Supplementary data

Mn Substitution and Distribution in Goethite and Influences on Photocatalytic Properties from First-principles Calculations and Experiments

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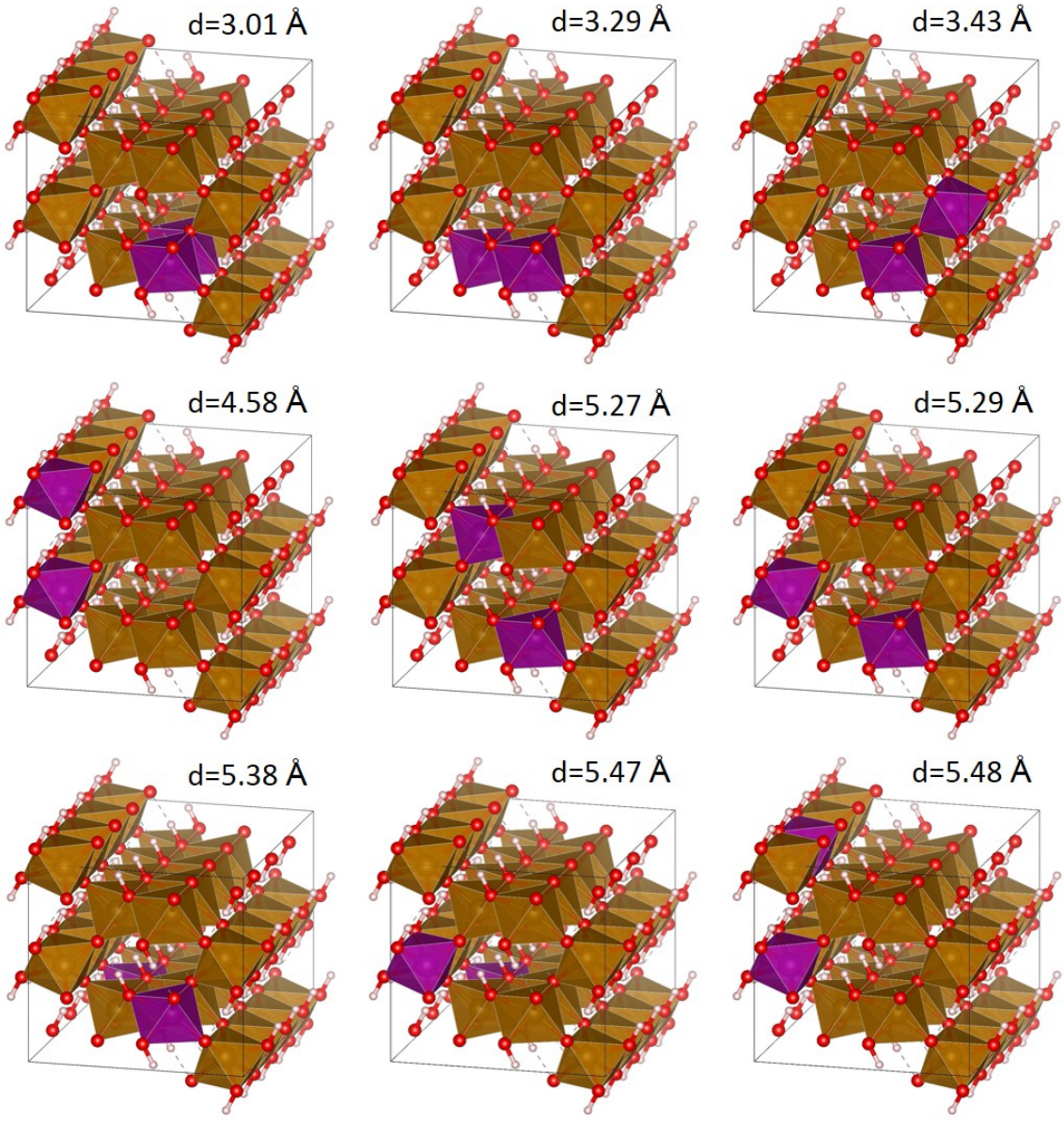
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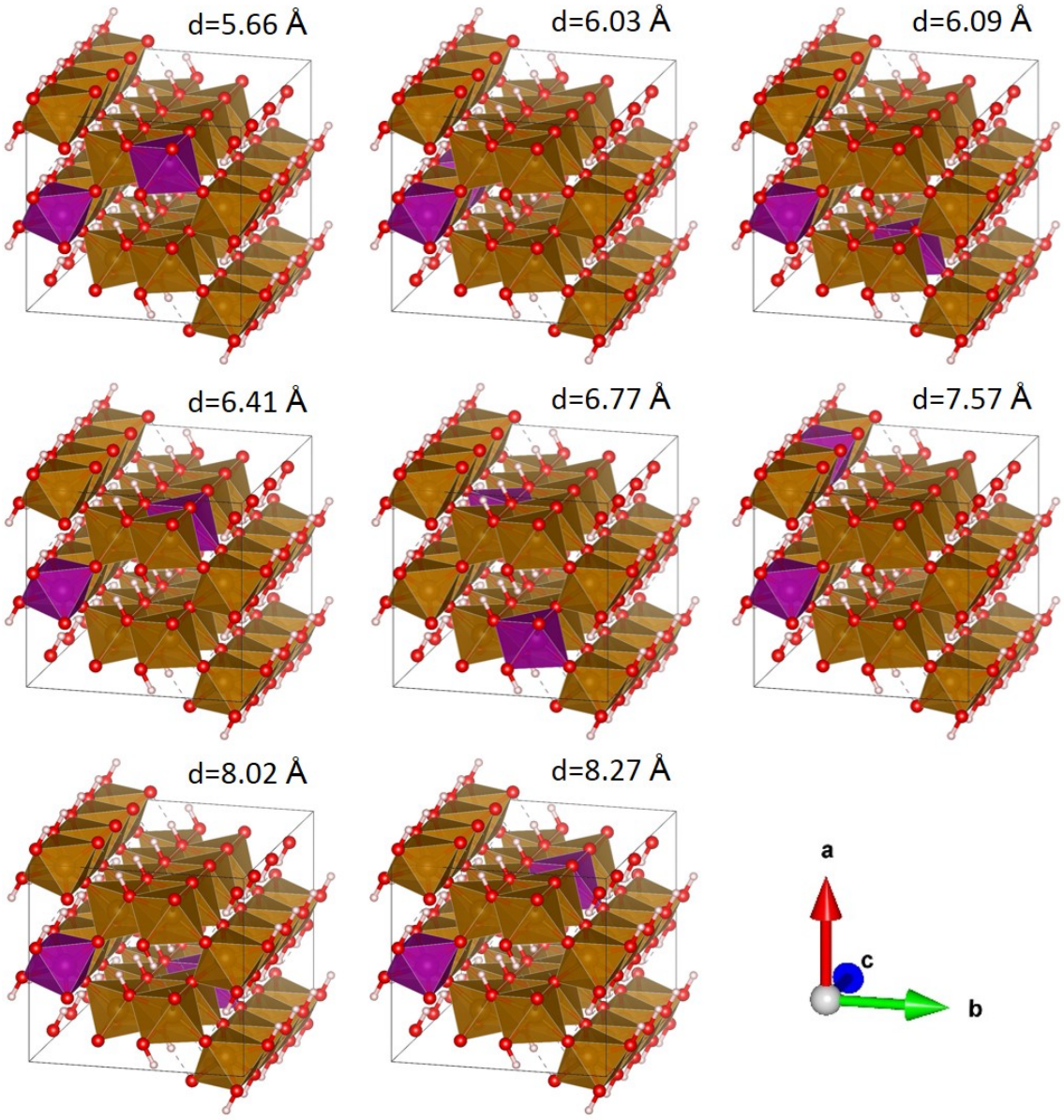

