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Biomimetic Dopamine Derivative for Selective Polymer Modification of Halloysite Nanotube Lumen

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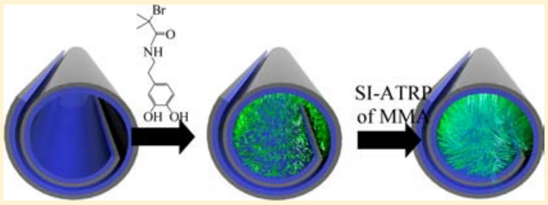
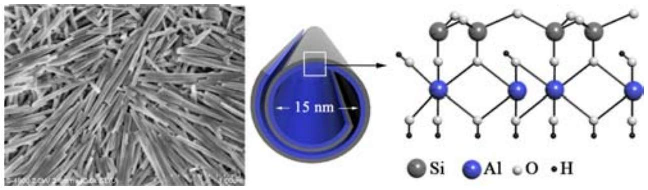
S *Supporting Information*

ABSTRACT: We demonstrate the use of a catecholic anchor (Dopa) for selective modification of the inner surface of an halloysite clay nanotube. Aqueous Dopa binds to alumina at the tube lumen and does not bind the silica surface under the same conditions. Selectivity of surface modification was evidenced using X-ray photoelectron spectroscopy (XPS) and ^{13}C solid state NMR spectroscopy. Surface-initiated atom transfer radical polymerization (SI-ATRP) was performed through selectively adsorbed Dopa to graft a layer of polymer brush into the nanotube lumen.



Among hybrid meso-materials, tubular clay minerals occupy a special place because they are readily available at low cost while constituting a specific nanoscale matrix for the assembly of organic components. The environmental friendliness and biocompatible nature make halloysite clay nanotubes [$Al_2Si_2O_5(OH)_4 \cdot nH_2O$] (Scheme 1) an important nanomaterial for developing new organic/inorganic composites. Halloysite, a hydrated polymorph of kaolinite consists of silica on the outer surface and alumina in the innermost surface.[1] Therefore, different inner and outer-compositions of these natural nanotubes allow for different chemical reactions in these tubes' interior and external surfaces.

Scheme 1. FE-SEM Image of Halloysite on Si-Wafer (Left) and Schematic Illustration of Crystalline Structure of Halloysite (Right)



Modification of the halloysite tube outer surface is usually intended to improve clay dispersal in polymer matrix/fluidic material,[2−9] and its selective interior modification by immobilization of functional groups via covalent bonds could open up new applications based upon molecular recognition, such as molecular separation, molecular storage, catalysis, and drug delivery.[10−12] However, selective modification of interiors remains a difficult task; so far, only organophosphate has been successfully used for stable selective modification of halloysite inner surface.[13]

A new tool for selective modification of silica−metal oxides materials is catechol derivative inspired by strong wet adhesion systems developed by nature: 3,4-dihydroxyphenylalanine (dopamine) is found in mussel adhesive proteins that contribute to the high sticking ability of marine adhesives.[14−17] Although the binding mechanism is still under debate, the chemisorption to metal oxide surfaces was proposed to comprise the monodentate−bidentate bond.[18−20] The binding of catechol to silica is noncovalent; its binding energy amounted to 14 kcal/mol, which is smaller than that for the covalent binding with a metal oxide.[21,22]

Catechol or dopamine derivatives have recently been used to anchor small functional biomolecules onto ferromagnetic Fe_2O_3 and semiconductor TiO_2 nanoparticles for biomedical applications.[23−28] While polydopamine/melanin films can be deposited on almost all kinds of substrate,[29−34] film detachment occurs from Si or Ge substrate, probably due to the weak interactions of catechol with these nonmetal surfaces.[35−37] In the research for simple and versatile strategies to functionalize tubular clay minerals and encouraged by the successful selective modification of halloysite nanotube lumen with alkyl phosphonic acid, we demonstrate here that the dopamine derivative can also be covalently linked in aqueous conditions to the alumina innermost surface but not to the silica outermost surface of halloysite. The modified halloysite with dopamine bearing bromo-group was further used as an initiator for the surface initiated-ATRP (SI-ATRP) polymerization to selectively graft a layer of PMMA brush in the lumen (Scheme 2).

