Versatile Nanostructured Materials via Direct Reaction of Functionalized Catechols

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Mussel-adhesive proteins have been the subject of intensive scientific research over the past decades,^[1,2,3,4] associated to the remarkable ability of marine invertebrates to strongly adhere to virtually all surfaces, even low-fouling materials.^[3,5] Albeit diverse in structure, this behavior has been attributed to their varying amounts of the non-essential catecholic aminoacid DOPA.^[1,5] Since this discovery, an ever-increasing number of bioinspired catechol-based polymers have been reported and shown to constitute powerful tools for the fabrication of water-resistant adhesives,^[6] protective layers,^[7] and primers for functional adlayers and nanoscale coatings,^[8] among others.^[9] One simple strategy for the preparation of this type of materials was introduced by Messersmith and co-workers^[10], who reported an easy and straightforward method for the synthesis of polydopamine by oxidative polymerization of catecholic dopamine.^[11] The process allowed for the *in situ* deposition of - otherwise highly insoluble- polymeric material on a wide variety of substrates,^[12] which could

be further functionalized on a second step in a versatile way, though with an uncontrolled degree of functionalization. A different approach consisted in the preparation of macromolecular systems bearing “adhesive” catecholic moieties, plus one or more functional chains grafted to a common polymeric backbone.^[7c-e] This design strategy afforded control of the polymer structure and degree of functionalization, and the possibility of deposition by means of *ex situ* treatments, but otherwise involved the use of careful polymerization procedures to circumvent undesired or premature catechol reactivity.

Here we report an alternative and simple polymerization method for the preparation of functional catechol-based materials. Although the self-assembly (e.g. quinhydrone^[13]) and polymerization of catechol groups induced by basic media,^[14] enzymes^[15] and electrochemically^[16] have been known for long, our novel approach relies on the copolymerization reaction between a catechol moiety substituted with appropriate functional chains and an excess of aqueous ammonia. In addition to maintaining a mildly basic pH necessary for the fast oxidation of the catechol ring under aerobic conditions, ammonia acts as a nucleophile on the reactive *o*-quinones thus formed, in a way reminiscent of melanization reactions such as that used in the preparation of polydopamine. This provides the desired covalent cross-link between adjacent catechol rings, regardless of their substitution pattern. The molecule of choice for these studies was the amphiphile 4-heptadecylcatechol **1** that, in addition to exhibiting a considerable tendency to adhere to surfaces,^[17] is structurally similar to alkylcatechol urushiol,^[18] used for thousands of years to manufacture protective lacquered coatings. The resulting polymerization product is amenable to deposition on representative nanostructures, as well as coating flat and convoluted bulk surfaces of very different chemical nature, by simple and fast *ex situ* procedures on organic solvents. Moreover, as befitting the structure of monomer **1**, these coatings were shown to confer a robust hydrophobic character to the surfaces, which can be modulated from oleophobic to highly hydrophilic upon extending the polymerization methodology to other functional catechol moieties. Finally,

thanks to the amphiphilic character of **1**, the new material can also be structured and isolated in the form of nanoparticles upon direct reaction in polar solvents exhibiting an excellent adhesion to substrates, such as textile materials, thanks to the presence of surface catechol groups.

