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

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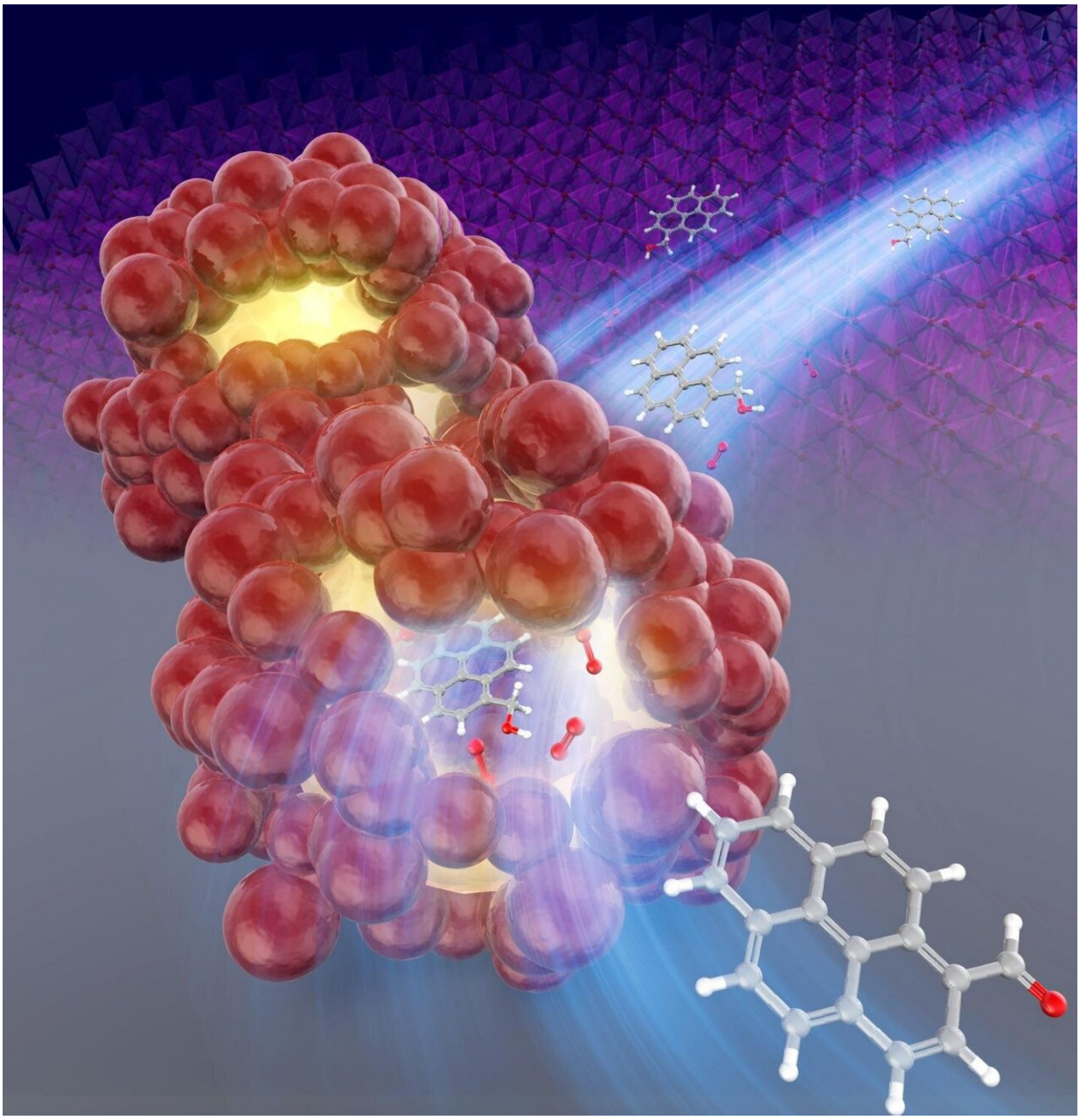


Acceleration of the chemical reaction by β-MnO_2 catalyst in the nanospace of the particles. Credit: Keiko Kamata, Tokyo Institute of Technology

