Iron oxide frameworks with hierarchical pore structure from pyrolysis of Prussian blue nanocrystals

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Adsorption, catalysis, or substrates for tissue growth: porous materials have many potential applications. In the journal *Angewandte Chemie*, a team of Chinese and Australian researchers has now introduced a method for the synthesis of ultralight three-dimensional (3D) iron oxide frameworks with two different types of nanoscopic pores and tunable surface properties. This superparamagnetic material can be cut into arbitrary shapes and is suitable for applications such as multiphase catalysis and the removal of heavy metal ions and oil from water.

Materials with hierarchically organized pore systems—meaning that the walls of macropores with diameters in the micrometer range contain mesopores of just a few nanometers—are high on the wish lists of materials researchers. The advantages of these materials include their high surface area and the easy accessibility of the small pores through the larger ones. The great desirability of these materials is matched by the degree of difficulty in producing them on an industrial scale.

Scientists at Fudan University (China) and Monash University (Australia) have now successfully produced an ultralight iron oxide framework with 250 µm and 18 nm pores in a process that can be used on an industrial scale. A team led by Gengfeng Zheng and Dongyuan Zhao used highly porous polyurethane sponges as a "matrix", which were soaked with yellow potassium hexacyanoferrate ($K_4[Fe(CN)_6]$). Subsequent hydrolysis resulted in cubic nanocrystals of Prussian blue (iron hexacyanoferrate), a dark blue pigment, which were deposited all over the surfaces of the sponge. The polyurethane sponge was then fully burned away through pyroloysis and the Prussian blue was converted to iron oxide. The result is a 3D framework of iron oxide cubes that are in turn made of iron oxide nanoparticles and contain mesopores. The material is so light that the researchers were able to balance a 240 cm^3 piece on an oleander blossom.

Simple modifications allow the surface of the 3D framework to be varied from strongly hydrophilic to strongly hydrophobic for different applications. The researchers demonstrated this by removing arsenic ions from contaminated water and by separating water from gasoline. In the latter experiment, the resol-coated iron oxide framework absorbed more than 150 times of its own weight in gasoline.

The resol-coated frameworks are also suitable for use as nanoreactors for catalytic multiphase reactions between hydrophilic and hydrophobic reactants, which can normally only be made miscible through addition of various phase-transfer reagents and cosolvents. With the resol-coated iron oxide framework, the reaction runs much faster and more selectively without these additives, giving high yields. This is because of the tunable hydrophilic/hydrophobic surfaces of the mesopores, which take in both reagents and bring them into contact with each other. The catalyst can be retrieved magnetically, because the iron oxide nanoparticles of the 3D frameworks are superparamagnetic.

More information: Kong, B., Tang, J., Wu, Z., Wei, J., Wu, H., Wang, Y., Zheng, G. and Zhao, D. (2014), "Ultralight Mesoporous Magnetic Frameworks by Interfacial Assembly of Prussian Blue Nanocubes." *Angew. Chem. Int. Ed.*. DOI: 10.1002/anie.201308625

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