In a typical experiment, a large excess of aqueous ammonia (100:1) was slowly added under vigorous stirring in the presence of air to a solution of **1** (0.2 % , w/v) in methanol, at 40 °C. The transparent, colorless solution turned bright orange, and later to a turbid dark-brown dispersion after several hours, which was attributed to the onset and further progress of the oxidative polymerization. Thin-layer chromatography (TLC) was used to follow the reaction, showing that approximately 80% of monomer **1** had already reacted after 3 hours, and consumed quantitatively within 24 hours, after which a dark-brown amorphous solid (**2**) could be extracted with chloroform and isolated by evaporation. Lower ammonia excesses (2, 5 and 10:1) caused the reaction to advance extremely slowly, while a molar excess of 1000:1 did not result in significant improvements in polymer yield or shortening of the reaction time. The characterization of **2** obtained upon filtration and drying processes was performed by NMR, EPR, FT-IR, mass-spectrometry (MS), elementary analysis and XPS (see supplementary material). Although a univocal molecular structure could not be established on the basis of these experiments, relevant structural information of the polymeric material was obtained: The MS results pointed out to a low polymerization degree with no more than 6-7 average units while elementary analysis results and XPS indicate the presence of nitrogen. EPR investigation showed that oligomer **2** is essentially diamagnetic. Finally, combined NMR studies including ^1H and ^{13}C NMR recorded in C_6D_6 and CDCl_3 , temperature-variable experiments, Diffusion-Ordered Spectroscopy (DOSY) and solid ^{13}C NMR confirms that material **2** consists of a heterogeneous mixture of oligomers of catechol derivatives with no presence of starting monomer **1**, with a wide dispersion of high molecular weights and under strong dynamic effects. According with this, and taking into account the many possible

variations in the reaction pathway that may be occurring simultaneously (Michael-type additions, Schiff-base formation, direct radical aryl-aryl couplings, a.o.), the difficulty in the elucidation of the structure of **2** is not surprising, and seems otherwise likely related to those encountered in the study of natural and synthetic melanins,^[19] and polydopamine^[20] itself. Interestingly, the morphological characterization by SEM and TEM of polymer **2** as *directly* obtained from the (polar) reaction medium upon evaporation of the ammonia excess, revealed its structuration into solid nanoparticles (NPs) with diameters ranging from 100 to 350 nm (see **Fig. 1a-b**). The surface charge of the NP solution (measured as zeta potential) was found to be around -45 mV in water at pH $\approx$ 7, which would be in agreement with the presence of a certain amount of catecholate groups in the outermost layer, affording a stable colloidal suspension for many days. **2**-NPs also exhibit fluorescence emission spanning over the whole visible spectral region, as shown in **Fig. 1c**. This indicates that conjugated polymeric segments are formed by polymerization, since the absorption spectrum of **1** lies within the UV region. On the other hand, the extremely broad fluorescence spectrum measured for **2**-NPs further confirms that they must be constituted by a polydispersed mixture of oligomers/polymers of **1**, which should present different conjugation lengths depending on the polymerization degree and, therefore, distinct absorption and emission spectra within the UV-vis region.

Finally, as expected from the presence of exposed catecholate groups in the outermost layer, the adhesiveness of **2**-NPs was tested on polyester fibers. This was done simply by dipping a piece of polyester in a water suspension of **2**-NPs, without any specific pre-treatment or functionalization. SEM images of the treated polyester fabric (**Fig. 1d-e**) showed that a large number of nanoparticles are adhered around individual fibers nicely distributed over the whole sample, even after drying under a vigorous nitrogen flow. This result is relevant in view of the challenge posed by the functionalization of textile fabrics with organic nanoparticles, since adhesion yields reported so far in this field are low.^[21]

-Insert Figure 1 here-

When compound **2** is dissolved in non polar solvents, such as chloroform or hexane, SEM images reveal the conversion of the NPs into an amorphous material that is subsequently used to coat nanoscopic materials by the simple and quick dipping method schematically depicted in **Fig. 2a**. As a proof-of concept, iron oxide nanoparticles of 500-650 nm in diameter were dispersed in a 0.5% (w/v) *n*-hexane solution of **2** for 30 minutes and filtered. TEM images showed that treated NPs appear surrounded by a brighter halo (not apparent in the non-treated sample) that corresponds to the presence of a 5 to 50 nm thin film of **2**, (see supplementary material).^[22] Similar results were obtained for 250-600 nm mesoporous silica NPs, affording coating thicknesses ranging from 7 to 20 nm (see supplementary material). Finally, multi-walled carbon nanotubes (MWCNTs) were also coated upon dispersion by ultrasonication in a methanol solution of **2**. As can be seen in **Fig. 2b**, the coating can be differentiated as an outer layer with brighter contrast (orange arrows), around the darker nanotube walls (green arrows). Different concentrations (0.1, 1 and 5% w/v) and dipping times (5 and 60 minutes) led to very similar results with very homogeneous coating layers around the MWCNTs, ranging in all the cases from 4 to 7 nm.^[23] The coating modifies the surface characteristics of the MWCNTs conferring a more hydrophobic character (**Fig. 2c**), so MWCNTs tend to float on a water solution without settling, even after vigorous ultrasonication and stirring, as opposed to uncoated nanotubes, which disperse temporally upon sonication. In contrast, long standing - though not perfectly homogeneous- suspensions of treated MWCNTs are obtained in a less polar solvent such as ethyl acetate, where uncoated MWCNTs exhibit a more pronounced tendency to aggregate.