The lumen of the halloysite tubes was immobilized with 2-bromo-*N*-[2-(3,4-dihydroxyphenyl)ethyl]-isobutyryl amide (Dopa), which also served as an ATRP initiator.[38] The

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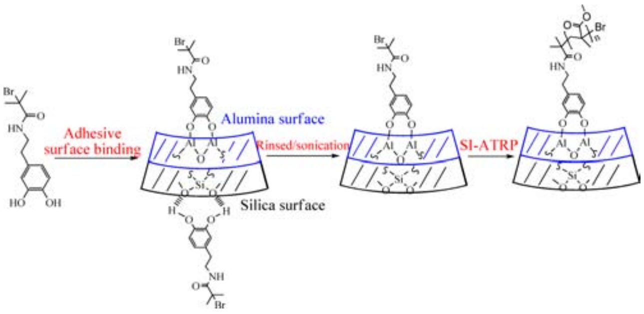
Scheme 2. Selective Modification of Halloysite Lumen with Dopa Biomimetic Initiator and Subsequent Polymerization



attachment of Dopa to the halloysite was confirmed from the characteristic C−H and carbonyl stretching vibrations centered at 2930 cm^{-1} and 1722 cm^{-1}, respectively in the FTIR spectrum (Figure S1, Supporting Information).[20,39,40] However, the C−H and C═O stretching bands are very weak. The quantity of the Dopa attached to the halloysite was determined by thermogravimetric analysis (TGA) to be 1.1 wt%, and the relative amount of grafted PMMA was 7.1 wt% (Figure S3, Supporting Information).

The presence of Dopa was confirmed by XPS measurement. The main difference between Figure 1 (a) and (b) is the presence of N 1s and Br 3d signal in the XPS spectra of Dopa treated Al substrate (after vigorous rinsing and sonication) but not detected in the Si substrate. The Al 2p and O 1s signal of Al substrate greatly reduced to 15.6% and 47.8%, respectively, after Dopa treatment while the Si 2p and O 1s of Si substrate remain same concentration (Table S1, Supporting Information). The Br 3d peak, a useful indicator because of its presence in organic molecule but not in the substrate, showed that Dopa was readily adsorbed to alumina but antiadsorptive to silica substrate.

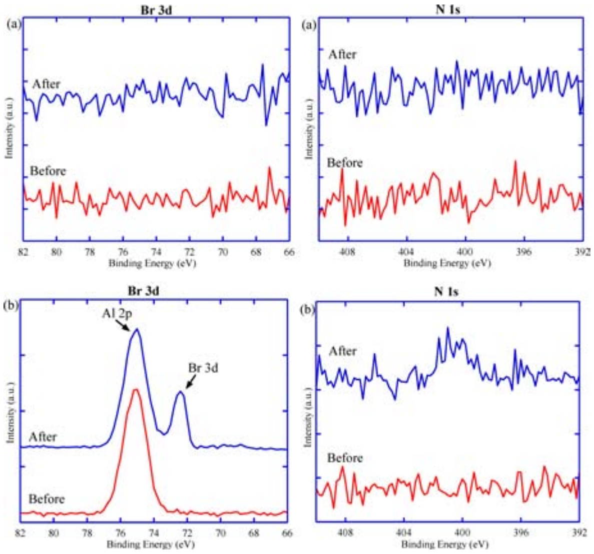


Figure 1. High resolution XPS of the Br 3d and N 1s region for Si (a) and Al (b) surfaces before and after treated with Dopa.

Information regarding the interaction of Dopa on halloysite was provided by solid-state ^{13}C NMR spectroscopy. The solid-state ^{13}C NMR spectrum of Dopa (Figure 2) displays sharp resonances for all eleven carbon environments of the molecule, which can be readily assigned; 177.0 ppm C(3), 144.3 ppm C(9), 142.2 ppm C(10), 130.2 ppm C(6), 118.8 ppm C(8), C(11), 116.7 ppm C(7), 62.7 ppm C(2), 60.0 ppm C(4), 39.5 ppm C(5), 34.0 ppm C(1). The spectrum of halloysite-Dopa shows broader resonances than that of the original molecule, suggesting slower motion of grafted Dopa inside the halloysite lumen.[41] The resonance corresponding to the catechol groups disappears in the composite or is at least strongly decreased, while the carbons of the aliphatic side chain are still predominant. The ^{13}C NMR spectra indicate that the chemical environment of grafted Dopa is somewhat different from the starting material due to strong catechol−alumina interaction in the halloysite lumen.[42]

