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Effect of the formation of open microcapsules with Mn_3O_4 walls during hydrolysis of the $MnSO_4$ salt solution droplets deposited on the alkaline solution surface

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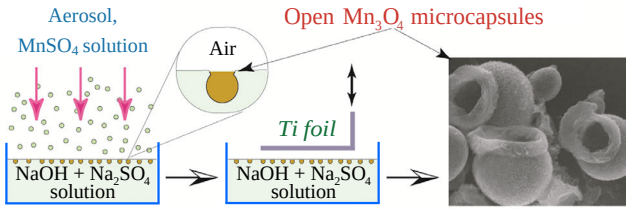
It was shown for the first time that open microcapsules 1–5 μm in size with Mn_3O_4 walls and unique morphology are formed as a result of spraying an aqueous $MnSO_4$ solution onto the surface of an alkali solution. The walls have a thickness of 80–120 nm and consist of an array of Mn_3O_4 nanosheets with a thickness of 2–3 nm, oriented predominantly in the radial direction towards the center of the microcapsule. There is a special rim with a height of 100–200 nm around the hole of the most microcapsules, which can be a kind of 'ground' when fixing such microcapsules on the surface of a substrate in the process of application by the Langmuir–Schaefer technique.



Keywords: Mn_3O_4, hausmannite, microcapsules, spray, air–solution interface.

The method of spraying reagent solutions is widely utilized in preparative chemistry to produce a variety of nanomaterials,[1–5] including manganese oxide with a microcapsule-like structure.[6] Such manganese-containing oxides are of great interest due to their distinctive combination of electrochemical and catalytic properties. These materials find applications as electrocatalysts in oxygen reduction reactions,[7] electrodes in batteries and other energy storage devices,[8] materials that are transparent to electromagnetic waves,[9] sorbents for chemical separation,[10] and agents in theranostics.[11] Hollow microcapsules of these oxides can be synthesized through hydrothermal or solvothermal methods at temperatures up to 180 °C, often involving surfactants.[9,12,13] An alternative approach involves the spraying of manganese salt solutions into a reactor heated to 600–1100 °C.[14,15]

In this work, the conditions for the synthesis of open microcapsules with Mn_3O_4 walls and unique vase-like morphology at room temperature without the use of special surfactants are presented for the first time. The synthesis was performed using the droplet spraying onto the solution surface (DSSS) technique, which was proposed by us earlier[16,17] and tested in the preparation of microcapsules with Ni^{II} and Fe^{III} double hydroxide walls. A feature of this technique is the isolation of the stage of microcapsule formation on the surface of the solution, where the droplets of the sprayed salt solution are applied and the free-floating microcapsules are obtained.† These microcapsules can be transferred to the surface of the substrate using the Langmuir–Blodgett (LB) or Langmuir–Schaefer (LS) methods. It should be noted that a number of works are known,[18,19] where microcapsules were also obtained by spraying a solution of one reagent onto the surface of a solution of another reagent, but with subsequent concentration at the bottom of a chemical vessel without isolating the stage of microcapsule formation at the interface.

The first experiments on the synthesis of the microcapsules in the above conditions using solutions of $MnSO_4$ and NaOH with different concentrations showed that when droplets of the $MnSO_4$ solution falls on the surface of the alkali solution, microcapsules are formed at concentrations of the first and second solutions above 0.2 and 0.8 M, respectively. At lower concentrations, the partially formed microcapsules with walls several tens of nanometers thick are formed, which disintegrate into separate fragments upon drying. At the same time, increasing the concentration of the $MnSO_4$ solution above 0.4 M leads to an increase in its viscosity and a decrease in the spray rate. It was also observed that the addition of Na_2SO_4 to the NaOH solution up to its concentration of 0.5 M promoted the formation of stronger microcapsule walls. Apparently, the presence of this salt increases the ionic strength of the solution and accelerates reactions of hydrolysis and oxidation of Mn^{II} cations and, thus, decreases the time of the formation of microcapsule walls. In this regard, the concentration of the $MnSO_4$ solution equal to 0.35 M and the concentration of the NaOH solution equal to 0.8 M were

† Aqueous solutions of $MnSO_4 \cdot 5H_2O$, Na_2SO_4 and NaOH (provided by JSC Vekton) were used as reagents for the synthesis. When preparing the solutions, the weighed portions of the reagents were dissolved in deionized water and stirred for at least 30 min. Two solutions were used for microcapsules synthesis, the first one was a 0.1–0.5 M $MnSO_4$ solution, which was sprayed as an aerosol, and the second one was a mixture of 0.8 M NaOH solution and 0.5 M Na_2SO_4 solution that was poured in a planar Teflon vessel. Spraying was carried out using an A&DUN-231 ultrasonic nebulizer with a generator with a power of 10 W and a frequency of 2.5 MHz. The duration of the treatment with an aerosol varied from 2 to 10 min. When the treatment was complete, the formed microcapsules were transferred from the solution surface to a titanium foil *via* the LS or LB