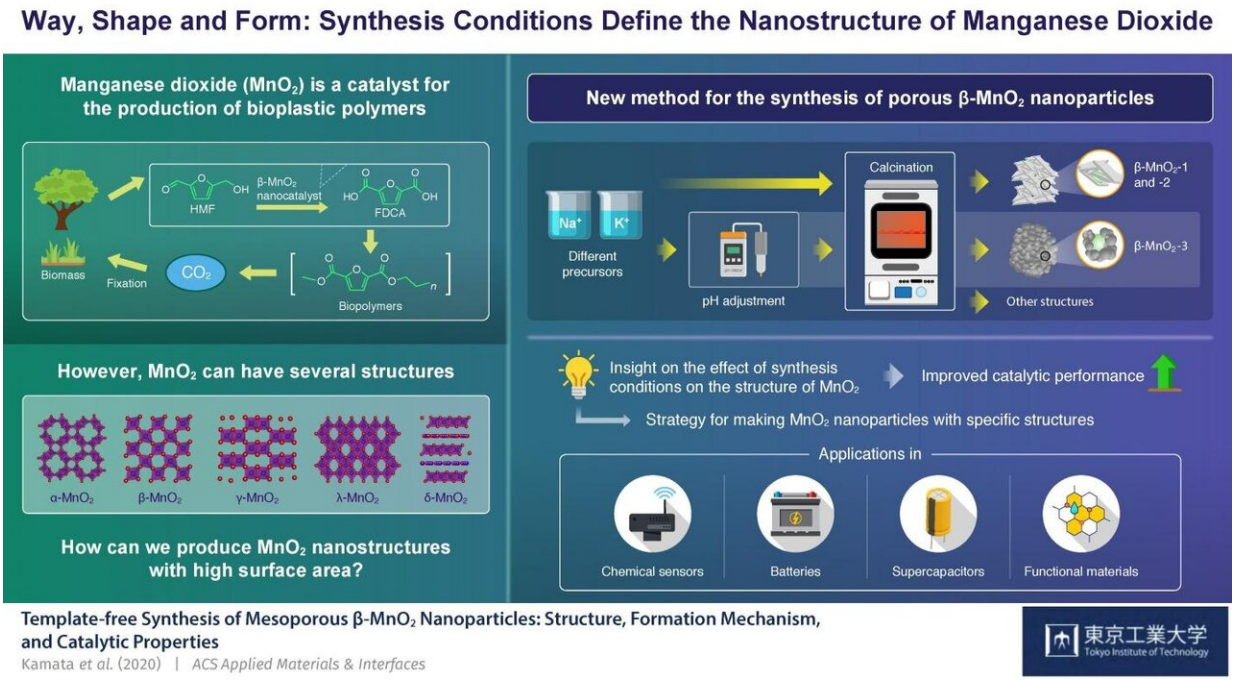
Scientists at Tokyo Institute of Technology explore a novel and simplistic method to synthesize manganese dioxide with a specific

crystalline structure called β-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.

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 MnO_2) nanostructured metal oxide that can form many different crystalline structures, with applications across various engineering fields. One important use of MnO_2 is as a catalyst for chemical reactions, and a particular crystalline structure of MnO_2, called β-MnO_2, 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 β-MnO_2 to maximize its catalytic performance is crucial.

However, producing β-MnO_2 is difficult compared with other MnO_2 crystalline structures. Existing methods are complicated and involve the use of template materials onto which β-MnO_2 '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 β-MnO_2 nanoparticles.



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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 β-MnO_2.

Most notably, the researchers found this porous β-MnO_2 to be much more efficient as a catalyst for synthesizing FDCA than the β-MnO_2 produced using a more widespread approach called the 'hydrothermal method.' To understand why, they analyzed the chemical, microscopic, and spectral characteristics of β-MnO_2 nanoparticles produced under different synthesis conditions.

They found that β-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, β-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 β-MnO_2 nanoparticles could efficiently catalyze the oxidation of HMF into FDCA in sharp contrast with β-MnO_2 nanoparticles obtained via the hydrothermal method. Further fine control of the crystallinity and/or porous structure of β-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.

More information: Yui Yamaguchi et al, Template-Free Synthesis of Mesoporous β-MnO2 Nanoparticles: Structure, Formation Mechanism, and Catalytic Properties, *ACS Applied Materials & Interfaces* (2020).

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