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The effect of gold nanoparticles on the impedance of microcapsules visualized by scanning photo-induced impedance microscopy

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ABSTRACT

Polyelectrolyte microcapsules have attracted great interest in drug delivery applications, and microcapsules modified with gold nanoparticles have been used in this way with triggered release when a laser can be used to remotely open shells through light-induced local heating. The electrical impedance of unmodified microcapsules has been studied due to its implications for their permeability, however, the impedance of functionalised microcapsules has not yet been investigated. Herein, the impedance of microcapsules modified with gold nanoparticles was studied for the first time. It was shown that the modification of microcapsules with gold nanoparticles leads to a much greater impedance than would be expected from the increase in the thickness caused by the presence of a layer of gold nanoparticles alone. The impedance of gold nanoparticle modified capsules was measured using scanning photo-induced impedance microscopy (SPIM), which is based on photocurrent measurements at an electrolyte-insulator-semiconductor (EIS) field-effect structure. High resolution and good sensitivity were achieved using a two-photon effect for charge carrier excitation and organic monolayer modified silicon-on-sapphire (SOS) as the SPIM substrate. SPIM allowed impedance imaging of collapsed microcapsules with unprecedented detail. SPIM images of capsules labelled with gold nanoparticles (AuNPs) showed a good agreement with the corresponding optical images, including the creases resulting from the collapse of the hollow shells. The significant increase in impedance caused by the impregnation with AuNPs was also verified by conductive Atomic Force Microscopy (C-AFM) measurements in the dry state.

1. Introduction

Polymeric multilayer capsules (PMLCs) assembled by layer-by-layer (LBL) approach on a sacrificial template continue to receive considerable attention because of their wide ranging applications in drug delivery, sensing, microreactors and smart materials [1–3]. Whilst the LBL assembly technique allows the design and modification of hollow microcapsules in a controllable way, the impregnation of the capsule shell with gold nanoparticles (AuNPs) is undoubtedly one of the most attractive ways to tailor their functionality [4–7]. For example, laser-induced remote drug release is based on localized heating due to surface plasmon resonance absorption by the nanoparticles [8–10]. Extensive research has also been carried out into the light sensitivity of AuNP modified PMLCs, and force deformation experiments have shown an improvement in the shell stiffness due to doping with AuNPs [11]. Moreover, a higher bending stiffness, elastic modulus and robustness have also been reported for free standing poly(allyl amine hydrochloride) (PAH)/poly(sodium 4-styrene sulfonate) (PSS) membranes with a central layer containing gold nanoparticles [12]. It has been reported that the ionic permeability and the integrity of the PMLC wall are closely related to their electrical impedance [13,14]. Electrorotation [13], and a microfluidic single particle impedance chip [14] have both been used to measure the impedance of PAH/PSS microcapsules reporting dielectric constants of 60 and 50 indicating a high water content of the capsule wall. However, the effect of AuNP doping on the electrochemical properties has not yet been studied. In this work, we investigated the effects of AuNPs on the impedance of the hollow microcapsules using scanning photo-induced impedance microscopy (SPIM) for

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the first time as this has implications for the permeability and stability of these capsules in physiological media and therefore their suitability for drug delivery.

The sensitivity and resolution of SPIM have recently been improved significantly [15,16], and SPIM is therefore an attractive tool for the investigation of the electrical impedance of PMLCs. SPIM is based on photocurrent measurement at electrolyte-insulator-silicon (EIS) field-effect structures and can provide a two-dimensional impedance image of the sample surface [17–19]. A bias voltage is applied between the semiconductor and a reference electrode immersed in the electrolyte to obtain an inversion layer, and a modulated light beam focused into the semiconductor scans across the substrate to generate electron/hole pairs. The separation of electron/hole pairs in the space charge layer results in ac photocurrents relating to the local impedance. High-quality impedance images of polymer films were obtained using SPIM, and a good agreement with the spectra measured with classical ac-impedance spectroscopy was confirmed [18]. By measuring local photocurrents while biasing the EIS structure towards depletion, local surface potentials could also be recorded—a technique termed light-addressable potentiometric sensors (LAPS) [20–22].

Submicrometre resolution for SPIM and LAPS has been achieved using silicon-on-sapphire (SOS, 0.5 μm silicon, 475 μm sapphire) as the semiconductor substrate and photoexcitation of charge carriers using a two-photon effect in the thin silicon layer by employing a femtosecond laser (1250 nm) with photon energy smaller than the bandgap of silicon [17]. By replacing the traditional insulator with a self-assembled organic monolayer that was bound to hydrogen-terminated silicon on the SOS substrate, we have significantly increased the sensitivity of SPIM and the measurement accuracy of LAPS recently [15,16]. The use of a self-assembled organic monolayer of 1,8-nonadiyne as the insulator has the advantage that different surface functionalities can be subsequently introduced using a simple Cu(I) catalysed "click" cycloaddition between the alkyne of the monolayer and an azide [15,16]. It was therefore decided to perform high-resolution SPIM measurements of PMLCs based on the well-established monolayer-modified SOS substrates and the femtosecond laser in order to investigate the effects of AuNPs on their impedance.

