

Nanomaterials, 2017, vol.7, N8

Halloysite nanotubes: Controlled access and release by smart gates

Cavallaro G., Danilushkina A., Evtugyn V., Lazzara G., Milioto S., Parisi F., Rozhina E., Fakhrullin R.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2017 by the authors. Licensee MDPI, Basel, Switzerland. Hollow halloysite nanotubes have been used as nanocontainers for loading and for the triggered release of calcium hydroxide for paper preservation. A strategy for placing end-stoppers into the tubular nanocontainer is proposed and the sustained release from the cavity is reported. The incorporation of Ca(OH)₂ into the nanotube lumen, as demonstrated using transmission electron microscopy (TEM) imaging and Energy Dispersive X-ray (EDX) mapping, retards the carbonatation, delaying the reaction with CO₂ gas. This effect can be further controlled by placing the end-stoppers. The obtained material is tested for paper deacidification. We prove that adding halloysite filled with Ca(OH)₂ to paper can reduce the impact of acid exposure on both the mechanical performance and pH alteration. The end-stoppers have a double effect: they preserve the calcium hydroxide from carbonation, and they prevent from the formation of highly basic pH and trigger the response to acid exposure minimizing the pH drop-down. These features are promising for a composite nanoadditive in the smart protection of cellulose-based materials.

<http://dx.doi.org/10.3390/nano7080199>

Keywords

Cellulose, Controlled release, Halloysite, Nanocomposite

References

- [1] Fakhrullina, G.I.; Akhatova, F.S.; Lvov, Y.M.; Fakhrullin, R.F. Toxicity of halloysite clay nanotubes In Vivo: A *Caenorhabditis elegans* study. *Environ. Sci. Nano* 2015, 2, 54-59.
- [2] Kryuchkova, M.; Danilushkina, A.; Lvov, Y.; Fakhrullin, R. Evaluation of toxicity of nanoclays and graphene oxide In Vivo: A *Paramecium caudatum* study. *Environ. Sci. Nano* 2016, 3, 442-452.
- [3] Shutava, T.G.; Fakhrullin, R.F.; Lvov, Y.M. Spherical and tubule nanocarriers for sustained drug release. *Curr. Opin. Pharmacol.* 2014, 18, 141-148.
- [4] Wei, W.; Minullina, R.; Abdullayev, E.; Fakhrullin, R.; Mills, D.; Lvov, Y. Enhanced efficiency of antiseptics with sustained release from clay nanotubes. *RSC Adv.* 2014, 4, 488-494.
- [5] Cavallaro, G.; Lazzara, G.; Massaro, M.; Milioto, S.; Noto, R.; Parisi, F.; Riela, S. Biocompatible poly(N-isopropylacrylamide)-halloysite nanotubes for thermoresponsive curcumin release. *J. Phys. Chem. C* 2015, 119, 8944-8951.
- [6] Lvov, Y.M.; DeVilliers, M.M.; Fakhrullin, R.F. The application of halloysite tubule nanoclay in drug delivery. *Expert Opin. Drug Deliv.* 2016, 13, 977-986.

