Reversible positioning at submicrometre scale of carbon nanotubes mediated by pH-sensitive poly(amino-methacrylate) patterns†

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The selective adsorption of carbon nanotubes (CNTs) on a pH-reversible PDMAEMA patterned gold surface is presented. In acidic conditions, a selective CNTs adsorption onto the polymer brushes is obtained due to ammonium–π interactions. The reversible behavior was shown by successive treatments in both alkaline and acidic solutions with CNTs.

Selectively-patterned surfaces exhibiting responsive properties represent very attractive platforms as "smart" devices in functional micro- or nano-arrays such as (bio)sensors. Accordingly, the design of these advanced materials can be achieved by micro- or nano-scale patterning of a surface with a template or a mask through lithographic techniques, electron-beam patterning or microtransfer-molding.[1] In addition, the micro-contact printing (μCP) technique enables the selective deposition of self-assembled monolayers (SAMs) on a substrate, *e.g.*, by means of a polydimethylsiloxane (PDMS) stamp.[1] In a subsequent step, the transferred relief pattern can be selectively functionalized through covalent or non-covalent methods such as *via* "*grafting from*" polymerizations.[1a] This simple and reliable procedure features high efficiency for large-area patterning of different substrates with spatial resolution down to the submicrometre range.

Carbon nanotubes (CNTs) are gaining a significant impact in the field of nanotechnology and more particularly for the design of future electronic devices and sensors[2] due to their unique mechanical, electrical and structural properties.[3] Amongst the methods available for the controlled positioning of CNTs, supramolecular chemistry offers a rational approach supported by its simplicity, cost-effective processes and the wide range of interactions available in the molecular recognition toolbox, without adversely affecting the structure of CNTs.[4] Recently, we have reported that poly(*N*,*N*′-(2-(dimethylamino)-ethyl)-methacrylate) (PDMAEMA) can selectively interact towards the CNTs in solution thanks to ammonium–π interactions.[5] In this respect, we have investigated the binding ability of PDMAEMA brushes on selectively-patterned gold surfaces in the immobilization and controlled release of CNTs. PDMAEMA endows a high pH sensitivity with a tunable amine/ammonium pending group capacity.[6] The pH-induced switching of PDMAEMA amino side groups is therefore expected to favor reversible anchoring of CNTs, due to stronger ammonium–π interactions with respect to the amine–π binding ability. To the best of our knowledge, such a method represents an unprecedented achievement combining both the controlled positioning and release of CNTs at the sub-micrometre scale in the realm of functional CNTs-based materials. Moreover, this system offers a smart platform for the development of future CNTs-containing sensing devices.[7]

Purposely, the patterned deposition of a disulfide initiator (see ESI† for synthetic pathway, Fig. S1), $[BrC(CH_3)_2COO(CH_2)_{11}S]_2$ active in atom transfer radical polymerization (ATRP), is performed by μCP on a gold surface (Fig. 1).

Such disulfide species are able to chemisorb onto gold substrates forming a close-packed monolayer.[8] It results in the sulfur–gold bond formation where the deposited monolayer at the outer surface points bromoisobutyrate functionalities. In this work, circular geometric shapes of 10 μm diameter are printed at repeat distances of 50 μm, representing

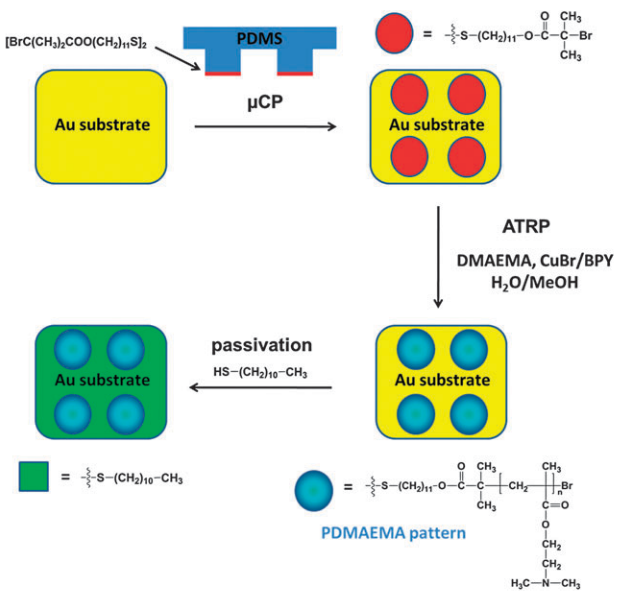

Fig. 1 Schematic representation of thiol derivative deposition by μCP on a gold surface, synthesis of PDMAEMA brushes by ATRP and passivation of the gold substrate.

