



Impact of polyelectrolyte coating in fluorescent response of Eu(III)-containing nanoparticles on small chelating anions including nucleotides



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ABSTRACT

The present work introduces a novel route to sense the permeability of the polyelectrolyte layer deposited onto luminescent core. The use of ternary Eu(III) complexes as the luminescent core enables to detect the permeability of the polyelectrolyte layers through the change of the Eu(III)-centered luminescence. The chelating anions, such as adenosine phosphates, glutamic acid and ethylenediaminetetraacetic acid disodium salt were used as substrates. The origin of the fluorescent response is the complex formation of the substrates with the Eu(III) complexes, which is greatly affected by the equilibrium concentration of the substrates at the surface of the core. The latter in turn is influenced by the permeability of the polyelectrolyte layer. The obtained results highlight the impact of the nature of the exterior layer in the penetration of the substrates through the negatively and positively charged polyelectrolyte layers.

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1. Introduction

The layer-by-layer deposition of oppositely charged polyelectrolytes is widely applied to build up capsules for drug delivery, as well as to protect hazardous magnetic or luminescent templates from the environment [1–9]. This sort of coating is soft, since it is based on a cooperative effect of rather weak non-covalent interactions [6]. Nevertheless the colloids that resulted from the adsorption and further layer-by-layer deposition of multi-charged polyelectrolytes onto hard templates are both stable enough and stimuli responsive. Thus a permeability of small molecules through a polyelectrolyte multilayer is a key point in the development of both polyelectrolyte capsules and core-shell nanomaterials. Moreover environmentally controlled gating of substrates is of particular importance in drug delivery development [10]. The covalent labeling of substrates by organic luminophores is the known route to reveal the penetration of substrates through polyelectrolyte layers [11,12]. Radiolabeling should be mentioned as another route to detect the ion exchange between the polyelectrolyte multilayer and the bulk of solution [6]. The encapsulation of the dye nanocrystals into polyelectrolyte capsules and following monitoring of its release exemplify more facile route to study the permeability of the polyelectrolyte multilayers [13,14]. The specified stability of these colloids in time is explained by the slowed down exchange between polyelectrolytes

within the multilayer and those in the solutions [15]. Taking into account that kinetic control is predominant versus thermodynamic one in the deposition of polyelectrolyte layers on templates, the mechanisms of release and/or penetration of substrates should significantly depend on their nature. Thus a development of facile procedure to monitor the penetration of small molecules through polyelectrolyte capsules is still an appealing task.

Our previous results highlight the encapsulation of the Eu(III) luminescent complexes as the hard templates or cores into capsules built through layer-by-layer polyelectrolyte deposition [16]. The encapsulation of [Eu(TTA)₃1] (TTA[−] and **1** are thenoyltrifluoroacetate and phosphine oxide derivative) in the form of nanosized templates into polyelectrolyte capsules built from the oppositely charged poly(sodium 4-styrenesulfonate) (PSS) and polyethyleneimine (PEI) represents a convenient route to develop stable in time colloids with efficient Eu(III) centered luminescence [16,17]. The ligand exchange at the nanoparticle/water interface is the reason of the substrate induced sensitization or quenching of the luminescence, which has been successfully applied in the sensing of fluoroquinolones in aqueous solutions [18]. Thus the ligand environment of Eu(III) ion is of great impact in the substrate induced luminescence response of the Eu(III) containing cores. Moreover our previous work highlights the nature of the exterior layer and the number of layers as the factors affecting the luminescence response arisen from the interfacial complex formation [18]. These results point to the permeability of the analytes through the polyelectrolyte layers as the key point in the improvement of the substrate

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