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Nanostructured microspheres of MnO_2 formed by room temperature solution processing†‡

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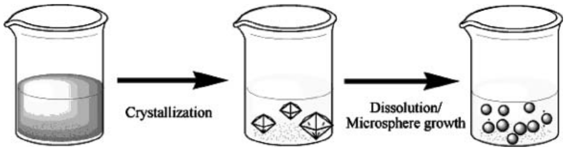
Nanostructured microspheres of manganese oxide have been prepared by the solution processing of manganese(II) salts using 1,4,7,10-tetraazacyclododecane and utilizing a crystalline intermediate stage.

Manganese oxides from mineral and synthetic sources are of significant technological importance.[1] For instance, they are used extensively in catalytic oxidations[2] or as battery materials.[3] More recently, other oxides have also been investigated for higher properties such as combinations of ferromagnetic and ferroelectric effects.[4] Now there is a significant trend towards identifying novel properties and perhaps uses based on the nanostructuring of these and other novel oxides.[5] Nanostructuring can be achieved by a variety of methods including templating,[6] self-assembly,[7] and thermolysis of coordination complexes.[8] The latter is of particular importance since precise control of the precursor complexes can be exercised giving products of predictable stoichiometry. One further methodology that is gaining increasing importance involves solution processing of inorganic materials into nanostructured forms, which is receiving attention because of its lower environmental impact and ease of implementation. Solution processing offers other advantages of operation at large scales and applicability to materials that are difficult to manage using vacuum processing. Thus the development of this approach holds significant promise as a means of accessing tailored materials. In this communication, we report the preparation of nanostructured manganese oxide in microspherical morphology using solution processing of appropriate precursor materials (Scheme 1), and which will subsequently be investigated as possible electrode materials for new high performance batteries. Nanostructured manganese oxides have been previously reported in several morphologies including nanoparticles,[9] nanosheets,[10] hollow nanoshells,[11] nanofibres[12] or mesoporous materials[13] but, to the best of our knowledge, microspheres with a lamellar internal nanostructure have not been reported.

In our investigations of biologically relevant systems we identified the coordination complexes of manganese as being potentially of interest. The use of such complexes of manganese with triazacyclononane (TACN) has been demonstrated for industrial bleaching applications.[14] Additionally, mixed valent complexes of manganese with TACN[15] or 1,4,8,11-tetraazacyclotetradecane (cyclam)[16] are well known while those of 1,4,7,10-tetraazacyclododecane (cyclen) have not been subjected to in depth investigation.[17] During work to assess the structures of dinuclear complexes of manganese with cyclen, we discovered a method for preparing nanostructured manganese oxide. Initially, we undertook structural studies, which revealed a supramolecular sheet structure involving chloride counteranions, but also found an aggregated, nanostructured form of a manganese oxide upon standing of the crystallization solutions.

When a methanolic solution of cyclen was mixed with manganese(II) chloride in aqueous solution and in the presence of sodium perchlorate a gradual colour change from pale pink to dark green occurred consistent with formation of a dioxo-dinuclear species similar to that found for cyclam.[16] Subsequent crystallization gave dark green prisms suitable for X-ray crystallographic analysis.§ The structure of the dioxo-dinuclear unit is given in Fig. 1 and it is consistent with a molecular formula $[Mn_2(\mu_2\text{-}O)_2(C_8H_{20}N_4)_2]\cdot 2Cl^-\cdot ClO_4^-$. The oxidation states of the manganese atoms were confirmed by bond valence sum analysis[18] with calculated valences 3.06 and 4.03 for Mn(1) and Mn(2), respectively (see caption of Fig. 1 for bond lengths), indicating valence localization in the Mn_2O_2 unit. Linear arrays of the dinuclear unit formed by double hydrogen bond bridging of a chloride ion with cyclen amine groups run parallel to the *b*-axis with these linear arrays being aligned within sheets by a further inter-array hydrogen bonding involving the remaining chloride counterion (see ESI‡). The single perchlorate counteranion per dinuclear unit is singly hydrogen bonded at one of the remaining cyclen amine groups and is not involved in the extended structure. Sheets formed by amine–chloride hydrogen bonding contain cavities, which are occupied by the perchlorate anions hydrogen bonded to adjacent sheets.



Scheme 1 Illustration of microsphere synthesis. Crystallization of the primary product is followed by its dissolution and redeposition as nanostructured microshperes.