- [7] Bonifacio, M.A.; Gentile, P.; Ferreira, A.M.; Cometa, S.; De Giglio, E. Insight into halloysite nanotubes-loaded gellan gum hydrogels for soft tissue engineering applications. *Carbohydr. Polym.* 2017, 163, 280-291.
- [8] Fakhrullin, R.F.; Lvov, Y.M. Halloysite clay nanotubes for tissue engineering. *Nanomedicine* 2016, 11, 2243-2246.
- [9] Ji, L.; Qiao, W.; Zhang, Y.; Wu, H.; Miao, S.; Cheng, Z.; Gong, Q.; Liang, J.; Zhu, A. A gelatin composite scaffold strengthened by drug-loaded halloysite nanotubes. *Mater. Sci. Eng. C* 2017, 78, 362-369.
- [10] Von Klitzing, R.; Stehl, D.; Pogrzeba, T.; Schomäcker, R.; Minullina, R.; Panchal, A.; Konnova, S.; Fakhrullin, R.; Koetz, J.; Möhwald, H. et al. Halloysites stabilized emulsions for hydroformylation of long chain olefins. *Adv. Mater. Interfaces* 2017, 4, N1.
- [11] Cavallaro, G.; Lazzara, G.; Milioto, S. Dispersions of nanoclays of different shapes into aqueous and solid biopolymeric matrices. Extended physicochemical study. *Langmuir* 2011, 27, 1158-1167.
- [12] Cavallaro, G.; Lazzara, G.; Konnova, S.; Fakhrullin, R.; Lvov, Y. Composite films of natural clay nanotubes with cellulose and chitosan. *Green Mater.* 2014, 2, 232-242.
- [13] Gorrasi, G.; Pantani, R.; Murariu, M.; Dubois, P. PLA/Halloysite nanocomposite films: Water vapor barrier properties and specific key characteristics. *Macromol. Mater. Eng.* 2014, 299, 104-115.
- [14] Machado, G.S.; de Freitas Castro, K.A.D.; Wypych, F.; Nakagaki, S. Immobilization of metalloporphyrins into nanotubes of natural halloysite toward selective catalysts for oxidation reactions. *J. Mol. Catal. Chem.* 2008, 283, 99-107.
- [15] Wang, R.; Jiang, G.; Ding, Y.; Wang, Y.; Sun, X.; Wang, X.; Chen, W. Photocatalytic activity of heterostructures based on TiO and halloysite nanotubes. *ACS Appl. Mater. Interfaces* 2011, 3, 4154-4158.
- [16] Luo, P.; Zhao, Y.; Zhang, B.; Liu, J.; Yang, Y.; Liu, J. Study on the adsorption of Neutral Red from aqueous solution onto halloysite nanotubes. *Water Res.* 2010, 44, 1489-1497.
- [17] Pasbakhsh, P.; Churchman, G.J.; Keeling, J.L. Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. *Appl. Clay Sci.* 2013, 74, 47-57.
- [18] Joussein, E.; Petit, S.; Churchman, G.J.; Theng, B.; Righi, D.; Delvaux, B. Halloysite clay minerals-A review. *Clay Miner.* 2005, 40, 383-426.
- [19] Lvov, Y.M.; Shchukin, D.G.; Mohwald, H.; Price, R.R. Halloysite clay nanotubes for controlled release of protective agents. *ACS Nano* 2008, 2, 814-820.
- [20] Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F. Steric stabilization of modified nanoclays triggered by temperature. *J. Colloid Interface Sci.* 2016, 461, 346-351.
