b' represents the number of ions attached to chalcogens

q' represents the charge value of ions attached to chalcogens

Schematic representation of the SILAR process is shown in **Figure 5**. The CdS Qds obtained by the LbL (SILAR) method can easily be used in the fabrication of Qds sensitized solar cells, which are very well suited for the creation of alternatives to silicon-based photovoltaic devices. A simple example of preparation of CdS-based Qds-sensitized solar energy converting construct is given by Chen and co. [51]. They sensitized ZnO nanosheets, obtained through the three-electrode electrodeposition method, with further coating them by CdS Qds. Such coating can be assembled through alternating dipping of ZnO nanosheets comprise a glass substrate into the liquid solutions. The whole process of LbL CdS assembling can be described as:

- (1) Immersing of negatively charged ZnO deposited glass substrate in a beaker containing 0.05 M  $\text{Cd}(\text{NO}_3)_2$  to adsorb  $\text{Cd}^{2+}$ . Resulting charge of the glass surface becomes positive.
- (2) Rinsing surface with deionized water to remove excess of ions.
- (3) Dipping of a positively charged substrate into dissolved 0.05 M  $\text{Na}_2\text{S}$  to deposit  $\text{S}^{2-}$ .
- (4) Final cleaning of surface is carried out by rinsing with clean water.

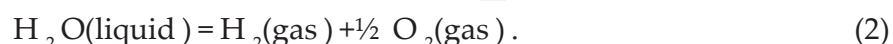


**Figure 5.** General scheme of the SILAR method for the fabrication of QDs.

### 3. Application of NPs immobilized via the LbL assembly in catalysis

#### 3.1. LbL-assembled layers for water splitting application

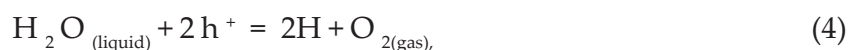
Hydrogen production by solar driving water splitting is a promising energy generation way. The development of hydrogen production is based on the fact that it is an ideal fuel for the future [52]. Among the different approaches to release hydrogen gas, photoelectrochemical (PEC) water splitting is the most promising. Overall water splitting reaction can be written as:



A PEC cell consists of two electrodes: one is called anode/photoanode and another is cathode/photocathode. On the surface of cathode, H<sub>2</sub>O molecule is reduced:



whereas on the anodes, it oxidized.



where e<sup>-</sup> is an electron and h<sup>+</sup> is a hole.

This process must take place under solar irradiation. Efficiency of this process depends on the following factors:

- (1) The ability of photoelectrodes to adsorb a photon
- (2) The performance of creation charge carries
- (3) The efficacy of charge carriers in the water splitting process.

To overcome these affecting factors on the efficiency of the cell, scientists need to develop more ideal electrodes. It means the control of all technical parameters including thickness of semiconducting layer, morphology, and density of particles, which forms active layer and so on. A simple way to control the distance between the electroactive species inside of multilayer structure is offered by LbL assembling [53]. Absorption of light by semiconducting materials results in creation an exciton, electron-hole pair. To use an exciton in the water splitting process, it must be separated. The separated electron and hole act as reduction and oxidation centers. Coupling of two different types of active materials allows the faster separation of exciton. For example, a couple of anatase and rutile phases of  $\text{TiO}_2$  improves the separation of exciton, created in the anatase structure [43]. In order to obtain a homogeneously distributed anatase/rutile, a heterostructure LbL approach is applied. The LbL assembling to building of anatase/rutile heterostructure is carried out in the presence of poly(sodium-4-styrenesulfonate) (PSS). This polymer serves as an adsorption layer. The rutile phase of  $\text{TiO}_2$  coated by PSS adsorbs an anatase structure. To remove polymer inter-layer and form good attachment between rutile and anatase the obtained material is heated up to  $500^\circ\text{C}$  (Figure 6).

