Pt-Doped Hematite Thin Films May Enable Solar-Powered Generation of Hydrogen

While today's debate over renewable energy sources has focused a great deal of attention on using sunlight to generate electricity, the possibility of solar-powered hydrogen generation is less well known to the public. However, a recent materials advance has brought the technology to derive hydrogen and other chemicals using sunlight one step closer to reality, and may eventually shift the contours of the energy debate. Y.-S. Hu, E.W. McFarland, and their colleagues at the University of California at Santa Barbara have synthesized a doped hematite material with significantly improved characteristics for harnessing sunlight to split water into oxygen and hydrogen. They reported their findings in the June 24 issue of *Chemistry of Materials* (DOI: 10.1021/cm800144q; p. 3803).

First demonstrated over 30 years ago, photoelectrochemical (PEC) electrolysis of water uses the electron–hole pairs liberated by the illumination of a semiconductor to drive oxidation-reduction reactions, releasing oxygen and hydrogen. The search has since been on for a semiconductor material that would enable high-efficiency solar-powered PEC electrolysis. Hematite (α-Fe_2O_3) has been extensively studied as a candidate material because of its relatively narrow bandgap (2.0–2.2 eV), good stability in several common electrolytes, safety, and low cost. However, the major limitations of pure hematite include its relatively low conductivity and its high electron–hole recombination rate. A number of studies have focused on introducing dopants, including Pt, to hematite in an effort to improve its PEC performance.

Despite previous unfavorable results by other researchers, the UC Santa Barbara team decided to investigate Pt-doped hematite for PEC applications. Using an electrodeposition technique, which had not previously been studied for synthesis of doped hematite, the team prepared samples of Pt-doped iron hydroxides, which they then calcined at 700ºC for 4 h to obtain doped crystalline hematite thin films. Scanning electron micrographs of the films showed a dramatic change in their morphology in the presence of a dopant molar ratio of 2–10% Pt in the electrolyte, to a much more uniform and dense structure than undoped samples. X-ray diffraction and x-ray photoelectron spectroscopy revealed that the doped thin films remained in a rhombohedral lattice with a fairly constant Pt concentration throughout the sample. The researchers found that when illuminated, the doped thin films showed significantly increased photocurrent generation (a measure of hydrogen production) compared with undoped hematite thin films, implying that a PEC electrolysis device built with these samples would display an overall energy efficiency of up to 3%, nearly four times greater than devices relying on undoped hematite.

While questions remain about the precise mechanism of the improvement of the PEC process from the Pt dopant and a bias is still required, this result suggests that cost-effective solar-powered generation of hydrogen and other chemicals using abundant and non-toxic materials may one day be feasible.

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Superhard Diamondlike BC_5 Predicted to Be a High-T_c Superconductor

Although boron-doped diamond ($B_\delta C_{1-\delta}$with $\delta = 0.028$) is superconducting with a critical temperature (T_c) of 7 K, other carbon materials, such as intercalated graphite, nanotubes, and alkali-doped fullerides, have substantially higher T_c values, ranging from 11–33 K. Superhard nanocrystalline BC_5 aggregates, with an effective δ of 0.167, were recently synthesized. The BC_5 crystal structure shows cubic symmetry with volume per atom (6.00 Å^3) 6% larger than diamond. However, the B and C atoms cannot be distinguished by diffraction (because of their similar atomic number), so that the position of the B atom in the cell is undetermined. While calculations based upon density functional theory (DFT) have shown that superconductivity in B-doped diamond (at low B content) is mediated by B-phonon states, it has been unclear whether superconductivity could scale with the doping level up to $\delta = 0.167$. Recently, M. Calandra and F. Mauri at CNRS and Institut de Minéralogie et de Physique des Milieux condensés, Paris, France, used DFT to resolve the BC_5 crystal structure and to predict that BC_5 is superconducting with a $T_c = 45$ K, which is larger than the T_c for MgB_2, experimentally found to be 39 K.

As reported in the July 4 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.101.016401; 016401), Calandra and Mauri replaced one of the two C atoms in the diamond cell with a B atom and performed volume and force optimizations on the 6-atom hexagonal supercell. The most

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