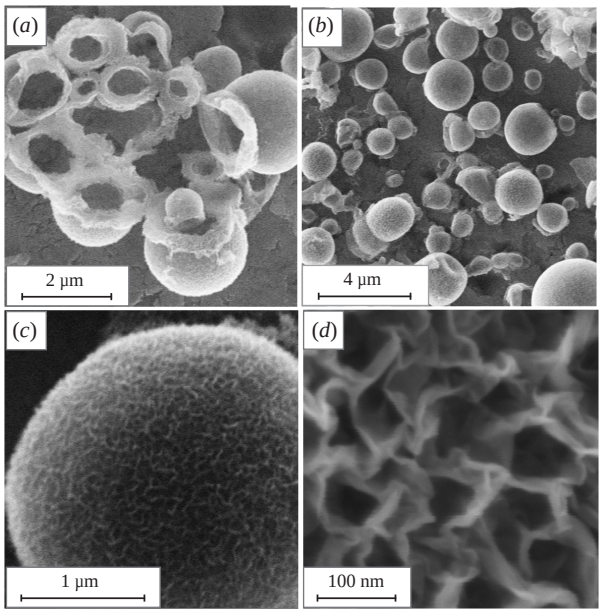


Figure 1 FESEM images of the microcapsules applied on a titanium foil surface using (*a*) LB and (*b*) LS methods and (*c*),(*d*) the surface of the walls of the corresponding microcapsules.

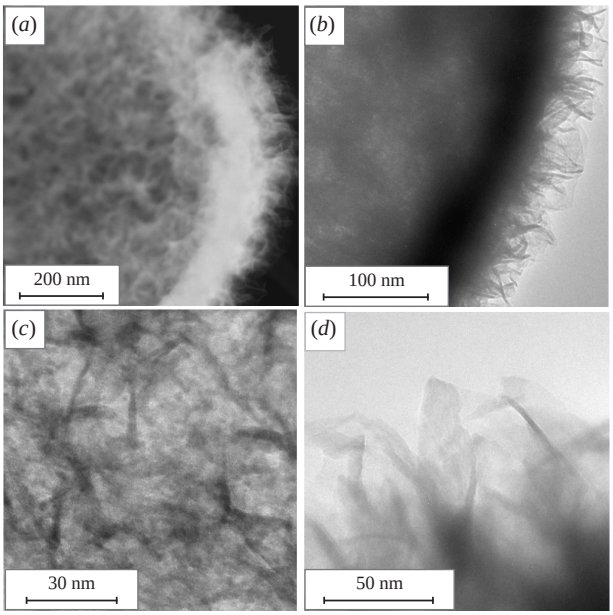


Figure 2 (*a*) STEM and (*b*–*d*) TEM images of the microcapsule walls: (*a*),(*b*),(*d*) cross-sectional images of the microcapsule, and (*c*) the wall viewed along the normal to its surface.

chosen as optimal, and Na_2SO_4 was also added to the second solution up to a concentration of 0.5 M. The time of aerosol treatment with the $MnSO_4$ solution equal to 8 min was chosen as optimal. During this time a layer of mainly separately floating microcapsules was formed at the surface of the NaOH–Na_2SO_4 mixed solution with a relatively high density of their arrangement suitable for investigation.

As follows from the microphotographs shown in Figure 1, the microcapsules obtained under above conditions have a size of 1–5 μm corresponding to the size of droplets in aerosol generated by the device used. As can be seen in Figure 1(*a*), the microcapsules have holes with a diameter of 0.5–1.5 μm and a peculiar rim with a height of 100–200 nm around them. It can also be observed that the walls of the microcapsules are formed by arrays of nanosheets that have pores up to 100 nm in size and these nanosheets are oriented predominantly in the radial direction towards the center of the microcapsule [Figures 1(*c*),(*d*)]. The EDX study showed that Mn, Na and O atoms are present in the wall composition with an Mn : Na atomic ratio of 10 : 1 (Figure S1, Online Supplementary Materials). In this experiment, we did not evaluate the oxygen atom content because it is also a part of the adsorbed water molecules.

More detailed information about the morphology of the nanosheets was obtained by analyzing STEM and TEM micrographs (Figure 2). Thus, it can be observed, firstly, that the walls of the microcapsules do not have clearly defined outlines due to the fact that they are formed by nanosheets of arbitrary shape [Figures 2(*a*),(*b*),(*d*)] and, secondly, the thickness of the nanosheets is about 2–3 nm [Figure 2(*d*)]. Nevertheless, it can be noted that the conventional thickness of such walls is in the range of 80–150 nm.

techniques, washed with deionized water and ethanol, and dried in air at 60 °C. The titanium foil substrates were about 5 × 15 mm in size and 0.2 mm thick. Before synthesis, the substrates were washed with acetone in an ultrasonic bath, then etched in a 7 : 3 v/v concentrated H_2SO_4–H_2O_2 solution, washed with deionized water, and dried in air.

Electron micrographs were obtained using a Zeiss Merlin or a Zeiss EVO-40EP scanning electron microscopes and a Zeiss Libra 200 transmission electron microscope. The composition of the synthesized microcapsules was determined using an Oxford INCA 350 EDX spectrometer integrated with a Zeiss EVO-40EP electron microscope.

