Versatile Bionanostructured Materials via Direct Reaction of Functionalized Catechols

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Mussel-adhesive proteins have been the subject of intensive scientific research associated to their remarkable ability to strongly adhere to virtually all surfaces. Albeit diverse in structure, this behavior has been attributed to their varying amounts of the non-essential catecholic aminoacid DOPA. Since this discovery, an ever-increasing number of bioinspired catechol-based polymers have been used for the fabrication of water-resistant adhesives, protective layers, primers for functional adlayers and nanoscale coatings, among others.[1]

Herein we report a new approach for the preparation of catechol-based materials based on a simple polymerization process in the presence of ammonia,[2] in a way reminiscent of melanization reactions. This strategy represents a significant advance in combining many advantages of methods reported previously: ease of preparation, solubility in appropriate solvents and a high ratio of adhesive (catecholic)-to-functional moieties.

EXPERIMENTAL METHODS

In a typical experiment, a large molar excess of aqueous ammonia was slowly added under vigorous stirring in the presence of air to a solution of the corresponding monomer (0.2 % , w/v) in methanol, at 40 ºC. Thin-layer chromatography (TLC) was used to follow the reaction, showing that the majority of monomer had already reacted after 3 hours, and consumed quantitatively within 24 hours, after which a dark-brown amorphous solid could be extracted with chloroform and isolated by evaporation.

RESULTS AND DISCUSSION

As a proof of concept, the first molecule of choice was a catechol bearing a long alkyl chain. The material resulting from its reaction with ammonia 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 synthetic polydopamine nanoparticles resembling eumelanin particles that constitute sepia ink have already been described in the literature, to our knowledge this is the first example where chemically-related NPs have been reported to exhibit adhesive properties.

On the other side, when this 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. Whereas catechol monomers bearing a long alkyl chain afford coatings with a persistent hydrophobic character, it was shown that this methodology can be extended to several other catechols with different ring pendant groups, providing varied surface functionalities such as oleophobic/hydrophilic, anti-fouling, anti-bacterial activities and water remediation.

CONCLUSION

A new methodology for the fabrication of bionspired catechol-based nanoparticles and coatings is reported. The chemical versatility of the approach allows for a broad range of functionalities that can be added, opening new paths in the realization functional and bioactive materials, an ever growing field of interest.

REFERENCES

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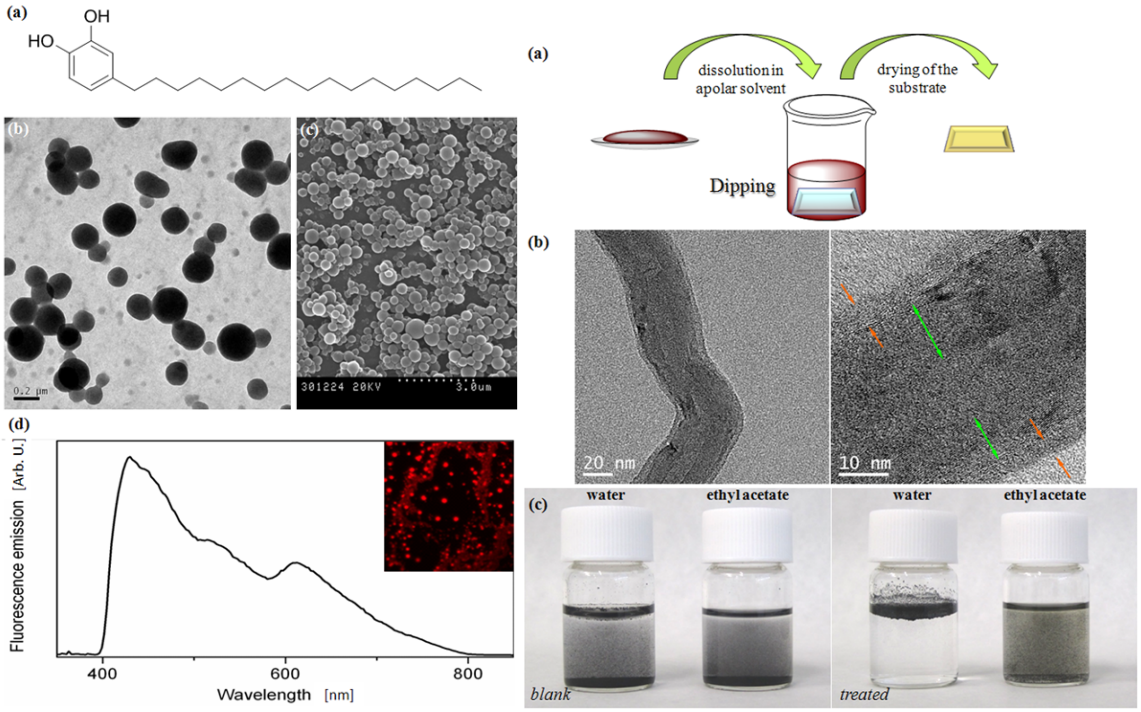
ACKNOWLEDGMENTS

This work was supported by MICINN through projects MAT2012-38318-C03-02, MAT2012-38319-C02-01, CTQ2010-15380 and CTQ2009-07469. We are also grateful to Generalitat de Catalunya for project 2010VALOR00039.



Left: (a) Molecular structure of the building block. (b) TEM and (c) SEM images of the polymerization product. (d) Fluorescence emission spectrum of the polymer in aqueous solution (λexc=355 nm, λdet>400 nm) and (inset) fluorescence microscopy image of 2-NPs deposited onto glass (λexc=540-552 nm). **Right**: (a) Schematic representation of the process carried out for coating the substrates with compound 2. (b) TEM images of MWCNT coated with the polymer 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.