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Hydrophobic perfluoro-silane functionalization of porous silicon photoluminescent films and particles

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ABSTRACT

Luminescent structures based on semiconductor quantum dots (QDs) are increasingly used in biomolecular assays, cell tracking systems, and in-vivo diagnostics devices. In this work we have carried out the functionalization of porous silicon (PSi) luminescent structures by a perfluorosilane (Perfluoro-octyltriethoxysilane, PFOS) self assembly. The PFOS surface binding (traced by X-ray photoelectron spectroscopy) and photoluminescence efficiency were analyzed on flat model PSi. Maximal photoluminescence intensity was obtained from PSi layers anodized at 110 mA/cm². Resistance to hydroxylation was assayed in H₂O₂:ethanol solutions and evidenced by water contact angle (WCA) measurements. PFOS-functionalized PSi presented systematically higher WCA than untreated PSi. The PFOS functionalization was found to slightly improve the aging of the PSi particles in water giving rise to particles with longer luminescent life. Confirmation of PFOS binding to PSi particles was derived from FTIR spectra and the preservation of luminescence was observed by fluorescence microscopy. Such functionalization opens the possibility of promoting hydrophobic-hydrophobic interactions between biomolecules and fluorescent QD structures, which may enlarge their biomedical applications catalogue.

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1. Introduction

Semiconductor quantum dots (QDs) are increasingly used in biomedical applications in view mainly of their luminescent properties. They have been tested both in-vitro as cell labelling [1] and diagnostic systems [2], as well as in-vivo in animal models for tissue imaging purposes [3]. Given the temperature induced emission shift they have further been explored as thermometers [4].

Porous silicon (PSi) in the form of particles (PSps) is a well known source for silicon QDs specially adapted to biomedical applications [5–7] in view of the reliability of the biofunctionalization processes through silanization and the intrinsic biocompatibility of Si degradation products [8,9]. Furthermore, PSps can be used to allocate nanomaterials to provide additional functionalities such as magnetic properties [10] or drug delivery potential [11,12]. The drawbacks stem from the chemical instability of PSi, which leads to a decay of intensity and red-shift of luminescence that should be prevented through surface passivation [8].

Biofunctionalization has been traditionally focused on providing surface groups on semiconductor nanostructures allowing a covalent binding with target biomolecules. Amino-silanes stand as the most prominent molecules for surface biofunctionalization of PSps [13]. In the opposite approach, hydrophilic antifouling groups from polyethylene-glycol have been promoted on PSps surface to inhibit the interactions with biomolecules [8]. However, covalent binding does not allow exploiting the multiple interaction mechanisms among PSps and biomolecules. In particular, reversible interactions with drugs are preferred for delivery applications. Furthermore, proteins carry a diversity of hydrophobic residues that shall be exploited for promoting such reversible interaction with PSps. For instance, serum proteins such as serum albumin exhibit pH dependent conformational changes induced by hydrophobic interactions [14]. The relevance of these processes on interactions with surfaces has been outlined previously [15].

Hydrocarbon surfaces are reputed hydrophobic systems and cover typically silicones [16], thermally passivated porous silicon [17], and carbonaceous materials [18], unless oxidative processes are used to induce surface polar (hydrophilic) groups. To maximize the hydrophobicity of the surfaces, fluorocarbon groups [19] are preferred to natural hydrocarbon moieties. When dealing

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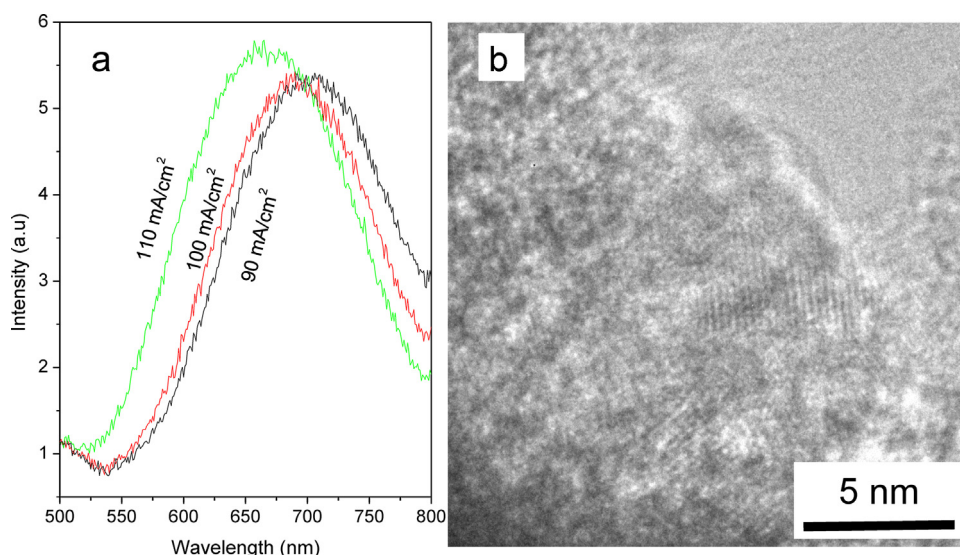