The SAED study revealed [Figure 3(*a*)] that the nanoparticles were characterized by the interplanar distances of 0.30, 0.25, 0.21 and 0.15 nm. These values are close to the interplanar distances in Mn_3O_4 oxide with a hausmannite-like crystal structure;[20] namely, it is characteristic for the reflection planes (112), (211), (220) and (431), respectively. The results of the HRTEM study confirm these conclusions. In particular, the 0.25 nm distance related to the (211) direction of the marked crystal can be observed in the interference pattern shown in Figure 3(*b*).

At first, it should be noted that when such microcapsules are transferred to the titanium surface using the LS technique, they are oriented with the open part and rim towards the substrate [Figure 1(*b*)]. Another important issue to discuss is the presence of sodium atoms in the composition of the samples. In our opinion, the main part of these atoms can be on the surface of nanosheets in adsorbed state and, considering their ultrasmall thickness of 2–3 nm, makes a significant contribution to the total composition. Although, on the other hand, it can be assumed that in the process of hydrolysis and oxidation of Mn^{II} cations at the droplet–alkali solution interface, a part of manganese cations can be oxidized to Mn^{IV} and form nanosheets with a crystalline structure similar to birnessite Na_xMnO_2.[21–23] In this structure, sodium ions are located in the interplanar spaces between nanosheets of MnO polyhedra. The latter assumption is supported by the results of HRTEM, where nanocrystals characterized by

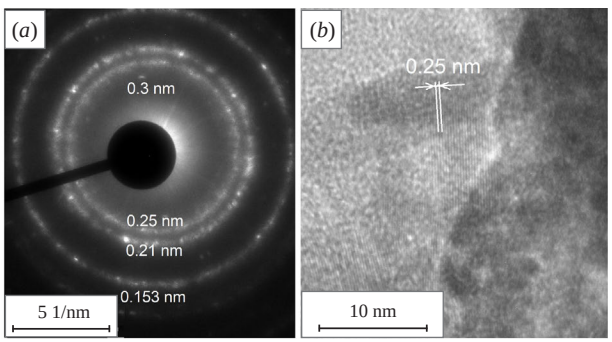


Figure 3 (*a*) SAED pattern and (*b*) HRTEM image of the Mn_3O_4 microcapsule wall.

interplane distances of above 5 nm corresponding to the plane (001) in this crystal can be detected in some micrographs (Figure S2). Unfortunately, we were not able to clearly detect such a diffraction maximum by SAED because of its proximity to the intense central maximum and, perhaps, the relatively small number of such nanocrystals.

To explain the observed results, it should be noted that when a droplet of the $MnSO_4$ solution falls on the surface of the $NaOH–Na_2SO_4$ mixed solution, the simultaneous immersion of a droplet into solution and the hydrolysis reaction of Mn^{II} cations with the formation of $Mn(OH)_2$ having the morphology of nanosheets is observed. Since the hydrolysis reaction takes place in air, some of the Mn^{II} cations are oxidized to Mn^{III} and form the Mn_3O_4 crystal lattice. After the formation of the first seeds of such crystals at the initial stage of the wall formation around the droplet, their growth begins with the process of mixing reagents due to the mutual diffusion of hydroxyl anions from the alkali solution into the interior of the droplet and Mn^{II} cations from the droplet solution into the alkali solution. And it is for this reason that the growth of nanocrystals with nanosheet morphology in the radial direction seems to occur. It is obvious that there are no OH^- anions at the solution boundary of such a partially immersed droplet with air, and therefore the wall formation does not occur in this area and such microcapsules turn out to be open. However, as they are immersed in the $NaOH–Na_2SO_4$ mixed solution, a meniscus is formed around this hole in the upper part, which leads to the formation of a kind of rim around it.

In conclusion it can be stated that when droplets of an aqueous solution of $MnSO_4$ are applied to the surface of the alkali solution using the DSSS technique, the rapid hydrolysis of Mn^{II} cations and their partial oxidation by air oxygen to Mn^{III} are observed. In this case, nanocrystals of hard-soluble manganese oxide Mn_3O_4 with the morphology of nanosheets each having a thickness of 2–3 nm are formed. These nanosheets form arrays and microcapsule walls at the droplet–alkali solution interface. Moreover, these nanosheets are oriented predominantly in the radial direction towards the center of the microcapsule. Importantly, such microcapsules have a 0.5–1.5 μm diameter hole at the air interface, around which a 100–200 nm high rim is formed. Such a rim can be a kind of ‘ground’ when fixing a layer of such microcapsules on the surface of a titanium substrate in the process of transferring them from the surface of the solution according to the LS technique. Due to this, a layer of microcapsules with an open part oriented towards the substrate can be obtained.

We believe that the described DSSS method has a great potential in the synthesis of complex manganese oxides and will find application in the creation of new, for example, biomedical and electrode materials, microreactors for various chemical processes and so on.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.038.

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