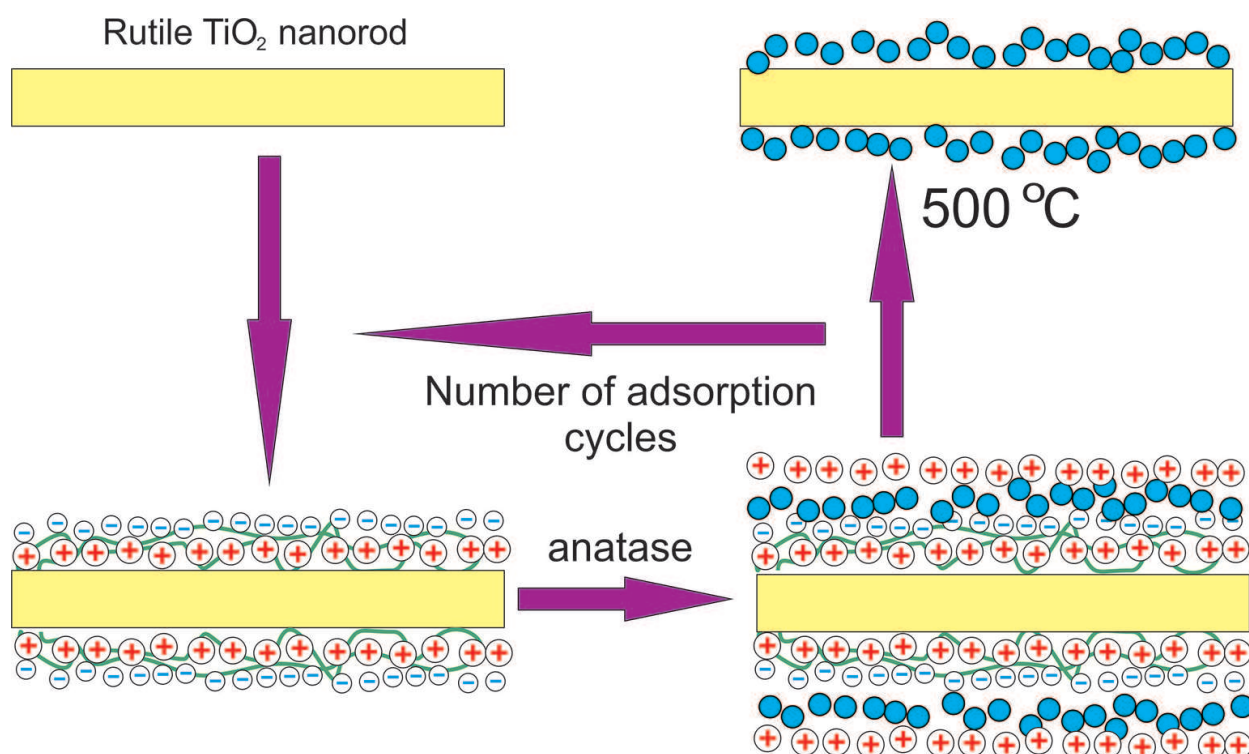
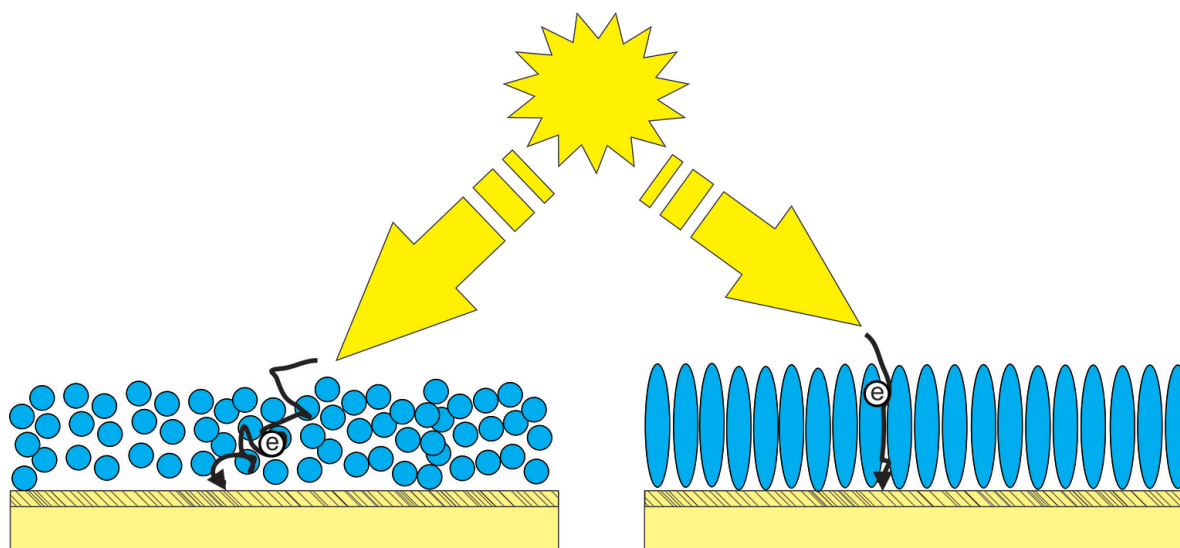


Figure 6. Formation of rutile/anatase heterostructure by LbL assembling.

