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Thin polymer films as sacrificial layers for easier cleaning

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ABSTRACT

We propose a new approach for the removal of fouling agents from an interface. The interface is pre-coated with a polymer layer of a few nanometers thick that can be removed by a simple trigger such as a change in pH or salt concentration. When fouling agents adsorb on the interface, they can be removed by simply desorbing (sacrificing) the polymer coating. We show a proof of principle of this concept on the basis of two different types of sacrificial layers. The first system consists of a silica surface that is pre-coated with a polyelectrolyte multilayer of poly(allyl amine) hydrochloride (PAH) and poly(acrylic acid) PAA. The outer layer of the polyelectrolyte multilayer is the positively charged PAH and on top of that silica particles are adsorbed. We investigated the release of silica particles upon a pH drop (leading to desorption of the multilayer) as a function of the number of polyelectrolyte layers in the multilayer. Four layers are already enough to significantly enhance desorption of the silica particles (70% removal). With fourteen layers (total adsorbed amount of polymer approximately 6 mg/m^2) the silica particles are completely removed.

The second system consists of a weak poly(acrylic acid) (PAA) brush, coated with an extra layer of PAA. At low pH the polyelectrolytes are uncharged, and the double polyelectrolyte layer is stable. However, when the pH is increased, the polyelectrolytes become charged and the extra PAA layer is removed, including any attached fouling agents. For this system, we show proof of principle of the sacrificial layer approach by measuring the hydrodynamic force necessary to remove PS particles (radius 3 μm) from a PAA brush. We show that the hydrodynamic force for removal is two orders of magnitude lower for the sacrificial layer system (PAA brush plus extra layer of PS-PAA), than for the PAA brush alone.

1. Introduction

Over the years much research has been dedicated to making cleaning easier. This has brought forward a number of very different approaches. The oldest approach is to use surfactants [1,2], amphiphilic molecules that can significantly reduce the attractive interaction between a surface and a fouling agent. Another approach is to use self-cleaning surfaces such as ultra-hydrophobic coatings [3,4]. These coatings are so hydrophobic that water will form almost spherical droplets that “roll off” the (tilted) surface taking with it any dust or dirt particles. A third approach is to prevent the fouling of surfaces by using anti-fouling layers. The polymer brush [5,6] is the best known example of such a layer, where the steric hindrance from the polymers in the brush prevents fouling agents such as proteins to reach the interface [5,6].

What all these approaches have in common is that, although they have been proven to work very well for a large number of fouling agents, none of them is universally applicable. This means that for every system there are fouling agents for which they are unsuitable. Surfactants in aqueous solution work extremely well to remove hydrophobic fouling agents but are much less effective in removing hydrophilic objects, especially from hydrophilic surfaces. For example, the polymer poly(ethylene oxide) (PEO) adsorbs cooperatively with the surfactant sodium dodecyl sulphate (SDS) to a silica surface [7]; non-ionic surfactants can remove PEO from a silica surface, but this happens only if the PEO chain is short [8]. The ultra-hydrophobic surfaces work well for the removal of larger particles, but will never work for hydrophobic particles in the nanometer range, or for protein molecules, as these objects are smaller than the roughness on which the ultra-hydrophobicity depends. Brushes, often made of PEO chains, are very suited to prevent the adsorption of proteins, but silica particles are found to adsorb in large adsorbed amounts to these brushes [9].

In this paper we present a new approach to cleaning surfaces: the use of a sacrificial layer of a few nanometers thick. A surface can be pre-coated with a thin polymer layer that can be desorbed from the surface by a simple trigger, such as a change in pH or in salt concentration. Any fouling agent that is adsorbed to the interface can then be removed by desorbing (or sacrificing) the polymer layer. This approach has a great advantage: as no direct contact between the interface and the fouling agent needs to be broken, it has the potential to work for any fouling agent. Limitations, however, are

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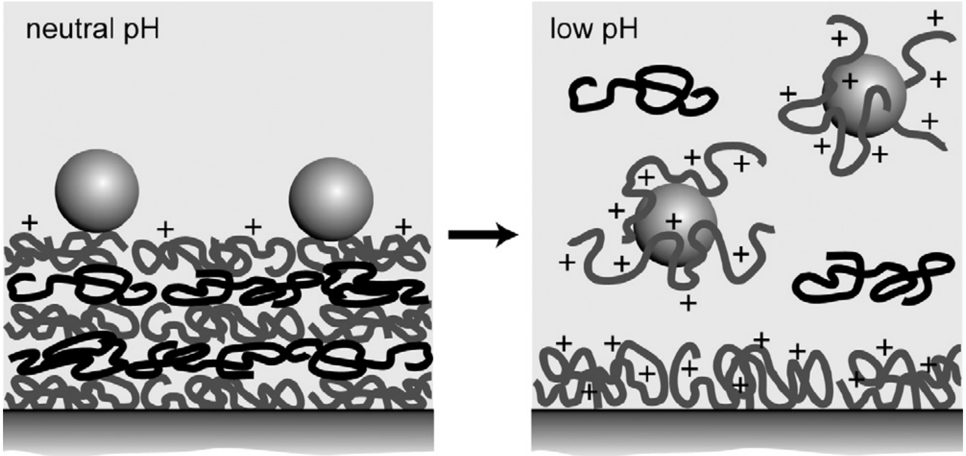

