Synthesis and Characterization of Manganese Doped Silicon Nanoparticles: Bifunctional Paramagnetic-Optical Nanomaterial

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Experiment

All manipulations for the synthesis of Si nanoparticles were performed in a N_2-filled glovebox or Ar inert atmosphere Schlenk line. $NaSi_{0.95}Mn_{0.05}$ was synthesized by direct reaction of stoichiometric amounts of the elements in sealed niobium tubes, sealed under vacuum in fused silica tubes, at 650 ºC for 3 days. X-ray powder diffraction of the product was consistent with NaSi with no evidence for unreacted Mn.[S1] In a typical reaction, 50 ml dioctyl ether (DOE, 260 ºC) was added via cannula to $NaSi_{0.95}Mn_{0.05}$ (0.1 g, 2 mmol) in a three-neck bottle and heated to reflux, and formed a black opaque suspension. NH_4Br (0.2 g, 2 mmol) was added and the mixture was stirred for 48 hours resulting in a yellow solution. The reaction mixture was allowed to cool to room temperature. After removing the black precipitate, 2 ml octyne was added by anaerobic syringe. The solution was stirred overnight at 150 ºC and the solvents were then removed via vacuum evaporation. The resulting product obtained was dissolved in chloroform. The chloroform solution was purified by extraction with a water/hexane mixture to remove any impurities such as NaBr and any unreacted NH_4Br. The hexane extract was further centrifuged to acquire a clear and light yellow solution. The light yellow solution can be dried to obtain a waxy, light-yellow solid which can be resuspended in many organic solvents, such as hexane, ethanol, and chloroform. The sample was sent out for elemental analysis.[S2] The result shows that the molar ratio of Si to Mn is 18.2:1.

The products were characterized by XRD, TEM, photoluminescence spectroscopy, EPR, FT-IR, and Transient Absorption Spectroscopy. XRD data were collected on an INEL CPS120 diffractometer using Cu K□ radiation. Transmission Electron Microscopy (Phillips CM-120, operating at 100 kV) was used to analyze the size distribution of the prepared product. TEM samples were prepared by dipping holey-carbon-coated, 400-mesh electron microscope grids into the hexane colloid solution and drying them at 120 ºC overnight. PL spectra of silicon colloid solution were obtained on a FluoroMax-3P fluorometer. Photoluminescence quantum yield was obtained by comparison of the PL intensity of a nanoparticle sample with that of fluorescein (laser grade) in 0.1M H_2SO_4 solution. Isolated samples were dissolved in chloroform and measured in a standard 1-cm quartz cell with controlled optical densities below 0.10 at the excitation wavelength. Continuous wave EPR was taken on a Bruker ECS106 X-Band spectrometer, equipped with an Oxford Instruments liquid helium cryostat. Typical experimental conditions were frequency 9.68 GHz, temperature 4.2 K, modulation amplitude 10 G, microwave power 0.50 m, conversion time 40.96 ms, time constant 40.96 ms, resolution 2048 pts, average of 6 scans. Samples were dissolved in chloroform solution. The FT-IR spectra were collected on a Shimadzu IR Prestige 21 spectrophotometer by dropping the hexane colloid on a KBr plate and allowing the solvent to evaporate.

Charge carrier dynamics were probed by ultrafast transient absorption spectroscopy using an amplified Ti:Sapphire laser system (Spectra Physics Spitfire Pro) producing 40 fs, 800 nm pulses at 1 kHz. The fundamental pulse was frequency doubled in a 1-mm BBO nonlinear crystal to produce 3.1 eV pulses for band-edge excitation of the Si nanoparticles. A fs white light (450 -750 nm) probe pulse generated in sapphire was focused into the sample following a variable time delay, and was subsequently dispersed and collected by a 256-pixel silicon diode array on a shot-by-shot basis. The pump source was optically chopped at 500 Hz and pump-induced absorption changes were calculated from an average of ~500 pumped/unpumped pairs of spectra. Samples of doped and undoped Si nanoparticles were suspended in chloroform and held in a 1-mm path length static quartz cuvette. The pump fluence was varied over the range 0.3 - 20 $\mu J/cm^2$. The measured decay kinetics was found to be independent of laser fluence, indicating a carrier density on average < 1 electron-hole pair per nanoparticle.

References:

(S1) Mayeri, D.; Phillips, B. L.; Augustine, M. P.; Kauzlarich, S. M. *Chem. Mater,* **2001**, 13, 765-770

(S2) Elemental analysis was performed by Desert Analytics (Tucson, AZ).

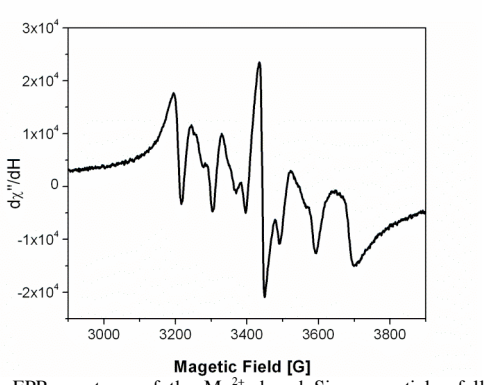

Figure S1 EPR spectrum of the Mn^{2+} doped Si nanoparticles followed by successive purification in order to remove Mn^{2+} from the surface of the particles.

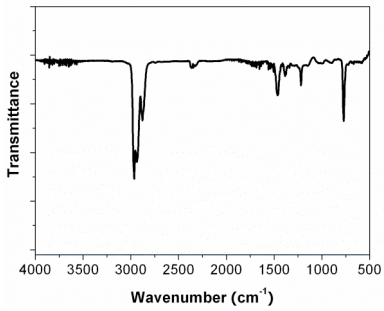

Figure S2 FT-IR spectrum of the Mn^{2+} doped Si nanoparticles.