Improvement of solar energy conversion can be achieved using an aligned structure, such as ZnO nanorods, because of reducing the charge pathway (**Figure 7**). The ZnO is a broadly used as a wide band gap semiconductor [37], and it plays a great role in gas sensing, optical and electrical devices. In spite of similarity of band structures between ZnO and  $\text{TiO}_2$ , electron mobility on ZnO is much higher. But negligible instability of ZnO in an aqueous solution makes it unfavorable for this material in the water splitting process. Recently, protection of ZnO was offered by building a core/shell structure, where a core is ZnO and a shell is represented by narrow band gap semiconductors. Covering of ZnO nanorods by narrow band gap CdS was studied a lot. The most attractive approach for it is using of SILAR technique [20, 54, 55]. The covering of free-standing ZnO nanorods by  $\text{CeO}_2$ , CdS, and Ag nanoparticles proceeds, as shown in **Figure 8**. The negative charges on the ZnO surface are formed by immersing the substrate into PAH and PSS. Then, the oppositely charged ions ( $\text{Ce}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ) are adsorbed on the surface of negatively charged ZnO nanorods due to strong electrostatic attraction. Reduction of metal ions is performed by  $\text{NaBH}_4$ . To use such composition for PEC water splitting or in dye-sensitized solar cells they should have a good contact to the electrode.



**Figure 7.** Schematic representation of the electron transport process through nanoparticles (a) and nanorods (b).

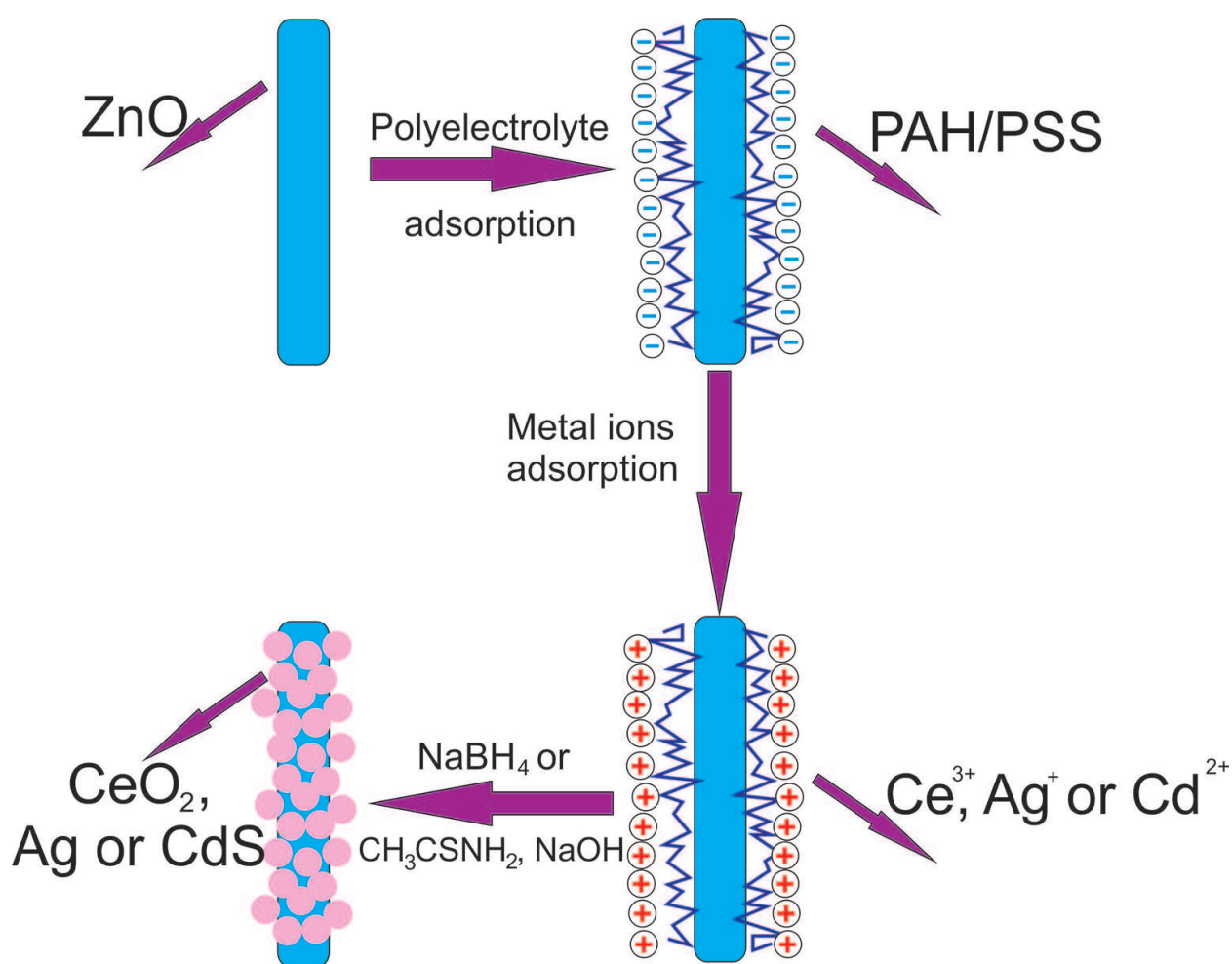
The immersing of the conductive substrate coated by aligned ZnO nanorods in two different aqueous solutions of  $\text{Cd}^{2+}$  cations and  $\text{S}^{2-}$  anions for 20 second allows to obtain a ZnO/CdS core-shell structure, which is a suitable heteromaterial for water splitting application. Effectiveness of such PEC water splitting of the ZnO/CdS core-shell composition has been showed an increased open voltage of around  $-1.55$  V vs. bare ZnO arrays whose open voltage is  $-0.8$  V [56].