Fig. 1. Schematic depiction of the potential application of a polyelectrolyte multilayer as a sacrificial layer. Fouling agents are adsorbed to the multilayer but upon a change of the pH, the layer desorbs, taking with it the adsorbed fouling particles. Released polyelectrolytes cover the particles and prevent re-adsorption.

that a specific trigger is necessary to remove the sacrificial layer, and that after every cleaning step, the surface has to be re-coated. On a macroscopic scale this kind of approach is already commonly used in, for example, consumer electronics. View screens in mobile phones, etc. are protected by a thin sheet of plastic called a tear-off. When the consumer buys the product, any grease or dust on the view screen can simply be removed by peeling of the tear-off. However, as far as we know this concept has never been studied before using molecular 'tear-off' layers that are only a few nanometers thick.

Here we consider two systems that would both be well suited as sacrificial layers. The first is a system of polyelectrolyte multilayers [10,11]. By subsequent adsorption of two oppositely charged polyelectrolytes one forms a dense polymer layer at the surface. The thickness of the layer can be tuned simply by the number of adsorption steps, while by choosing the right polyelectrolytes one can provide a trigger (such as a change in pH or salt concentration) that leads to the destruction of the layer [12]. An extra benefit might be that the polyelectrolytes that are released into solution upon destruction of the layer could well act as so-called anti-redeposition agents: by adsorbing to the released fouling agents they might prevent possible re-adsorption of the fouling agents. We schematically show this concept in Fig. 1. To give a "proof of principle" for the application of such multilayers as sacrificial layers we use polyelectrolyte multilayers in combination with silica particles.

The second system that we investigate consists of a weak polyelectrolyte brush that has been coated with an extra layer of the same weak polyelectrolyte. The polyelectrolyte in the coating is connected to a short hydrophobic block inherent to the preparation method (see Section 2). This system is stable at a pH at which the polyelectrolyte is uncharged. Changing the pH so that the polyelectrolyte becomes charged leads to the removal of the extra layer, including any attached fouling agents. This approach is schematically shown in Fig. 2. To determine how well this system is suited to remove fouling agents, we measure the hydrodynamic force necessary to remove 50% of previously attached PS particles (radius 3 μm). This so called critical removal force is a measure for the adhesive force between the particle and the interface [13,14].

2. Materials and methods

2.1. Polyelectrolyte multilayers

The adsorption and desorption of polymers and particles was followed with fixed-angle optical reflectometry using an impinging jet flow-cell. A detailed description of the reflectometer setup is provided by Dijt et al. [15]. It contains a He-Ne laser (monochromatic light, $\lambda = 632.8$ nm) with linearly polarized light. Change in polarization is measured by simultaneously detecting the parallel (R_p) and the perpendicular (R_s) reflectance and dividing R_p by R_s

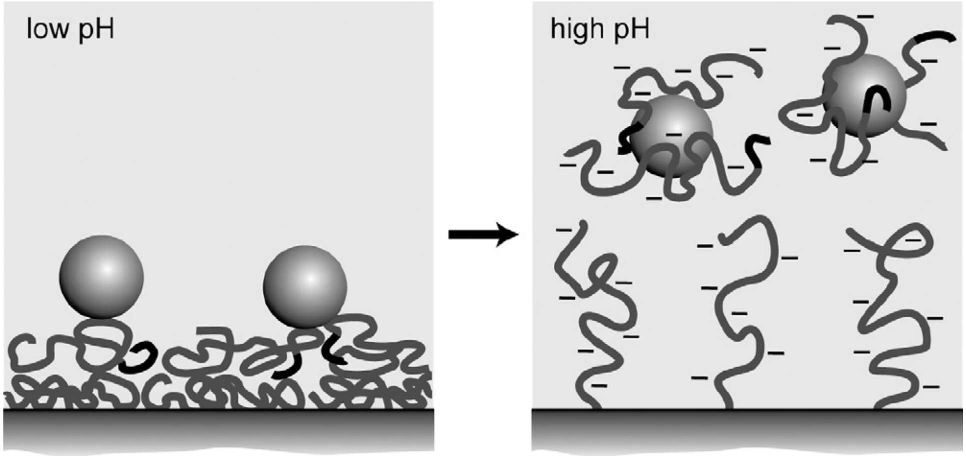

Fig. 2. Schematic representation of the approach to use as a sacrificial layer, a weak polyelectrolyte brush (anionic in this figure) coated with an extra layer of the same weak polyelectrolyte. At low pH the polymers are uncharged and the layer is stable, at high pH the polyelectrolytes are charged and the extra polyelectrolyte layer, including adsorbed fouling agents, desorbs from the interface.