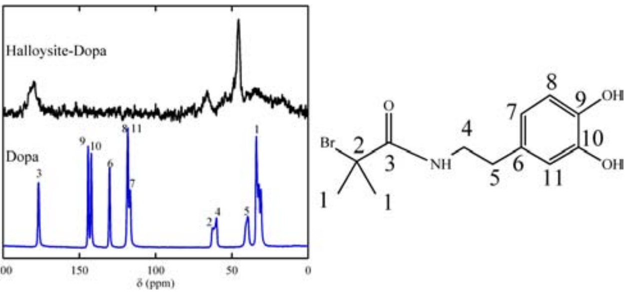


Figure 2. Solid-state ^{13}C NMR spectra of Dopa and halloysite-Dopa (Dopa formula is given at the right).

The selective adsorption nature of Dopa on metal oxide over silica was evidenced from solid-state ^{13}C NMR of silica and alumina nanoparticle before and after treatment.[43] In the model experiment, alumina nanoparticles were treated with Dopa in a mixture solvent of THF:H_2O (4:1), then sonicated and rinsed with THF:H_2O solution five times and dried under vacuum at 70 °C. For alumina−Dopa, the ^{13}C NMR spectra of the resulting powders (Figure 3a) displayed two resonances. The broad resonances at 20−50 ppm (aliphatic) and 181.1 ppm C(3) were attributed to the grafted Dopa species through formation of alumina−catechol covalent bonds. However, when silica nanoparticles were treated with Dopa in THF:H_2O, Dopa

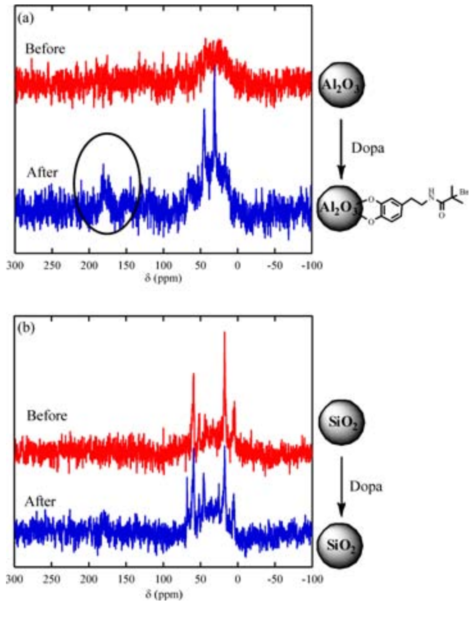


Figure 3. Solid-state ^{13}C NMR spectra of (a) alumina and (b) silica nanoparticles before and after Dopa treatment.

species could no longer be detected as shown in Figure 3b (broad resonances at 0−80 ppm were adventitious hydrocarbon contamination). This behavior may be ascribed to a weak silica−catechol bond, which can be readily removed by sonication and THF:H_2O rinses. These results are also applicable to the alumina and silica surfaces of halloysite.

Alumina-catechol bonds are much more stable than silica−catechol bonds, allowing selective modification of aluminol group of halloysite lumen by catechol group under aqueous conditions.

The growth of PMMA brush from tube lumen can be ascertained from transmission electron microscopy (TEM) study. Figure 4 shows the TEM images of halloysite (a) and lumen PMMA grafted halloysite (b,c). For the purpose of easier visualization of the polymer portion of the sample, the halloysite underwent prolonged polymerization time. After being polymerized for 24 h, the interior cavity was completely filled with the PMMA brush and some polymer extension is visible at the tube opening. The droplet presumably corresponding to polymer protruded from the tube opening is clearly seen in Figure 4(b,c). This provides further evidence that the PMMA brush grows through selectively grafted halloysite lumen.

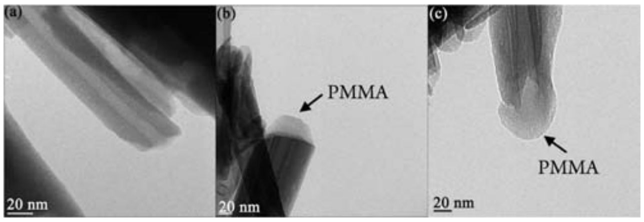


Figure 4. TEM images of halloysite before (a) and after SI-ATRP of MMA (b,c). The arrows in (b) and (c) indicate the extruded PMMA from the tube openings