-Insert Figure 2 here-

The coating capacity of **2** was also confirmed and evaluated on a bulk material such as glass, following the same procedure described in Fig 2a and using a 1% (w/v) *n*-hexane solution of **2** for 1 minute. The corresponding AFM image shown in **Fig. 3b** reveals a very homogeneous coating with a surface roughness inferior to 0.2 nm, and an average thickness of approximately 150 nm, as determined by measuring the topographic profile of a scratched zone (see supplementary material). Coated glasses exhibit reproducible contact angles (CA) around 100° considerably higher than those of the untreated glass (15-20°) and well in the hydrophobic limit expected for smooth surfaces.^[24] CA values were found to be insensitive to longer dipping times, revealing no significant differences between treatments lasting up to 24 hours. On the contrary, CAs were found to depend on parameters such as solvent nature or concentration, being the optimized experimental parameters those already used in the previous section (for more info about the influence of both parameters on CAs see supplementary material). These results are comparable with those already described for polydopamine coatings already used for surface modification.^[25]

In order to test resistance of the outside layer, coating glass substrates were subsequently subject to thermal treatment by heating in an oven at 90 °C, and washing stress tests (with water and methanol). In both cases, CA remained approximately unchanged, with slight variations that lay within experimental error. This behavior is in contrast with that of the hydrophobic coating obtained upon self-assembly of a monolayer of unreacted compound **1** on glass, which exhibits smaller CA values and especially, much lower thermal and wear resistance (see supplementary material). Both facts confirm the need for the polymerization of **1** into the cooperatively cross-linked product **2** to ensure a sufficiently robust coating.

The hydrophobic character was also investigated on 2 x 2 cm² polyester samples treated with a 1% w/v *n*-hexane solution of **2** for 1 minute. SEM images of the coated textiles are shown in **Fig. 3a-b**. Differences in fabric thickness between treated and non-treated substrates are not

discernible in SEM images at first sight, unless a defect area lacking the coating is magnified. The presence of a thicker coating layer becomes more evident when concentrations as high as 10% are used (see supplementary material), though in all the cases fibers still show ample room between each other, which is relevant to ensure that the mechanical properties and breathability of the textiles are preserved upon deposition of **2**. In accordance with the hydrophobic nature of monomer **1** and the intrinsic roughness of the textile substrate, a high CA value of 130° is obtained, which is maintained indefinitely, in contrast with the quick absorption of water on the pristine textile. No significant improvement of the CA can be detected along the whole concentration range of **2** used.

The methodology previously described also allowed us to systematically widen the range of surface energies of coated substrates by means of the same ammonia-reacted methodology, by choosing an appropriate catecholic monomer. For instance, the use of a catechol molecule bearing a partially fluorinated alkyl chain (**3**) was shown to impart oleophobic character, whereas the use of simple pyrocatechol (**4**), lacking any side chains, was found to confer high hydrophilicity to the substrates, with a large tendency to attract water, due to the higher density of polar groups. With regard to oleophobic surfaces, treatment of a glass slide and a piece of polyester textile with the polymerization product of **3** in THF afforded CAs of 115° and 150°, respectively (see **Fig. 3c** and video on supplementary material). On the other hand, treatment of a hydrophobic aluminum substrate with an aqueous solution the polymerization product of **4** caused the CA to drop dramatically from an initial value of 80° to ca. 0° upon coating.