- [21] Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F.; Sanzillo, V. Modified halloysite nanotubes: Nanoarchitectures for enhancing the capture of oils from vapor and liquid phases. *ACS Appl. Mater. Interfaces* 2014, 6, 606-612.
- [22] Cavallaro, G.; Lazzara, G.; Milioto, S. Exploiting the colloidal stability and solubilization ability of clay nanotubes/ionic surfactant hybrid nanomaterials. *J. Phys. Chem. C* 2012, 116, 21932-21938.
- [23] Tully, J.; Yendluri, R.; Lvov, Y. Halloysite clay nanotubes for enzyme immobilization. *Biomacromolecules* 2016, 17, 615-621.
- [24] Della Porta, V.; Bramanti, E.; Campanella, B.; Tine, M.R.; Duce, C. Conformational analysis of bovine serum albumin adsorbed on halloysite nanotubes and kaolinite: A Fourier transform infrared spectroscopy study. *RSC Adv.* 2016, 6, 72386-72398.
- [25] Ruiz-Hitzky, E.; Aranda, P.; Darder, M.; Ogawa, M. Hybrid and biohybrid silicate based materials: Molecular vs. block-assembling bottom-up processes. *Chem. Soc. Rev.* 2011, 40, 801-828.
- [26] Nagy, D.; Firkala, T.; Drotar, E.; Szegedi, A.; Laszlo, K.; Szilagy, I.M. Photocatalytic WO/TiO nanowires: WO polymorphs influencing the atomic layer deposition of TiO. *RSC Adv.* 2016, 6, 95369-95377.
- [27] Szilagy, I.M.; Santala, E.; Heikkilä, M.; Pore, V.; Kemell, M.; Nikitin, T.; Teucher, G.; Firkala, T.; Khriachtchev, L.; Räsänen, M. et al. Photocatalytic properties of WO/TiO Core/Shell Nanofibers prepared by Electrospinning and Atomic Layer Deposition. *Chem. Vap. Depos.* 2013, 19, 149-155.
- [28] Andres, C.M.; Larraza, I.; Corrales, T.; Kotov, N.A. Nanocomposite microcontainers. *Adv. Mater.* 2012, 24, 4597-4600.
- [29] Lvov, Y.; Abdullayev, E. Functional polymer-clay nanotube composites with sustained release of chemical agents. *Prog. Polym. Sci.* 2013, 38, 1690-1719.
- [30] Abdullayev, E.; Price, R.; Shchukin, D.; Lvov, Y. Halloysite tubes as nanocontainers for anticorrosion coating with Benzotriazole. *ACS Appl. Mater. Interfaces* 2009, 1, 1437-1443.
- [31] Viseras, M.T.; Aguzzi, C.; Cerezo, P.; Viseras, C.; Valenzuela, C. Equilibrium and kinetics of 5-aminosalicylic acid adsorption by halloysite. *Microporous Mesoporous Mater.* 2008, 108, 112-116.
- [32] Fix, D.; Andreeva, D.V.; Lvov, Y.M.; Shchukin, D.G.; Möhwald, H. Application of inhibitor-loaded halloysite nanotubes in active anti-corrosive coatings. *Adv. Funct. Mater.* 2009, 19, 1720-1727.
- [33] Shchukin, D.G.; Möhwald, H. Surface-engineered nanocontainers for entrapment of corrosion inhibitors. *Adv. Funct. Mater.* 2007, 17, 1451-1458.