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† Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Packing diagrams, EDX and XPS spectra, FTIR spectra, magnetic susceptibility data. See DOI: 10.1039/b713201h

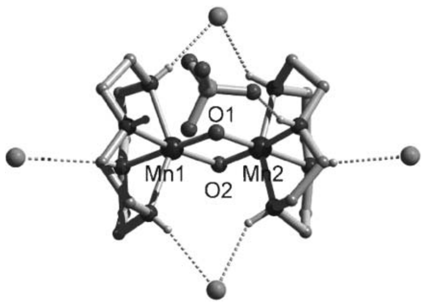

Fig. 1 X-Ray crystal structure of the initial product from the reaction between cyclen and manganese(II) chloride tetrahydrate in water–methanol solution in the presence of sodium perchlorate. Important bond lengths and angles about the Mn_2O_2 unit: Mn(1)–O(1) 1.814(4), Mn(1)–O(2) 1.868(5), Mn(2)–O(1) 1.765(5), Mn(2)–O(2) 1.786(4) Å, Mn(1)–O(1)–Mn(2) 97.7(2), Mn(1)–O(2)–Mn(2) 95.0(2)°.

Cyclen reacts in a similar fashion with other manganese salts including manganese(II) acetate and manganese(II) oxalate. In the case of oxalate, allowing the crystallization solutions to stand for periods longer than required for the collection of crystals resulted in formation of a dark brown precipitate concurrent with dissolution of the crystalline or microcrystalline primary products. Observation by optical microscopy revealed the particulate nature of these precipitates (Fig. 2(a)). Scanning electron microscopy (SEM, Fig. 2(b)–(d)) was used to probe further the structure of these particles and revealed that they possess a secondary structure of lamellar appearance.

X-Ray diffraction (XRD) patterns for the manganese(II) oxalate system are shown in Fig. 3. Fig. 3(a) is the XRD pattern of the dark green microcrystalline primary product.[19] Upon standing of this product under the reaction liquors (*i.e.* the product was not filtered) a broad peak appears in the diffraction patterns of the materials filtered later (see Fig. 3(b)). Peaks due to the primary product gradually decrease in intensity with a concurrent increase in intensity of the broad peaks. Additionally, further sharp peaks appear, which are due to a yet-to-be-identified colourless crystalline byproduct (Fig. 3(c)). This impurity can be removed manually yielding samples having the XRD pattern in Fig. 3(d). The *d*-spacings of the broad peaks are of a ratio 1 : 1/2 : 1/3 indicating a lamellar structure with a layer thickness of ∼1.2 nm. Further weak reflections with *d*-spacing values of 2.46 and 1.45 Å are at angles expected for known examples of layered MnO_2, respectively being the 10 and 11 reflections due to its two dimensional hexagonal architecture (Fig. 3(e)).[20] The layer thickness deduced from the XRD data (1.2 nm) indicates that there is a species intercalated in the structure and infrared spectroscopy (see ESI‡) suggests that this is cyclen or its decomposition product(s).

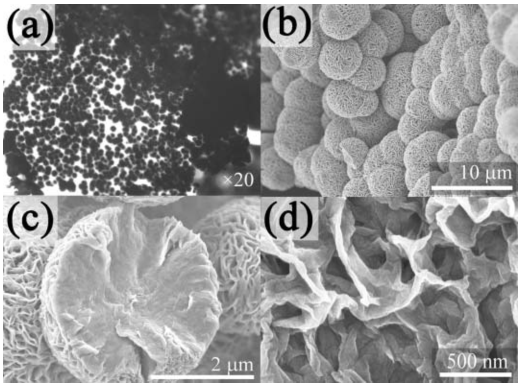

Fig. 2 (a) Optical microscopy image of the microspherical product of the reaction between cyclen and manganese(II) oxalate in water–methanol. (b) SEM image of the same sample. (c) Texture at the interior of a microsphere. (d) Texture at the surface of a microsphere.

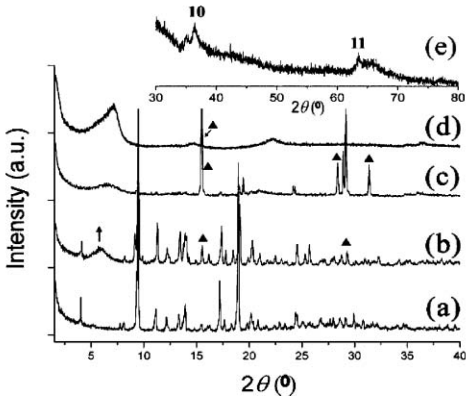

Fig. 3 X-Ray diffraction patterns of the products from the reaction between cyclen and manganese(II) oxalate in water–methanol. (a) Initial microcrystalline product. (b) During crystal decomposition. (c) After completion (∼3 months). (d) Purified nanostructured microspheres. (e) Wide angle region of the XRD spectrum of nanostructured microspheres. Solid triangles denote peaks due to unknown compound.