Figure S1. All 17 kinds of crystal models used in calculating pairwise interaction energies. Here only Mn substituted goethites are supplied.

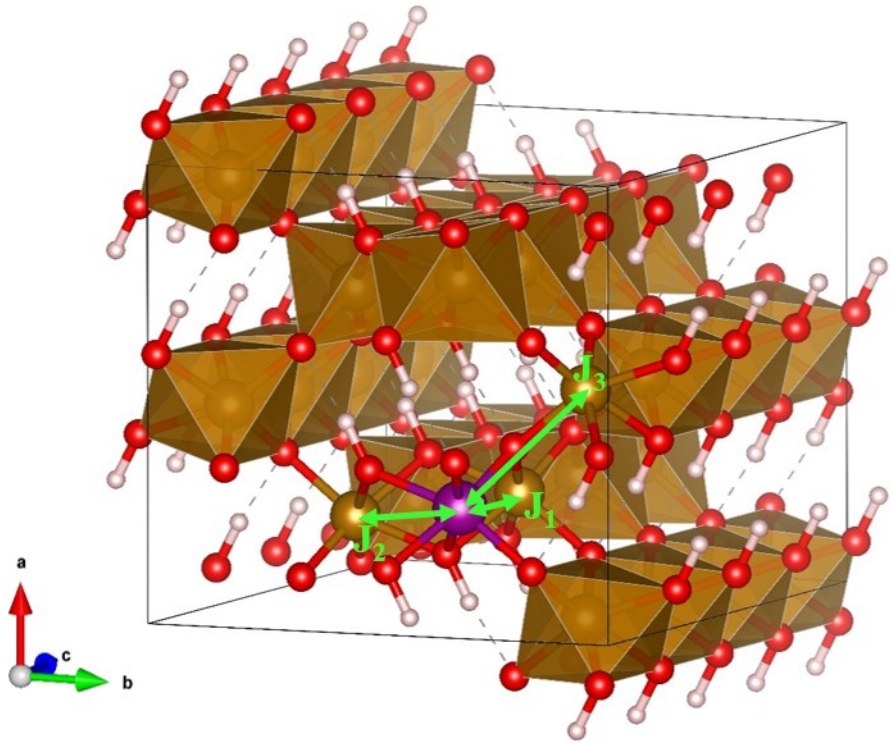

Figure S2. The first three pairwise interactions J_1, J_2, J_3.

