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Multilayer lectin–glyconanoparticles architectures for QCM enhanced detection of sugar–protein interaction

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Multivalent biorecognition of lectin layers by glyconanoparticle sugar-clusters has been used to generate multilayer nanoplatform architectures in a QCM sensing setup.

Constitutional Dynamic Chemistry (CDC) provides an evolutional approach to the generation of chemical diversity through the synergetic implementation of reversible covalent reactions at a molecular level and non-covalent intermolecular interactions at a supramolecular level.[1] The self-assembly of the components into well-defined architectures across size scales, controlled by mastering constitutional affinities, embodies the flow of structural information from the molecular level toward nanoscale dimensions. Constitutional materials composed of 2-D/3-D architectures of reversibly interacting components are becoming increasingly important as a viable solution to post-synthetically assembled systems.[2] Multilayers fabricated through layer by layer (LBL) assembly with nanoparticles (NPs) appear to be a promising route towards controlled film morphologies at the nanoscale. Previous examples are predominantly based on bifunctional covalent cross-linkers and electrostatically passivated NPs.[3] Supramolecular multivalent layer by layer assembly has been described for dendrimers and functionalised NPs.[4,5] The assembly using large biomolecules is limited to a few cases such as NPs–myoglobin[5] or lysozyme–NPs[6] multilayers. Gold NPs–biomacromolecule hybrid multilayer films have attracted interest again, based on their colorimetric properties as well as electrochemical sensing capabilities.[7] Nanoparticles layers have been used to enhance Quartz Crystal Microgravimetry (QCM) sensitivity.[8] QCM frequency change enhancement probes have already been demonstrated for the biotin–streptavidin interactions,[8a] for enhanced DNA detection[8b] and glycoNPs–lectin or glyco-vesicles–lectin interactions.[8c-f] All these applications are related to the formation of a single glyco-nanoplatform layer on the lectin immobilized surfaces. With all these in mind, herein our efforts have been concentrated on preparing glycoNPs–lectin composite multilayers organised through specific carbohydrate–lectin multivalent recognition. Our strategy relies on specific very weak sugar–lectin interactions. Evidence is presented that such multivalent interactions between gold glycoNPs and Concanavalin A (Con A) can be efficiently used for the construction of multilayered composite architectures and for important enhancement of QCM detection and quantification of carbohydrate–lectin interactions.

It has been previously demonstrated that Con A retains its activity upon physical immobilisation on hydrophobic surfaces.[10] For this study, Con A was immobilised on QCM quartz crystals by combinations of a non-specific hydrophobic interaction and by recognition of mannan polysaccharide. Specific adsorption through mannoside recognition is a useful method for Con A immobilisation and can be accomplished with self-assembled hydrophobic monolayers (SAMs) or adsorbed films of high specificity.[8] Mannan adsorbed on a polystyrene surface of a QCM electrode was demonstrated as an effective Con A immobilisation procedure in experiments by Pei *et al.*[9]

Here we extended this procedure to a more hydrophobic surface of octadecanethiol (ODT) monolayer obtained on a gold surface of

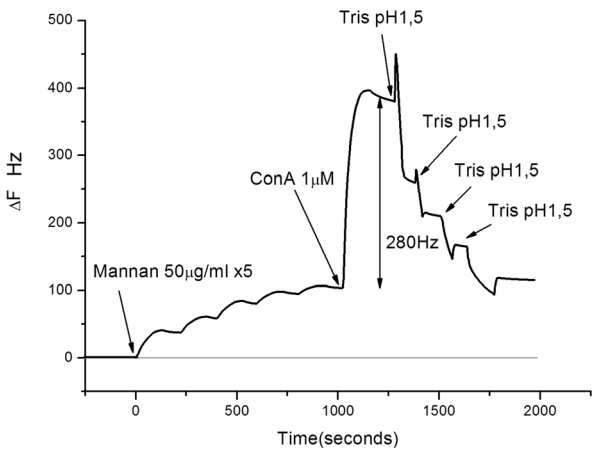

Fig. 1 Con A immobilization on mannan film on a ODT hydrophobic surface of a QCM electrode.

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