2. Experimental

2.1. Materials

Monodisperse melamine formaldehyde (MF) microparticles (~10 μm, dispersed in water) were purchased from Microparticles GmbH, Germany. A suspension of gold nanoparticles stabilised with citrate (~15 nm, dispersed in water) were prepared following a procedure described elsewhere [23].

Silicon-on-sapphire (SOS) with a 1 μm thick silicon (100) layer (boron doped, 0.1 Ω cm) on a 475 μm thick sapphire substrate was purchased from Monocrystal, Russia. Double polished silicon (100) (boron doped, 10–30 Ω cm) was purchased from Si-MAT, Germany. All chemicals and reagents, unless otherwise noted, were purchased from Sigma-Aldrich and were used as received. Dichloromethane (DCM) used for cleaning was redistilled prior to use. 1,8-Nonadiyne (98%) was redistilled from sodium borohydride (99+%) and stored under argon as reported [24,25]. Argon was dried and purified through an oxygen/moisture trap (Agilent Technologies, USA).

2.2. Microcapsule preparation and characterisation

To study the effect of AuNPs on the impedance of capsules, hollow capsules with AuNPs (~15 nm) $(PSS/PAH)_2$-AuNPs-$(PSS/PAH)_2$ and without AuNPs $(PSS/PAH)_4$ were prepared using MF microparticles as templates following a previously established procedure [26] (see ESI for further details).

The distribution of AuNPs in the shell of microcapsules was observed by a transmission electron microscope (TEM, JEOL 2010) operated at 200 kV. The diluted capsule suspension was deposited on a carbon-coated copper grid, and air-dried for 2 h. Then, the copper grid was installed in a sample holder and placed into the vacuum chamber of the TEM for characterisation.

Zeta potentials of hollow capsules containing AuNPs were measured with a Malvern Nano ZS zetasizer (Malvern Instruments Ltd, UK). For measurements, a small volume of sample solution was transferred to a transparent cuvette, diluted with pure water and placed in the thermostatted cavity. Fifteen measurements were taken on each sample and averaged. Atomic Force Microscopy (AFM, Dimension Icon, Bruker, US) in PeakForce TUNA mode was used to image the morphology and conductivity distribution of collapsed microcapsules. A Bruker PeakForce TUNA tip (Au coating, spring constant of 0.4 N/m) was used for scanning and a dc bias voltage at 1 V was applied between the AFM tip and the sample substrate.

2.3. SPIM substrate preparation and characterisation

SOS wafers and double polished silicon wafers were cut into 7 mm × 7 mm pieces. In order to form the ohmic contact for SPIM/LAPS measurements, 30 nm Cr and 150 nm Au were thermally evaporated onto one corner of the chip and subsequently heated to 300 °C for 5 min as previously reported [15]. The substrate was cleaned in a hot piranha solution (3:1 H_2SO_4 (96%)/H_2O_2 (30%), caution: highly corrosive) at 100 °C for 30 min and then rinsed copiously with ultrapure (Milli-Q) water. The assembly of the 1,8-nonadiyne monolayer followed the procedure reported by Ciampi et al. [24,25]. The cleaned SOS or silicon sample was transferred to a 2.5% HF solution and chemically etched for 90 s to obtain the H-terminated surface (caution: HF is highly corrosive). During the cleaning and etching time, the redistilled 1,8-nonadiyne was transferred into a Schlenk tube and was degassed by freeze-pump-thaw cycles until no gas bubbles evolved from the solution. Then, the freshly prepared H-SOS or H-Si sample was

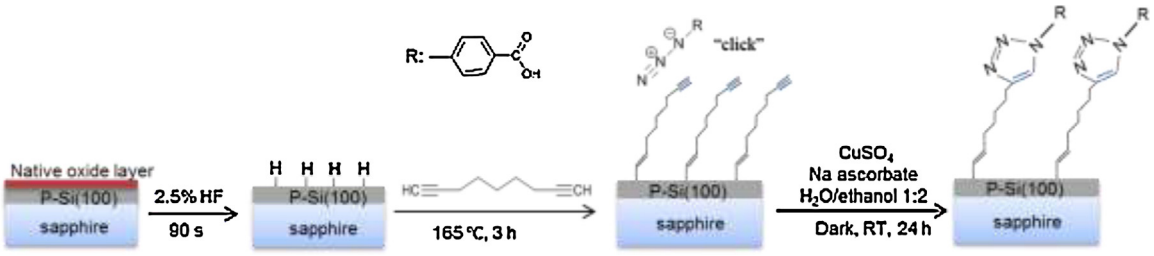

Fig. 1. Modification of 1,8-nonadiyne monolayers on SOS substrates using "click" cycloaddition to generate CO_2H-terminated monolayers.