In conclusion, the selectivity of the Dopa coating for halloysite lumen may be ascribed to the high affinity of the catechol group for metal oxides located at the tube inner surface and weaker catechol−silica bond (tube's outer surface). A similar selectivity is expected for other silica−metal oxides systems, such as silica−titania, silica−zirconia, and silica−ITO. The silica outermost surface of the halloysite−Dopa composite can also be covalently bound with a second class of organic groups via silylation reaction.[13] Moreover, the use of mussel-inspired binder dopamine as a site-specific anchor on natural clay under mild aqueous conditions for the design of an organic−inorganic hybrid embraces the "Green Chemistry" principles that promise to reduce the utilization and generation of hazardous substances.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental details, figures, and tables showing XPS, FTIR, and TGA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bates, T. F.; Hildebrand, F. A.; Swineford, A. *Am. Mineral.* **1950**, *35*, 463−484.

(2) (a) Li, C.; Liu, J.; Qu, X.; Guo, B.; Yang, Z. *J. Appl. Polym. Sci.* **2008**, *110*, 3638−3646. (b) Du, M.; Guo, B.; Jia, D. *Polymer Intern.* **2010**, *59*, 574−95.

(3) Wang, L.-P.; Wang, Y.-P.; Pei, X.-W.; Peng, B. *React. Funct. Polym.* **2008**, *68*, 649−655.

(4) (a) Vergaro, V.; Abdullayev, E.; Lvov, Y. M.; Zeitoun, A.; Cingolani, R.; Rinaldi, R.; Leporatti, S. *Biomacromolecules* **2010**, *11*, 820−826. (b) Lvov, Y.; Price, R.; Gaber, B.; Ichinose, I. *Colloids Surf.: Eng.* **2002**, *198*, 375−382.

(5) Matsuno, R.; Yamamoto, K.; Otsuka, H.; Takahara, A. *Chem. Mater.* **2002**, *15*, 3−5.

(6) Matsuno, R.; Otsuka, H.; Takahara, A. *Soft Matter* **2006**, *2*, 415−421.

(7) (a) Ma, W.; Otsuka, H.; Takahara, A. *Chem. Commun.* **2011**, *47*, 5813−5815. (b) Ma, W.; Yah, W. O.; Otsuka, H.; Takahara, A. *J. Mater. Chem.* **2012**, *22*, 11887−11892.

(8) Terayama, Y.; Kikuchi, M.; Kobayashi, M.; Takahara, A. *Macromolecules* **2010**, *44*, 104−111.

(9) Horiuchi, S.; Hanada, T.; Ebisawa, M.; Matsuda, Y.; Kobayashi, M.; Takahara, A. *ACS Nano* **2009**, *3*, 1297−1304.

(10) Lvov, Y. M.; Shchukin, D. G.; Möhwald, H.; Price, R. R. *ACS Nano* **2008**, *2*, 814−820.

(11) Abdullayev, E.; Sakakibara, K.; Okamoto, K.; Wei, W.; Ariga, K.; Lvov, Y. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4040−4046.

(12) Abdullayev, E.; Lvov, Y. *J. Mater. Chem.* **2010**, *20*, 6681−6687.

(13) Yah, W. O.; Takahara, A.; Lvov, Y. M. *J. Am. Chem. Soc.* **2012**, *134*, 1853−1859.

(14) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. *Science* **2007**, *318*, 426−430.

(15) Holten-Andersen, N.; Fantner, G. E.; Hohlbauch, S.; Waite, J. H.; Zok, F. W. *Nat. Mater.* **2007**, *6*, 669−672.

(16) Harrington, M. J.; Masic, A.; Holten-Andersen, N.; Waite, J. H.; Fratzl, P. *Science* **2010**, *328*, 216−220.

(17) Wilker, J. J. *Nat. Chem. Biol.* **2011**, *7*, 579−580.

(18) McBride, M. B.; Wesselink, L. G. *Environ. Sci. Technol.* **1988**, *22*, 703−708.

(19) Redfern, P. C.; Zapol, P.; Curtiss, L. A.; Rajh, T.; Thurnauer, M. C. *J. Phys. Chem. B* **2003**, *107*, 11419−11427.

(20) (a) Connor, P. A.; Dobson, K. D.; McQuillan, A. J. *Langmuir* **1995**, *11*, 4193−4195. (b) Xu, H.; Nishida, J.; Ma, W.; Wu, H.; Kobayashi, M.; Otsuka, H.; Takahara, A. *ACS Macro Lett.* **2012**, *1*, 457−460.