Fig. 1. (a) Optimization of photoluminescence of the PSi layers by varying current density and (b) typical Si QDs within PS as observed by TEM.

with Si-based materials (silicas, glass, silicates, silicon) and other affine materials, the hydrophobic functionalization can be however performed through perfluoro-silanes [20] as an alternative to more generic plasma [21], or photoactivated [22] hydrosilylation processes. Such functionalization provides the surfaces not only with hydrophobic and oleophobic properties, but also increases the range of functionality to frosting conditions [23]. Thus, perfluoro-silane modified materials present improved dielectric [24], anticorrosion and tribological properties [25], and increase the stability of organic solar cells [26] or transistors [27].

In the present work we aim at the surface functionalization of PSi structures with Perfluorooctyl-triethoxysilane (PFOS) in order to provide a compact synthetic surface on PSi, analogue to what promoted naturally using hydrophobin proteins for PSi based drug delivery systems [28]. Silane self-assembly is generally driven by surface OH groups, but such intermediate modification is detrimental for photoluminescence properties. We explore the influence of exciton generation using white light to carry out the surface modification with PFOS as an alternative to other methods that preclude deep PSi oxidation [29] and use intermediate Li compounds [30]. We aim at the description of the assembly efficiency by using X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), Fourier transformed infrared spectroscopy (FTIR) and study the stability in critical conditions by the photoluminescence aging in particularly oxidizing conditions.

2. Experimental

2.1. Porous Silicon preparation and functionalization

PSi layers were formed by the electrochemical etch of p-type low resistivity Si wafers (boron doped, single side polished, orientation (1 0 0) and 0.01–0.02 Ω cm resistivity) in an HF:ethanol (1:2) solution. The non-polished side of the Si wafers was previously coated with an Al layer and annealed to provide low resistance ohmic contacts. Samples were galvanostatically etched without illumination. The etching current density was varied from 90 to 110 mA cm⁻² and the etching time was 30 s. To produce PSps, an additional final etch step of 5 s at 180 mA cm⁻² was applied to sacrifice the PSi layer. The induced instability of the PSi/Si interface induced a fragmentation of the layer in the form of PSi flakes, which were easily scrapped from the surface and were further mortar grinded to reduce their size. The whole extraction process was carried out in ethanol to prevent atmospheric exposure thus

minimizing oxidation and photoluminescence extinction. Surface functionalization with solutions of PFOS 0.2% (pur. >98%, Sigma Aldrich) in ethanol (Panreac) were carried out under a 100 W halogen illumination for 30 min, which is known to slightly oxidize the PSi surface [31]. After modification, the PSi structures (whether films or particles) were changed of ethanol medium twice and dried at room temperature for analysis. When aiming at studying the stability of the particles, two aging conditions were considered. For wettability aging purposes H₂O₂:ethanol (1:2) solutions were used in view of their oxidation potential. For PL studies, milder oxidation conditions in milliQ water were used to avoid a drastic decay of emission intensity.

2.2. Characterization techniques

Photoluminescence (PL) was measured using a fluorimeter (Aminco Bowman series 2) operating with a 150 W continuous wave Xe lamp. Samples were excited with wavelengths between 350 and 400 nm (2 nm bandwidth) in order to excite the different energy levels. Signal was recorded using a photomultiplier tube detector polarized at 500 V. The emission scan was performed between 475 and 675 nm (4 nm bandwidth), avoiding the second harmonic diffraction peak from the excitation wavelength. PL response from PSps has been also observed directly by fluorescence microscopy using a IX81 Olympus inverted microscope linked to a DP72 digital camera controlled by cellD software. The excitation source of this device is a 100 W Hg lamp operating at stabilized direct current, suitable for UV fluorescence.

The internal structure of PSi was observed by transmission electron microscopy (TEM) in a JEOL 2100F operated at 200 kV. Plane sections were prepared by subsequent steps of mechanical (dimpler) and ion beam milling (dual Ar ion gun). XPS measurements were performed in an AXIS ULTRA Spectrometer (KRATOS Analytical, UK). The samples were irradiated with monochromatic Al-K _{α} X-rays ($h\nu = 1486.6$ eV) using X-ray spot size of 400 \times 700 μ m² and different take-off angles (TOA) with respect to the sample surface. Surface charging was compensated by means of a filament inserted in a magnetic lens system and all spectra were corrected by setting the C1s hydrocarbon component to 284.50 eV. For the core level spectra, a pass energy of 40 eV was selected, determining a resolution of 0.63 eV as measured both on the Ag 3d_{5/2} peak and on the Ag Fermi edge. The data were processed using the Vision2 software (Kratos, UK) and CasaXPS v16R1 (Casa Software, UK). Curve fitting of core level peaks was carried out using the same

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