

# Highly Stable & Oppositely charged Hybrid Nanomaterials

## Fine tuning of their Electro-static interactions to fabricate Functional surfaces

S. Sekar\*, E. Feltrin\*, J. Giermanska\*, J.-F. Berret\*\*, J.-P. Chapel\*

\*Centre de Recherche Paul Pascal (CRPP), UPR CNRS, Université Bordeaux 1, 33600 Pessac, France

\*\*Matière et Systèmes Complexes (MSC), UMR 7057 CNRS, Université Denis Diderot Paris-VII,  
Bâtiment condorcet, 75205 Paris, France

chapel@crpp-bordeaux.cnrs.fr

### ABSTRACT

We report on the generation of Smart hybrid functional surfaces via a novel surface functionalization pathway termed as Surface Grown Hybrid Functional Layers or SgL, which competes with the conventional Layer-by-Layer (LbL) approach. In SgL approach, the smart surfaces were generated in a single step at a fluid/solid interface through fine tuning of electro-static interaction between the *stable* oppositely charged building blocks (BBs) as a function of the ionic strength of the dispersion. Admixing of the oppositely charged BBs at high ionic strength resulted a dormant solution, where the electrostatic interaction is completely *switched off*. The complexation between the BBs can be triggered by *switching back on* the interaction via a controlled removal of salt (desalting) by dialysis or dilution with water yield a reactive solution. The onset of this *desalting transition* at a given substrate enabled the fabrication of smart hybrid layers with unique morphology, properties and applications.

**Keywords:** electro-static complexation, hybrid materials, desalting transition, layer-by-layer, functional surfaces.

### 1 INTRODUCTION

Over the past two decades, an extensive body of research works have been devoted to the development of versatile hybrid functional surfaces, one of the final goals of modern chemistry, physics and biology. The fabrication of such functional surfaces at nanometer level has enabled their applications in a wide range of fields. In particular, the electrostatic complexation between the oppositely charged inorganic nanomaterials and organic macromolecules at an interface is a promising pathway to generate versatile hybrid layers, combining the advantageous properties of organic and inorganic worlds. So far, the conventional and very popular Layer-by-Layer (LbL) [1] is the most widely used technique to perform such interfacial hybrid complexation. But has a serious drawbacks such as it is a time consuming and tedious process to fulfill many industrial requirements. We propose an alternate approach that overcomes the drawbacks of LbL, named Surface grown hybrid functional layers or SgL, based on the

concept of “desalting transition” inspired from molecular biology by Berret et al [2]. In which, the ionic strength ( $I_s$ ) is used as a key factor to fine tune the electrostatic complexation between the oppositely charged BBs, when the interaction between them is *solely* driven by electrostatic forces. The mixing of oppositely charged components at high  $I_s$  resulted a “clear dormant” solution, where the electrostatic interaction is completely *switched off* by the screening effect of salt. The interaction between them can be *switched back on* by the controlled removal of salt either by dialysis or dilution resulting in a “turbid-reactive” solution via the spontaneous association of the reacting species. The bulk transition from a clear state to a turbid state is known as the critical ionic strength  $I_b$  of a specific system put under scrutiny. Beyond which electrostatic clusters were formed. By fine tuning the rate of removal of salt, the size of the clusters can be tuned from nanometer to micrometer level. We have extended this *bulk desalting transition* at an interface to generate hybrid functional surfaces with tunable thickness as function of  $I_s$ . Therefore the most important criteria to meet the concept is that the individual BBs *must* be stable under high  $I_s$ .

The fine tuning of the electro-static interaction cannot be enabled on the bare inorganic colloidal dispersions, as they are not generally stable beyond  $10^{-2} M$  [3]. An extra repulsive force must then be added to overcome the van der Waals attraction that drives the aggregation which is better played by macromolecules. The surface functionalization of inorganic nanomaterials with macromolecules resulting the hybrid materials were extensively studied by many authors. But not much attention has been paid on their stability issues especially under high salt content. In this frame work, we address the issue in overcoming the saline barrier via the formulation of various novel hybrid materials composed of inorganic ceria ( $CeO_2$ ), silica ( $SiO_2$ ) and multi-walled carbon nanotubes (MWCNTs) as core and charged organic polyelectrolytes as corona. Those electrostatically stabilized hybrid BBs were formulated via various synthetic routes including the “non-covalent” and “covalent” approach. The resultant highly saline stable cationic and anionic  $CeO_2$ ,  $SiO_2$  and MWCNTs exhibited the “desalting transition” in bulk. The onset of their bulk desalting transition at an interface generated different

functional surfaces with specific surface properties and applications include anti-corrosive, superhydrophobic and thin transparent conductive surfaces.