-Insert Figure 3 here-

In summary, we report a new methodology for the obtaining of catechol-based materials derived from the polymerization of functionalized catechols with ammonia. Overall, the strategy reported combines advantages such as ease of preparation, solubility in appropriate

solvents, improved surface functionalization and *a priori*, a good overall density of functional moieties because each catechol ring may be designed to support a given functional chain. The as-synthesized material **2** obtained upon reaction of **1** with this new methodology, represents a nice example of the versatility of this approach. Compound **2** is shown to spontaneously structure in the form of nanoparticles a few hundred nanometers in diameter in water, which easily stick to polyester fibers affording stable NP coatings. Even though polydopamine nanoparticles resembling eumelanin particles that constitute *Sepia* ink have already been described in the literature,²⁶²³ to our knowledge this is the first example where chemically-related NPs have been reported to exhibit adhesive properties. On the other side, when the material is dissolved in non-polar solvents such as hexane, robust coatings on a representative variety of substrates, both at the nano-/macroscale are obtained, by means of a quick and *ex-situ* approach without any pretreatment or modification. Upon polymerization, the presence of a long alkyl chain in **1** affords functional coatings with a persistent hydrophobic character, whereas functional catechols with different ring pendant groups allowed us to modify of the surface tension of coated surfaces by means of an analogous polymerization methodology. Overall, these results would lead us to expect potential applications in the near future for materials developed with this new approach.

Experimental Section

Experimental materials and methods, the synthesis and characterization of partially fluorinated catechol **3**, along with as well as additional results can be found in the Supporting Information

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Figure captions

Fig. 1. (a) Molecular structure of **1**. (b) TEM and (c) SEM images of **2**-NPs. (d) Fluorescence emission spectrum of **2**-NPs in aqueous solution ($\lambda_{\text{exc}}=355$ nm, $\lambda_{\text{det}}>400$ nm) and (inset) fluorescence microscopy image of **2**-NPs deposited onto glass ($\lambda_{\text{exc}}=540\text{-}552$ nm) and. (e) SEM images of a polyester fibers treated with a dispersion of **2**-NPs, where large amounts of these nanoparticles can be observed adhered to the fibers even after the drying process and (f) detail of one of such fibers with the attached NPs.

Fig. 2. (a) Schematic representation of the process carried out for coating the substrates with compound **2**. (b) TEM images of MWCNT coated with compound **2** after being dispersed in a 0.5% (w/v) *n*-hexane solution for 30 minutes. The green arrows mark the MWCNT wall; the orange arrows point at the coating thickness. (c) Different behavior of blank and treated MWCNT dispersed in water and ethyl acetate.

Fig. 3. (a) Molecular structure of **3**. (b) molecular structure of **4**. (c) SEM image of a treated polyester fiber and the corresponding magnification from where the coating can be clearly differentiated. (d) AFM Topography image of a glass substrate (5 μm x 5 μm) treated *ex situ* with a 1% (w/v) *n*-hexane solution of **1** for 1 minute. (e) Contact angles obtained with different liquid on different substrates coated with the polymerization product of **3**.

Figure 1

Figure 2

Figure 3

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A facile one-step polymerization strategy is explored to achieve uniform catechol-based materials. Depending on the functionality of the catechol, the as-prepared product can be used to systematically modify the surface tension from oleo-/hydrophobic to highly hydrophilic materials, both on nano and bulk structures, as well as to self-assemble as solid nanoparticles with sticky properties in polar solvent media. Such a versatile concept is ideal for the development of catechol-based multifunctional materials.

Keyword: catechol, adhesiveness, multifunctional, surface tension, nanoparticles

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