### 3.2. Reduction and oxidation of organic substrates by metal nanoparticles immobilized within LbL films and membranes

In the past few years, LbL films and membranes are more commonly used in catalytic processes. Films with incorporated metal nanoparticles synthesized by the LbL technique are commonly used for multifunctional catalytic applications, including photocatalysis, thermal



catalysis, and electrocatalysis, which means the reduction [57] and oxidation of various organic substrates [18, 58]. Authors [59] showed that LbL covalently stacked multilayer structure of immobilized metal nanoparticles ensure the stability of particles against aggregation. Such multilayer structure can be achieved by embedding the nanoparticles into a porous polymer membrane. The porous structure of polymer membrane is utility to creation of concentration gradient between the aqueous medium and reaction centers, which accelerate the reaction rate. The catalytic activity of immobilized metal nanoparticles within the polymer scaffold depends on the number of bilayers as well as the size of the particles. For instance, 10 bilayers show higher catalytic activity than the higher numbers of layers. While the high number of bilayers exhibits good stability. The optimization of such criteria is possible by modulating the number of layers in the LBL structure, which allows to prepare highly catalytic active and stable films using this simple and versatile approach.



**Figure 8.** Using the LbL technique for covering free-standing ZnO nanorods by  $\text{CeO}_2$ , CdS, and Ag nanoparticles.

The multilayered metal nanoparticles deposited onto  $\text{TiO}_2$  nanotubes demonstrate efficient thermal catalytic activities toward reduction of nitrophenol to nitroaniline under ambient conditions [60]. The catalytic properties of metal nanoparticles/ $\text{TiO}_2$  nanotubes (M/TNT) nanocomposites are



achieved mainly due to the distribution of monodispersed metal nanoparticles on TNT [61, 62]. It is evident that distribution of nano objects onto a substrate affects the catalytic performance of multilayer films. Therefore, surface modification of 1D semiconductors through the LbL assemble strategy can be used as an effective way to achieve a uniform deposition of metal nanoparticles for various catalytic applications. The electrocatalytic performances of LbL-assembled multilayers are also extensively exploit for selective hydrogenation of a series of unsaturated alcohols [34] and methanol oxidation. For example, a strong synergistic catalytic behavior exhibits polyaniline-Pt (PANI/Pt) nanocomposites fabricated by the modification of LbL assembly by electrodeposition [42]. Such synergic catalytic activity is used for methanol oxidation. But the catalytic activity of such composites depends not only on a number of layers (and hence the Pt loading) but mostly on nature of the outermost layer. The catalytic activity of such multilayers can be enhanced when they end by the PANI layer as the oxidation of methanol by Pt particles facilitated by the formation of hydrogen bonds with the outer PANI layer.

#### 4. Concluding remarks

Immobilization of metal and semiconducting nanoparticles within the multilayer structure by the LbL self-assembling technique is an effective process to design drug delivery systems, capacitors, sensors, solar and fuel cells, quantum dots, catalysts with unique properties. Gold, silver, palladium, and platinum nanoparticles incorporated into the polymer thin films leads to enhancement of plasmonic and catalytic properties, which can be easily tuned by changing multilayer structure. Preparation of nanocatalysts using the LbL assembly technique represents a comparatively simple, robust, efficient, and highly versatile method and demonstrates significant advantages over routine methods. The multilayer thin films containing metal nanoparticles demonstrate efficient catalytic activities toward reduction of nitrophenol, oxidation of methanol, and selective hydrogenation of unsaturated alcohols under ambient conditions. One of the promising areas is to use the LbL technology for photocatalytic decomposition of water. Photoelectrochemical cells can be develop by alternately applying of organic and inorganic semiconducting materials and dyes on transparent conductive substrates such as indium tin oxide glass, aluminum-doped zinc oxide glass, and so forth. It is anticipated that the LbL methods and technologies will definitely expand its horizon toward practical applications in the commercial realm and to new discoveries in the fields of polymer and materials science and engineering.

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