## 2 UNIVERSALITY OF BULK DESALTING TRANSITION

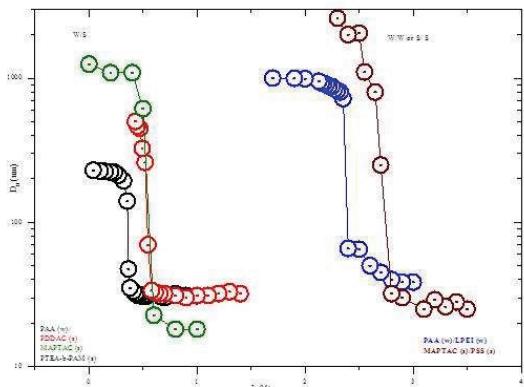


Figure 1. Hydrodynamic Diameter  $D_H$  as a function of  $I_s$  for PEs system. [complexation of PAA with PTEA-b-PAM, black; PDDAC, red; MAPTAC, green; PEI, blue; complexation of MAPTAC with PSS, brown;]

The figure 1 indicates that the measurement of hydrodynamic diameter ( $D_H$ ) as a function of  $I_s$  for the oppositely charged pure polyelectrolytes (PEs) of weak/strong and weak/weak or strong/strong systems. All the PEs, except the block copolymer, were purchased from sigma aldrich. Whereas PTEA-b-PAM was synthesized by MADIX technology. In all the five systems investigated, a small  $D_H$  at initial ionic strength ( $I_0$ ) (1M or 4M of  $\text{NH}_4\text{Cl}$ ) indicates the effective screening and “dormant” nature of the oppositely charged species. Step-dilution with water triggered the co-assembly and resulting in the formation of “organic” clusters with decreasing  $I_s$ . Just before passing through a sharp transition at  $I_b$  (specific to the PEs systems), very large organic electrostatic complexes were generated due to the charge compensation between the cationic and anionic species. The above feature concluded that “desalting transition” is a “universal phenomenon” [4], as it showed the transition for all the systems investigated, independent of the nature of PEs considered. However the sizes of the complexes were found to be strongly depend on the conformation and Mw of PEs. This specific desalting experiment serves as a reference experiment for the desalting transition of oppositely charged hybrid BBs as these PEs were used as stabilizers for various inorganic cores of  $\text{CeO}_2$  (provided by Rhodia),  $\text{SiO}_2$  and MWCNTs (Arkema).

## 3 FORMULATION OF HYBRID BBs

The figure 2 represents the synthesis of MWCNT-PEs nanocomposites via the covalent and non-covalent approach. The cationic branched polyethyleneimine (bPEI, Mw ~25000) and anionic polyacrylic acid (PAA, Mw ~5000) were covalently attached with carboxylic acid and ethylenediamine functionalized MWCNTs respectively via amide linkage mediated by the carbodiimide cross-linkers such as 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, hydrochloride and N-hydroxysuccinimide (EDC.HCl/NHS). The stability assessment by dynamic light scattering (DLS) technique concluded that among the various approaches and stabilizers investigated, the covalent attachment of PEs is a promising way to obtain stable hybrid dispersions which are stable up to 4M of  $\text{NH}_4\text{Cl}$ . By using this approach, highly saline stable dispersions of cationic and anionic  $\text{CeO}_2$  and  $\text{SiO}_2$  hybrid BBs were formulated similarly. The stability property turned out these hybrid BBs as a suitable candidate for the “desalting transition”. As a proof of this concept, preliminary desalting kinetics experiments were reported on the stable anionic  $\text{CeO}_2/\text{Fe}_2\text{O}_3$  nanoparticles and oppositely charged PEs [4,5].

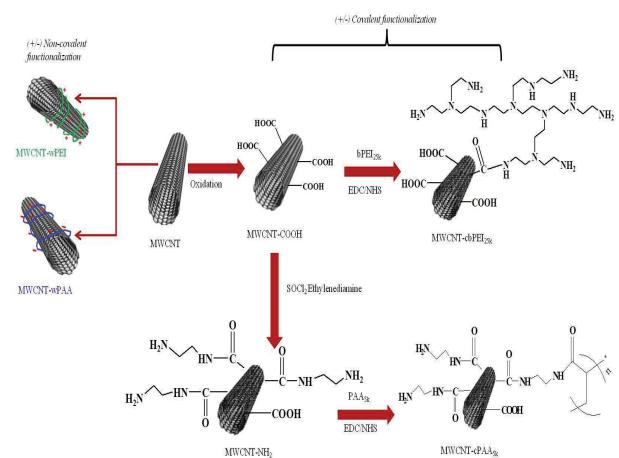


Figure 2. Schematic representation of non-covalent and covalent functionalization of MWCNTs with PEs and small ligands.

The observations encouraged us to use this trigger to control the co-assembly of oppositely charged formulated hybrid BBs. The fine tuning of electro-static interaction by  $I_s$ , indeed resulted various electrostatic “hybrid clusters” with versatile morphologies and properties. This “bulk” behaviour provokes us to extend this approach at a fluid/solid interface.

## 4 FABRICATION OF FUNCTIONAL SURFACES

### 4.1 Layer-by-Layer approach (LbL)

As mentioned earlier, the conventional LbL possess many drawbacks. However, used as the benchmark, where the hybrid functional surfaces were developed via the sequential deposition of oppositely charged BBs, as shown below.