EPR measurement

The production of free radical of goethites induced by light was investigated by Electron Paramagnetic Resonance Spectroscopy (EPR). EPR spectrum was recorded on EPR spectrometer (JES X320 JEOL Co.) operated at the same parameters for all the measurements (9.045GHz, scan width 10mT, centerfield 323.3mT, time constant 0.1s, scan time 1 min, modulation width 0.1 mT, gain 500, power 1mW). 20 mg pure goethite or Mn-substituted goethite samples were added to 20 ml solution with 10 mg/L MB and 50 mmol DMPO, then added 1.5 ml H_2O_2 (30%, w/w). The solution sample was taken out into a small tube, then analyzed by EPR to obtain the dark line. Subsequently, one sample of reaction solution was irradiated with 20W infrared light (>800 nm) for 10 min, then analyzed by EPR and shown as the infrared light line.

Figure S3 shows Electron Paramagnetic Resonance (EPR) experiments for pure goethite and Mn substituted gothite under dark condition and infrared light. Under infrared light, Mn substituted goethite can produce both a lot of O_2•$^-$ radicals and •OH radicals, but pure goethite can hardly produce any radicals. As a comparison, no matter Mn substituted goethite or pure goethite can hardly produce any free radical under dark condition. This data confirms that Mn substituted goethite can generate photo-induced electrons and holes but pure goethite can not under infrared light, making Mn substituted goethite has photoresponse ability in infrared light while pure goethite can not. The results quite coincide with our MB photocatalytic degradation experiments.

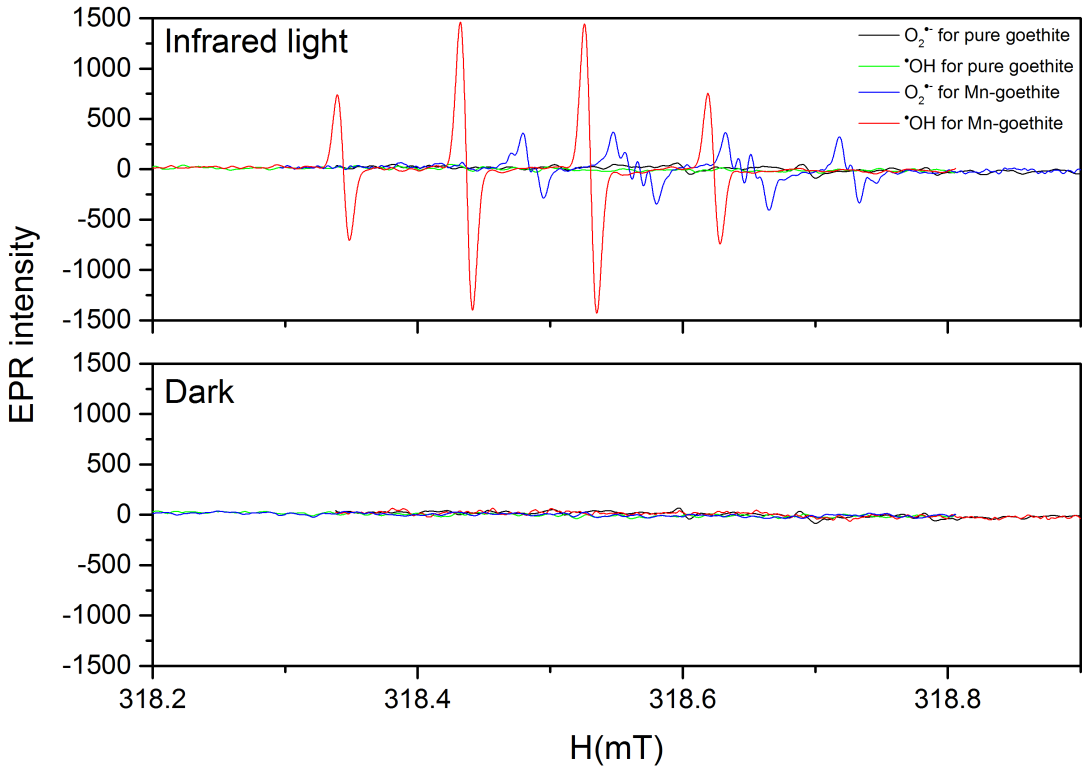

Figure S3. EPR spectrum of pure goethite and Mn substituted goethite under infrared light (> 800 nm) and dark condition.