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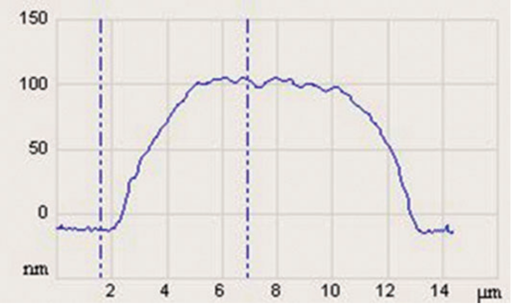

Fig. 2 TM-AFM height profile over one dot PDMAEMA.

localized initiating sites on the gold substrate. Subsequently, PDMAEMA brushes are readily obtained by ATRP initiated from the bromoisobutyrate group.[1c] The polymerization of 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) was carried out at room temperature in water/methanol (1 : 1) using CuBr and bipyridine as catalyst and ligand, respectively.

The chemical composition and the spatial confinement of resulting polymeric brushes were confirmed both by Atomic Force Microscopy in Tapping-Mode (TM-AFM) and X-ray Photoelectron Spectroscopy (XPS). The AFM analysis established the presence of PDMAEMA patterns through average thickness values of polymeric brushes of *ca.* 110 nm (Fig. 2). This "*grafting from*" polymerization technique proved highly reproducible, allowing for a good control over the polymeric chain length and related layer thickness, within a variation of *ca.* 5 nm.

The XPS spectrum confirmed also the brushes formation with the presence of all characteristic atoms of PDMAEMA: the N_{1s} element can adopt two binding energy positions (Fig. 3) in addition to the peaks of C1s (at 285 eV), O1s (at 531 eV), S2p (at 163 eV), and Br3d5 (at 67 eV) (see XPS survey spectra in ESI†, Fig. S2). According to our hypothesis, the recognition process could depend on a function of pH, namely ammonium *vs.* amine binding capability towards the π-unsaturated system. Consequently, the PDMAEMA patterns have been characterized by XPS under acidic and alkaline conditions in order to prove the protonation of amine side chains. When the sample was immersed in alkaline solution, we observed a single N_{1s} peak at 399.5 eV assigned to neutral nitrogen element (dimethylamino group). Under acidic condition, we observed a complete shift of this peak to 402.5 eV, which is attributed to the protonated nitrogen (*i.e.*, an ammonium group).

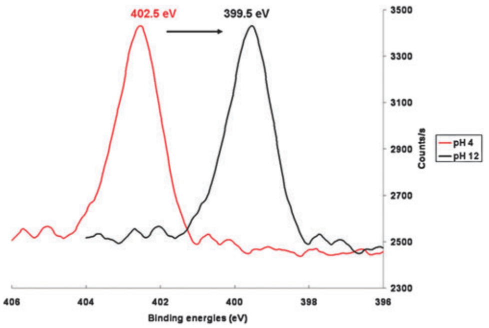

Fig. 3 N_{1s} XPS spectrum of PDMAEMA brushes under acidic and alkaline conditions.

Due to the inherent affinity between CNTs and gold,[9] the passivation of the uncoated substrate was required by immersing the gold substrate with undecanethiol (thiol–CH_3) in order to prevent any undesired CNTs adsorption (see ESI†, Fig. S3). The CNTs anchoring ability of the PDMAEMA brushes was then investigated in an acidic solution adjusted at pH 2. Indeed, the poly(amino-methacrylate) brushes adopt a fully extended form in acidic aqueous media due to interactions between the protonated amines and the solvent supplemented by electrostatic repulsion of the ionic groups. This results in the creation of positively charged sites along the polymeric backbone readily available for a "recognition" process with the unsaturated CNTs π-structure.[5a] This behaviour has been described by some of us in solution with PDMAEMA and MWCNTs and supported by molecular dynamic (MD) simulations.[5a] In practice, the patterned gold surface was immersed in the acid solution in the presence of 1 mg of multiwall CNTs (MWCNTs) and stirred overnight at room temperature. Then, the substrate was thoroughly washed and sonicated in neutral water in order to remove any unbound CNTs bundles.

The selective nanotubes location throughout the patterning system was first highlighted by optical microscopy. As seen in Fig. 4, large amounts of CNTs are selectively adsorbed on the surface at the polymeric circular anchoring sites. Clearly, the protonation of the PDMAEMA dimethylamino groups creates attractive cation-binding sites towards the electron-rich CNTs surface.[10]

In order to attest the preferential CNTs adsorption on the polymeric circular spots, Conducting Atomic Force Microscopy (C-AFM) was used as the appropriate tool to map the local electrical properties. Indeed, taking advantage of the inherent electrical conductivity of CNTs, C-AFM can readily reflect the CNTs distribution onto the PDMAEMA patterns.[11]

