Way, shape and form: Synthesis conditions define the nanostructure of manganese dioxide

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Materials engineering has advanced to a point at which not only are we concerned about the chemical composition of a material, but also about its structure at a nanometric level. Nanostructured materials have recently drawn the attention of researchers from a variety of fields and for good reason; their physical, optical, and electrical characteristics can be tuned and pushed to the limit once methods to tailor their nanostructure are available.

Manganese dioxide (chemical formula MnO₂) is a nanocrystallized metal oxide that can form many different crystalline structures, with applications across various engineering fields. One important use of MnO₂ is as a catalyst for chemical reactions, and a particular crystalline structure of MnO₂, called ?-MnO₂, is exceptional for the oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid (FDCA). Because FDCA can be used to produce environment-friendly bioplastics, finding ways to tune the nanostructure of ?-MnO₂ to maximize its catalytic performance is crucial.

However, producing ?-MnO₂ is difficult compared with other MnO₂ crystalline structures. Existing methods are complicated and involve the use of template materials onto which ?-MnO₂ 'grows' and ends up with the desired structure after several steps. Now, researchers from Tokyo Institute of Technology led by Prof. Keigo Kamata explore a template-free approach for the synthesis of different types of porous ?-MnO₂ nanoparticles.

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Scientists at Tokyo Institute of Technology explore a novel and simplistic method to synthesize manganese dioxide with a specific crystalline structure called \(\beta\)-MnO\(_2\). Their study sheds light on how different synthesis conditions can produce manganese dioxide with distinct porous structures, hinting at a strategy for the development of highly tuned MnO\(_2\) nanomaterials that could serve as catalysts in the fabrication of bioplastics. Credit: Keigo Kamata, Tokyo Institute of Technology

Their method, described in their study published in *ACS Applied Materials & Interfaces*, is outstandingly simple and convenient. First, Mn precursors are obtained by mixing aqueous solutions and letting the solids precipitate. After filtration and drying, the collected solids are subjected to a temperature of 400°C in a normal air atmosphere, a process known as calcination. During this step, the material crystallizes and the black powder obtained afterwards is more than 97% porous \(\beta\)-MnO\(_2\).

Most notably, the researchers found this porous \(\beta\)-MnO\(_2\) to be much more efficient as a catalyst for synthesizing FDCA than the \(\beta\)-MnO\(_2\) produced using a more widespread approach called the 'hydrothermal method.' To understand why, they analyzed the chemical, microscopic, and spectral characteristics of \(\beta\)-MnO\(_2\) nanoparticles produced under different synthesis conditions.

They found that \(\beta\)-MnO\(_2\) can take on markedly different morphologies according to certain parameters. In particular, by adjusting the acidity (pH) of the solution in which the precursors are mixed, \(\beta\)-MnO\(_2\) nanoparticles with large spherical pores can be obtained. This porous structure has a higher surface area, thus providing better catalytic performance. Excited about the results, Kamata remarks: "Our porous \(\beta\)-MnO\(_2\) nanoparticles could efficiently catalyze the oxidation of HMF into FDCA in sharp contrast with \(\beta\)-MnO\(_2\) nanoparticles obtained via the hydrothermal method. Further fine control of the crystallinity and/or porous structure of \(\beta\)-MnO\(_2\) could lead to the development of even more efficient oxidative reactions."

What's more, this study provided much insight into how porous and tunnel structures are formed in MnO\(_2\), which could be key to extending its applications, as Kamata states: "Our approach, which involves the transformation of Mn precursors into MnO\(_2\) not in the liquid-phase (hydrothermal method) but under an air atmosphere, is a promising strategy for the synthesis of various MnO\(_2\) nanoparticles with tunnel structures. These could be applicable as versatile functional materials for catalysts, chemical sensors, lithium-ion batteries, and supercapacitors." Further studies like this one will hopefully allow us to one day harness the full potential that nanostructured materials have to offer.


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