To probe the elemental composition of the microparticles and their precursors, electron X-ray dispersive analysis (EDX) was performed. EDX spectra revealed an increasing proportion of manganese going from crystals to the final nanostructured microspheres. The final composition according to EDX is Mn (51.2%), O (24.7%), C (16.6%), N (7.6%) suggesting a composition containing MnO_2 accompanied by 1/8 equivalents of cyclen, that is, $MnO_2(C_8H_{20}N_4)_{0.125}$, a formula consistent with the lamellar structure and with the continued presence of an organic species. An XPS survey scan (see ESI‡) confirmed the presence of manganese, oxygen and carbon although the peak due to nitrogen appears broad. These data are consistent with the formula obtained by EDX. The presence of an organic species, probably cyclen, is confirmed by FTIR spectroscopy (see ESI‡) and this is in line with the requirement of a cationic species for the electrostatic maintenance of the lamellar form so that the cyclen must be at least partially protonated in order to balance the charge of the oxide layers as in other similar materials[21] and leading to a formulation $MnO_{2-\delta}(C_8H_{20}N_4)_{0.125}$.

Flocculation of aqueous solutions of manganese salts by addition of basic reagents is a well known method for the preparation of manganese oxo-hydroxide aggregates, which are often gelatinous in nature and correspondingly difficult to handle. In this case, our primary sequestration of the manganese cations as the dinuclear cyclen complex prevents a rapid precipitation of the expected oxo-hydroxides. Rather, a preliminary crystallization process is followed by gradual deposition of the nanostructured product. This process is somewhat similar to the 'chelation-mediated' control reported by Oaki and Imai[22] although our process always involves a crystalline intermediate. Nucleation of the nanostructured product appears to occur in close association

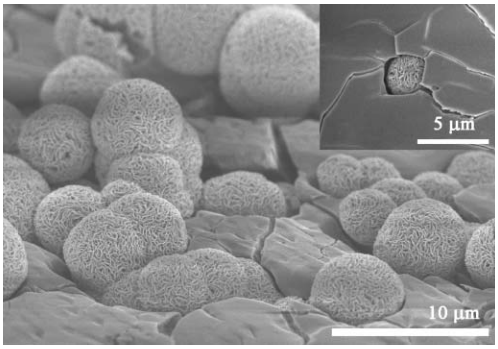

Fig. 4 Intermediate growth stage of the nanostructured microspheres on the surface of crystals of the primary product. Inset: growth of microspheres apparently at the interior of a crystal.

with the crystalline primary product. This is most likely due to the appearance of decompositional defects at the surfaces of the crystals, which provide appropriate sites for growth of the particles. Following this initial stage, growth of the microspheres proceeds also on the glass walls of the reaction vessel. SEM observations of the reaction solutions at intermediate stages of the process show that the nanostructured particles appear to grow both at the surface of the crystals and occasionally even at the interior. However, growth of particles at the interior appears to occur following the loss of integrity of the crystals, since at no time could particles be observed growing inside pristine crystals (by transmission optical microscopic observation). Fig. 4 shows the growth of particles at two sites on the crystalline primary product.

In summary, we have discovered a method for preparing nanostructured microspheres of manganese oxide $MnO_{2-\delta}$ with a lamellar internal structure. This solution process, which operates at room temperature, avoids the precipitation of the manganese oxo-hydroxides and permits preparation of these products with novel structures. Thus we have found a means of producing potentially useful nanostructured manganese oxide particles using a method which is an improvement in terms of environmental impact. The method should be applicable to other systems where precipitation is a problem. In this case, we could obtain microparticles having magnetic properties distinct from those of the common manganese oxides (see ESI‡). The form of these microparticles should endow them with significant surface areas and thus they would possess potential in the areas of catalysis or as electrode materials, and we are now embarking on testing of their suitability for these purposes.

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Notes and references

§ **Synthesis**. A solution of cyclen (0.1 g, 0.58 mmol) in methanol (10 mL) was added dropwise with stirring to a solution of manganese(II) chloride tetrahydrate (1 eq., 0.115 g) in water (10 mL). Then sodium perchlorate (0.4 g) was added and the mixture stirred until complete dissolution. The solution was filtered and allowed to stand in a vessel open to the air until crystals of the complex began to appear. Then the solution was allowed to stand for several weeks until a dark particulate matter was deposited, which was subjected to further analysis. Other divalent salts of manganese were treated similarly.