C-AFM experiments were performed in contact mode; the intensity of the local current is directly related to the presence of CNTs under the AFM tip. The images display a clear and unambiguous correlation between the nanotubes location in deflection and conducting mode (Fig. 5). Very low current values (~2–6 nA) are recorded on the CNTs-free polymeric brushes (β) and on the thiol–CH_3 monolayer (α), with only a very small number of isolated nanotubes (δ) present on the thiol–CH_3 surface. Interestingly, a high current (~30–100 nA) is measured on the polymeric patterns (χ), attesting for the presence of the specifically localized CNTs. In this case,

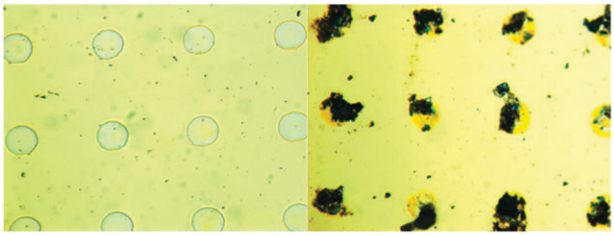

Fig. 4 Microscopic view (magnification 50×) of the naked PDMAEMA pattern (left) and after selective anchoring of CNTs on polymeric brushes (right). (Circular pattern diameter: 10 μm.)

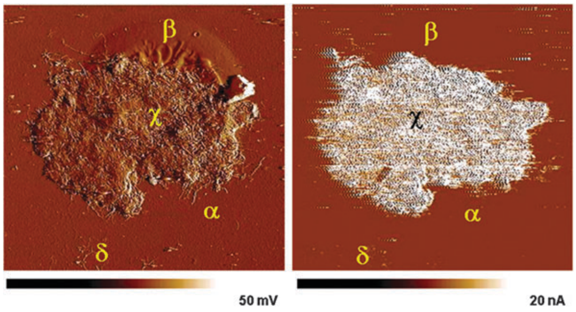

Fig. 5 20 × 20 μm AFM images in deflection mode (left) and current (right). (α) Self-assembled thiol–CH$_3$ layer on gold surface; (β) partially uncovered PDMAEMA brushes; (δ) isolated CNTs on the thiol–CH$_3$ layer; (χ) CNTs on PDMAEMA brushes.

the electronic response of CNTs matches well with the PDMAEMA pattern location on the gold surface.

The impact of alkaline conditions (pH 12) on the anchoring of CNTs has been also investigated. In this case, the successive treatment steps afford a polymeric substrate with only a tiny quantity of adsorbed CNTs (see ESI†, Fig. S4). It is known that in alkaline environment, the side chains of PDMAEMA brushes are mostly back-folded, and the residual ammonium species do not ensure enough interactions to anchor CNTs onto the gold surface.[12]

Based on those observations, subsequent experimental efforts have focused on the reversibility of the system, namely the controlled release of immobilized nanotubes under specific conditions. To address this issue, polymeric brushes with anchored CNTs, obtained under acidic treatment, were immersed in an alkaline sodium carbonate solution at ambient temperature. While a CNTs release would have been expected, a microscopic analysis revealed an unchanged quantity of adsorbed CNTs. The disanchoring process could result from different types of interactions, namely N(CH$_3$)$_2$–π, residual $^+$NH(CH$_3$)$_2$–π, π–π stacking between the deposited carbon nanotube walls and conformational changes of the polymeric brushes.[5a] However, the determination of this mechanism is under investigation. Since we are targeting the reversibility of our system, the sample was immersed for a few seconds in the alkaline solution, but at 50 °C under sonication. This treatment enabled the almost complete CNTs-release from the polymeric brushes. Again, the resulting gold surface was immersed in the acidic solution in the presence of CNTs, giving rise to a clear and unambiguous carbon nanotubes immobilization. This attests the reversibility of the PDMAEMA-brushes onto the gold surface as CNTs anchoring systems.

In summary, we described a simple and efficient method to achieve a localized and reversible CNTs anchorage on a gold substrate at the micrometre scale. The deposition of an ATRP initiator monolayer is performed straightforwardly by μCP soft lithography, followed by the "*grafting from*" of PDMAEMA brushes, and passivation of the uncoated gold areas. Under acidic conditions, MWCNTs are able to selectively adsorb on the polymeric patterns thanks to ammonium–π interactions. In contrast, only a very marginal CNTs amount remains adsorbed onto the polymer under alkaline conditions. As far as the reversibility is concerned, the selective desorption of CNTs occurs in a highly efficient manner, when the substrate is treated in alkaline solutions at 50 °C. A subsequent adsorption cycle can take place under the same conditions. The development of this system aiming at selectively anchoring and releasing CNTs upon external stimuli opens a very appealing strategy with broad applications in micro- or nano-array sensors, representing a hot topic in materials science.[7]

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