(21) Mian, S. A.; Saha, L. C.; Jang, J.; Wang, L.; Gao, X.; Nagase, S. *J. Phys. Chem. C* **2010**, *114*, 20793−20800.

(22) Mian, S.; Gao, X.; Nagase, S.; Jang, J. *Theor. Chem. Acc.* **2011**, *130*, 333−339.

(23) Xu, C.; Xu, K.; Gu, H.; Zheng, R.; Liu, H.; Zhang, X.; Guo, Z.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 9938−9939.

(24) Shultz, M. D.; Reveles, J. U.; Khanna, S. N.; Carpenter, E. E. *J. Am. Chem. Soc.* **2007**, *129*, 2482−2487.

(25) Rajh, T.; Saponjic, Z.; Liu, J.; Dimitrijevic, N. M.; Scherer, N. F.; Vega-Arroyo, M.; Zapol, P.; Curtiss, L. A.; Thurnauer, M. C. *Nano Lett.* **2004**, *4*, 1017−1023.
(26) Cheng, K.; Peng, S.; Xu, C.; Sun, S. *J. Am. Chem. Soc.* **2009**, *131*, 10637−10644.
(27) Wang, B.; Xu, C.; Xie, J.; Yang, Z.; Sun, S. *J. Am. Chem. Soc.* **2008**, *130*, 14436−14437.
(28) Na, H. B.; Palui, G.; Rosenberg, J. T.; Ji, X.; Grant, S. C.; Mattoussi, H. *ACS Nano* **2012**, *6*, 389−399.
(29) Bernsmann, F.; Ponche, A.; Ringwald, C.; Hemmerle, J.; Raya, J.; Bechinger, B.; Voegel, J.-C.; Schaaf, P.; Ball, V. *J. Phys. Chem. C* **2009**, *113*, 8234−8242.
(30) Bernsmann, F.; Ball, V.; Addiego, F.; Ponche, A.; Michel, M.; Gracio, J. J. d. A.; Toniazzo, V.; Ruch, D. *Langmuir* **2011**, *27*, 2819−2825.
(31) Yang, L.; Phua, S. L.; Teo, J. K. H.; Toh, C. L.; Lau, S. K.; Ma, J.; Lu, X. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3026−3032.
(32) Xing, B.; Yin, X.-B. *PLoS One* **2009**, *4*, e6451.
(33) Faure, E.; Halusiak, E.; Farina, F.; Giamblanco, N.; Motte, C.; Poelman, M.; Archambeau, C.; Van De Weerdt, C.; Martial, J.; Jerome, C.; Duwez, A.-S.; Detrembleur, C. *Langmuir* **2012**, *28*, 2971−2978.
(34) Kang, S. M.; Rho, J.; Choi, I. S.; Messersmith, P. B.; Lee, H. *J. Am. Chem. Soc.* **2009**, *131*, 13224−13225.
(35) Ryu, J.; Ku, S. H.; Lee, H.; Park, C. B. *Adv. Funct. Mater.* **2010**, *20*, 2132−2139.
(36) Malisova, B.; Tosatti, S.; Textor, M.; Gademann, K.; Zurcher, S. *Langmuir* **2010**, *26*, 4018−4026.
(37) Muller, M.; Kepler, B. *Langmuir* **2011**, *27*, 12499−12505.
(38) Fan, X.; Lin, L.; Dalsin, J. L.; Messersmith, P. B. *J. Am. Chem. Soc.* **2005**, *127*, 15843−15847.
(39) Fan, X.; Lin, L.; Messersmith, P. B. *Compos. Sci. Technol.* **2006**, *66*, 1198−1204.
(40) Gulley-Stahl, H.; Hogan, P. A.; Schmidt, W. L.; Wall, S. J.; Buhrlage, A.; Bullen, H. A. *Environ. Sci. Technol.* **2010**, *44*, 4116−4121.
(41) Park, T. J.; Kim, J.; Kim, T. K.; Park, H. M.; Choi, S. S.; Kim, Y. *Bull. Korean Chem. Soc.* **2008**, *29*, 2459−2464.
(42) Jaber, M.; Lambert, J.-F. *J. Phys. Chem. Lett.* **2010**, *1*, 85−88.
(43) Jaber, M.; Bouchoucha, M.; Delmotte, L.; Methivier, C.; Lambert, J.-F. *J. Phys. Chem. C* **2011**, *115*, 19216−19225.