- [34] Elumalai, D.N.; Tully, J.; Lvov, Y.; Derosa, P.A. Simulation of stimuli-triggered release of molecular species from halloysite nanotubes. *J. Appl. Phys.* 2016, 120, 134311.
- [35] Lvov, Y.; Wang, W.; Zhang, L.; Fakhrullin, R. Halloysite clay nanotubes for loading and sustained release of functional compounds. *Adv. Mater.* 2016, 28, 1227-1250.
- [36] Du, M.; Guo, B.; Jia, D. Newly emerging applications of halloysite nanotubes: A review. *Polym. Int.* 2010, 59, 574-582.
- [37] Joshi, A.; Abdullayev, E.; Vasiliev, A.; Volkova, O.; Lvov, Y. Interfacial modification of clay nanotubes for the sustained release of corrosion inhibitors. *Langmuir* 2013, 29, 7439-7448.
- [38] Abdullayev, E.; Lvov, Y. Clay nanotubes for corrosion inhibitor encapsulation: Release control with end stoppers. *J. Mater. Chem.* 2010, 20, 6681-6687.
- [39] Dzamukova, M.R.; Naumenko, E.A.; Lvov, Y.M.; Fakhrullin, R.F. Enzyme-activated intracellular drug delivery with tubule clay nanoformulation. *Sci. Rep.* 2015, 5, 10560.
- [40] Biddeci, G.; Cavallaro, G.; Di Blasi, F.; Lazzara, G.; Massaro, M.; Milioto, S.; Parisi, F.; Riela, S.; Spinelli, G. Halloysite nanotubes loaded with peppermint essential oil as filler for functional biopolymer film. *Carbohydr. Polym.* 2016, 152, 548-557.
- [41] Gorrasi, G. Dispersion of halloysite loaded with natural antimicrobials into pectins: Characterization and controlled release analysis. *Carbohydr. Polym.* 2015, 127, 47-53.
- [42] Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F. Halloysite nanotubes with fluorinated cavity: An innovative consolidant for paper treatment. *Clay Miner.* 2016, 51, 445-455.
- [43] Du, M.; Guo, B.; Jia, D. Thermal stability and flame retardant effects of halloysite nanotubes on poly(propylene). *Eur. Polym. J.* 2006, 42, 1362-1369.
- [44] Poggi, G.; Giorgi, R.; Toccafondi, N.; Katur, V.; Baglioni, P. Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper. *Langmuir* 2010, 26, 19084-19090.
- [45] Dong, C.; Cairney, J.; Sun, Q.; Maddan, O.L.; He, G.; Deng, Y. Investigation of Mg(OH) nanoparticles as an antibacterial agent. *J. Nanopart. Res.* 2010, 12, 2101-2109.
- [46] Giorgi, R.; Dei, L.; Ceccato, M.; Schettino, C.; Baglioni, P. Nanotechnologies for conservation of cultural heritage: Paper and canvas deacidification. *Langmuir* 2002, 18, 8198-8203.
- [47] Poggi, G.; Toccafondi, N.; Melita, L.N.; Knowles, J.C.; Bozec, L.; Giorgi, R.; Baglioni, P. Calcium hydroxide nanoparticles for the conservation of cultural heritage: New formulations for the deacidification of cellulose-based artifacts. *Appl. Phys. A* 2014, 114, 685-693.
- [48] Rodriguez-Navarro, C.; Vettori, I.; Ruiz-Agudo, E. Kinetics and mechanism of calcium hydroxide conversion into calcium alkoxides: Implications in heritage conservation using nanolimes. *Langmuir* 2016, 32, 5183-5194.
- [49] Cheradame, H.; Ipert, S.; Rousset, E. Mass deacidification of paper and books. I: Study of the limitations of the gas phase processes. *Restorator* 2008, 24, 227-239.
- [50] Baty, J.W.; Maitland, C.L.; Minter, W.; Hubbe, M.A.; Jordan-Mowery, S.K. Deacidification for the conservation and preservation of paper-based works: A review. *BioResources* 2010, 5, 1955-2023.
- [51] Abdullayev, E.; Sakakibara, K.; Okamoto, K.; Wei, W.; Ariga, K.; Lvov, Y. Natural tubule clay template synthesis of silver nanorods for antibacterial composite coating. *ACS Appl. Mater. Interfaces* 2011, 3, 4040-4046.
- [52] Cavallaro, G.; Lazzara, G.; Milioto, S.; Parisi, F. Hydrophobically modified halloysite nanotubes as reverse micelles for water-in-oil emulsion. *Langmuir* 2015, 31, 7472-7478.
- [53] Joo, Y.; Sim, J.H.; Jeon, Y.; Lee, S.U.; Sohn, D. Opening and blocking the inner-pores of halloysite. *Chem. Commun.* 2013, 49, 4519-4521.
- [54] Materic, V.; Hyland, M.; Jones, M.I.; Northover, B. High temperature carbonation of Ca(OH): The effect of particle surface area and pore volume. *Ind. Eng. Chem. Res.* 2014, 53, 2994-3000.
- [55] Materic, V.; Smedley, S.I. High temperature carbonation of Ca(OH). *Ind. Eng. Chem. Res.* 2011, 50, 5927-5932.
- [56] Blanco, I.; Abate, L.; Bottino, F.A.; Bottino, P. Thermal behaviour of a series of novel aliphatic bridged polyhedral oligomeric silsesquioxanes (POSSs)/polystyrene (PS) nanocomposites: The influence of the bridge length on the resistance to thermal degradation. *Polym. Degrad. Stab.* 2014, 102, 132-137.