X-Ray crystallography. $C_{64}H_{40}Cl_3Mn_2N_8O_6$, FW 656.79 g mol^{-1}, orthorhombic, *Pnma*, $a = 22.3850(14)$, $b = 9.1934(5)$, $c = 13.2424(10)$ Å, $V = 2725.2(3)$ Å^3, $T = 200$ K, $F(000) = 1364$, $\rho_{calc} = 1.601$ Mg m^{-3}, μ(Mo-Kα) = 1.267 m^{-1}. Stoe IPDS diffractometer, $\lambda = 0.71073$ Å, 15645 data measured to $2\theta_{max} = 52°$, of which 2709 unique ($R_{int} = 0.1230$), structure solution by direct methods and full-matrix refinement against F^2 (all data) using SHELXTL,[23] 192 parameters, final $wR_2 = 0.0903$, $S = 0.967$ (all data), $R_1 = 0.0480$ (1397 with $I > 2\sigma(I)$). CCDC 656863. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713201h

Scanning electron microscopy. A Hitachi S-4800 FE-SEM operating at an accelerating voltage of 4 kV was used to collect images.

X-Ray powder diffraction. XRD of powdered samples was performed using a Rigaku Ultima III diffractometer.

1 J. E. Post, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 3447; S. Roy, in *Manganese Materialization, Geochemistry and Minerology of Terrestrial and Marine Deposits*, ed. K. Nicholson, J. R. Hein, B. Bühn and S. Dasgupta, Geological Society, London, Spec. Pub. 119, pp. 5.
2 S. L. Suib, in *Studies in Surface Science and Catalysis*, ed. H. Chon, S. H. Woo and S. E. Park, Elsevier, Amsterdam, 1996, vol. 102, pp. 47–74.
3 J. O. Besenhard, in *Soft Chemistry Routes to New Materials – Chimie Douce*, ed. J. Rouxel, M. Tournoux and R. Brec, Trans Tech, Aedermannsdorf, 1994, pp. 152–153.
4 W. Eerenstein, N. D. Mathur and J. F. Scott, *Nature*, 2006, **442**, 759.
5 *Synthesis, Properties and Applications of Oxide Nanomaterials*, ed. J. A. Rodriguez and M. Ferdinandez-Garcia, Wiley-Interscience, New York, 2007.
6 G. J. A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
7 G. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418.
8 For example: W. Schmitt, J. P. Hill, S. Malik, C. A. Volkert, H. Ichinose, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2005, **44**, 7048.
9 S. L. Brock, M. Sanabria, S. L. Suib, V. Urban, P. Thiyagarajan and D. I. Potter, *J. Phys. Chem. B*, 1999, **103**, 7416.
10 X. Yang, Y. Makita, Z. Liu, K. Sakane and K. Ooi, *Chem. Mater.*, 2004, **16**, 5581; Y. Oaki and H. Imai, *Angew. Chem., Int. Ed.*, 2007, **46**, 4951.
11 L. Wang, Y. Ebina, K. Takada and T. Sasaki, *Chem. Commun.*, 2004, 1074; H. Chen and J. He, *Chem. Lett.*, 2007, **36**, 174.
12 Z. Tian, Q. Feng, N. Sumida, Y. Makita and K. Ooi, *Chem. Lett.*, 2004, **33**, 952.
13 Z. Tian, W. Tong, J. Wang, N. Duan, V. V. Krishnan and S. L. Suib, *Science*, 1997, **276**, 926.
14 K. F. Sibbons, K. Shastri and M. Watkinson, *Dalton Trans.*, 2006, 645.
15 K. Wieghardt, U. Bossek, D. Ventur and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1985, 347.
16 K. J. Brewer, M. Calvin, R. S. Lumpkin, J. W. Otvos and L. O. Spreer, *J. Am. Chem. Soc.*, 1989, **28**, 4446.
17 P. A. Goodson, D. J. Hodgson, J. Glerup, K. Michelsen and H. Weihe, *Inorg. Chim. Acta*, 1992, **197**, 141; Y.-W. Ren, J. Li, F.-X. Zhang, J.-H. Zhang and H. Guo, *Chin. J. Chem.*, 2005, **23**, 418.
18 W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102.
19 Crystals suitable for single crystal analysis could not be obtained during this work.
20 N. Sakai, Y. Ebina, K. Takada and T. Sasaki, *J. Phys. Chem. B*, 2005, **109**, 9651.
21 Y. Omomo, T. Sasaki, L. Wang and M. Watanabe, *J. Am. Chem. Soc.*, 2003, **125**, 3568; S. L. Brock, M. Sanabria, J. Nair, S. L. Suib and T. Ressler, *J. Phys. Chem. B*, 2001, **105**, 5404.
22 Y. Oaki and H. Imai, *Chem.–Eur. J.*, 2007, **13**, 8564.
23 G. M. Sheldrick, SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA, 1997.