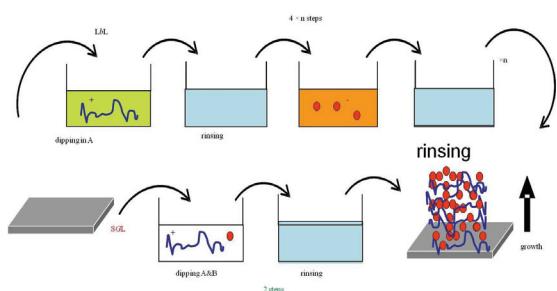


Figure 3. Schematic illustration of sequential Layer-by-Layer (LbL) and the surface grown layers (SgL).

The growth of the multilayer was monitored on a model surface with the help of Quartz Crystal Microbalance (QCM) technique. The amount of mass adsorbed ( $\Delta m$ ) was calculated from the frequency decrease ( $\Delta f$ ) using the Sauerbrey equation, as follows.

$$\Delta m = -C \frac{\Delta f}{n} \quad (1)$$

C = Sauerbrey constant

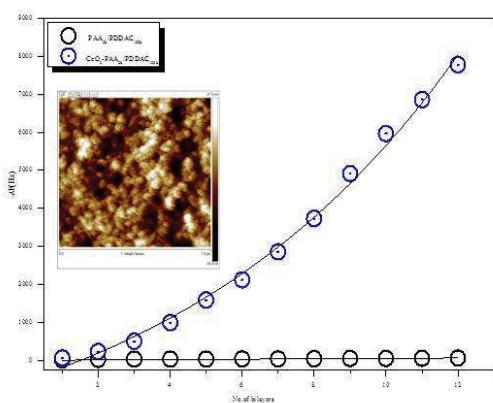


Figure 4. LbL between  $(\text{CeO}_2\text{-PAA/PDDAC})_{12}$  and the insert shows the AFM image of these layers.

The figure 4 represents the successful growth of multilayer from the LbL self assembly between anionic

PAA modified  $\text{CeO}_2$  and PDDAC, in comparison with the pure PEs scaffolds [6]. The increment in the  $\Delta m$  indicates the sequential deposition of BBs. Atomic Force Microscopy (AFM) analysis on these self assembled layers after drying under nitrogen flow showed the densely packed structures of  $\text{CeO}_2$ .

### 4.2 Surface grown Layers (SgL)

The desalting transition between the oppositely charged hybrid BBs at a fluid/solid interface generated different functional surfaces. The figure below shows the spontaneous growth at the interface triggered by salt for the oppositely charged anionic  $\text{CeO}_2$  and PDDAC. The functional surfaces from  $\text{CeO}_2$ , MWCNTs and  $\text{SiO}_2$  BBs respectively exhibited anti-corrosive, thin transparent conductive and superhydrophobic properties.

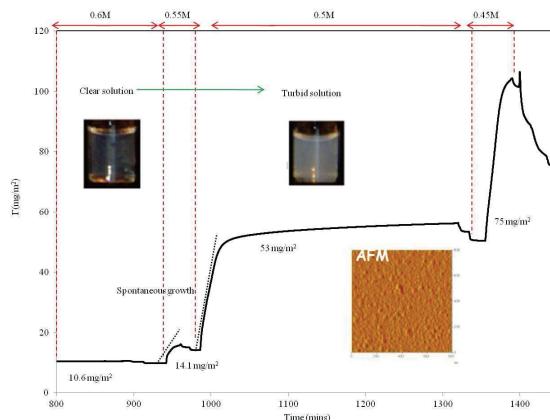


Figure 5. SgL between  $(\text{CeO}_2\text{-PAA/PDDAC})$  tuned by  $I_s$ .

## 5 CONCLUSION

Highly saline stable various oppositely charged hybrid BBs were formulated. The possibility to switch off/back on the electrostatic interaction was achieved by tuning the  $I_s$ . Versatile hybrid functional surfaces were successfully fabricated via both the LbL and SgL and showed unique surface properties and applications. In future this SgL approach can be used to develop heterostructured materials.

## REFERENCES

- [1] Decher, "Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites," *Science*, 277, 1232-1237, 1997.
- [2] Fresnais, "Nanoparticle Aggregation Controlled by Desalting Kinetics," *J. Phys. Chem. C*, 113, 16371-16379, 2009.
- [3] Buettner, "Aggregation kinetics of cerium oxide nanoparticles in monovalent and divalent

- electrolytes," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 366, 74-79, 2010.
- [4] Yan, "Magnetic Nanowires Generated via the Waterborne Desalting Transition Pathway," *ACS Applied Materials & Interfaces*, 3, 1049-1054, 2011.
- [5] Qi, "Influence of the Formulation Process in Electrostatic Assembly of Nanoparticles and Macromolecules in Aqueous Solution: The Interaction Pathway," *J. Phys. Chem. C*, 114, 16373-16381, 2010.
- [6] S.T.Dubas, "Polyelectrolyte Multilayers Containing a Weak Polyacid: Construction and Deconstruction," *Macromolecules*, 34, 3736-3740, 2001.