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EPR Study of Manganese-Doped TiO2 Nanorods TIJANA RAJH, ZORAN SAPONJIC, NADA DIMITRIJEVIC, Argonne National Laboratory, CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY TEAM Titanium dioxide nanoparticles and nanorods were prepared by a hydrothermal method using scrolled anatase nanotubes as the starting material. The addition of manganese ions to scrolled nanotube precursors was found to unroll the nanotubes into sheet-like structures indicating a strong adsorption of manganese ions at undercoordinated sites that terminate layers of scrolled titanium dioxide nanotubes. Hydrothermal treatment of Mn²⁺ unscrolled nanotubes was found to result in the formation of doped anatase nanorods (30 x 300 nm). Upon 1 % doping, the optical properties of nanorods change, resulting in the appearance of a broad absorption band at ~ 650 nm. X-band EPR spectra show unusual eleven line spectrum with 72 G hyperfine splitting and a g factor of 2.007. The total width of the spectrum was 890 G due to the appearance of second order effects. The same hyperfine coupling was found in samples having doping levels in the range 0.1-2 % of Mn²⁺, indicating specific interaction of manganese ions within the TiO_2 lattice. Adsorption of Mn^{2+} ions onto the surface of nanorods did not change their optical properties and exhibits the typical six line spectrum of Mn^{2+} with 90 G hyperfine splitting in addition to a broad, unresolved solution spectrum of Mn^{2+} . The effects of the size and shape of titanium dioxide nanoobjets on the spin multiplicity of manganese dopants are being investigated.

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