Electronic Supporting Information for: **Visible Light Induced Desorption fromGoethite**

Anna Šutka,[1] Martin Järvekülg,[2]KarlisAgrisGross,[1] Mati Kook,[2]Tanel Käämbre,[2]Meeri Visnapuu,[2]Gregor Trefalt,[3]* Andris Šutka[2,4]*

[1] Biomaterials Research Laboratory, Institute of Inorganic Chemistry, Riga Technical University, P. Valdena 3/7, Riga, LV-1048, Latvia

[2]Institute of Physics, University of Tartu, Wilhelm Ostwald Str. 1, 50411 Tartu, Estonia

[3] Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

[4] Research Laboratory of Functional Materials Technologies, Riga Technical University, P. Valdena 3/7, 1048 Riga, Latvia

Experimental details: For scanning electron microscopy Helios Nanolab, FEI was used. Transmission electron microscopy was performed onTecnai G2 F20, FEI operated at 200 kV. Crystal structure of synthesized goethite was analysed by Ultima+ X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation.Dfractograms were recorded from 15° to 80° at a scanning rate of 1°/min.

Nitrogen adsorption–desorption isotherms were recorded using a NOVA 1200e instrument (Quantachrome, UK).The zeta potentials of aqueous suspensions of goethite (1 mg/mL) were measured using a Zetasizer Nano ZSP (Malvern Instruments). To convert electrophoretic mobilities into the zeta potential values, Smoluchowski model was used.

The optical absorption spectra of the α-FeOOH in were measured by a UV-NIR spectrophotometer (Agilent, Cary 4000 UV–vis, Germany).Hard X-ray photoelectron spectroscopy (HAXPES) measurements (with an overall resolution of 0.4 eV) were done on the HIKE experimental station at the KMC- 1 beamline at the BESSY-II synchrotron source (Helmholtz-Zentrum Berlin, Germany). The large kinetic energy used increases the inelastic mean free path (imfp), and hence the probing depth, therefore becoming capable of providing chemical state information the same as typical XPS, but without being oversensitive to possible surface artefacts and modifications. Surface artefacts can easily dominate the photoelectron spectra recorded using excitation energies in the more common range from soft X-ray down to VUV.

In methylene blue (MB) adsorption-desorption tests the supernatant was transferred to UV-Vis measurements to determine MB concentration by using GENESYS™ 10S UV-Vis Spectrophotometer - Thermo Fisher Scientific. The pH value of the suspensions was controlled by using HCl and NaOH. The goethite suspensions were irradiated by light emitting diode lamp (light irradiation intensity:50mW/cm^2) with spectrum presented in Fig. S5. As band gap of synthesized α-FeOOH is 2.4 eV, the effective intensity was 13 mW/cm^2.

In the experiments, samples were irradiated in 20 ml glass vials and presented limited light penetration behaviour, thus the intensity triggering MB desorption from α-FeOOH nanowires was even lower. The same experimental conditions were used for photocatalysis tests for MB degradation by goethite under visible light at pH near the isoelectric point where weak MB adsorption is observed.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) measurements were recorded on a Spectrum One (Perkin Elmer, UK) FTIR spectrometer in the range of 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1} after 32 continuous scans. The ATR top plates have composite zinc selenide (ZnSe) and diamond crystals. Samples before measurements were subtracted from suspensions and dried at room temperature and dark.

Fig. S1. Goethite suspension.

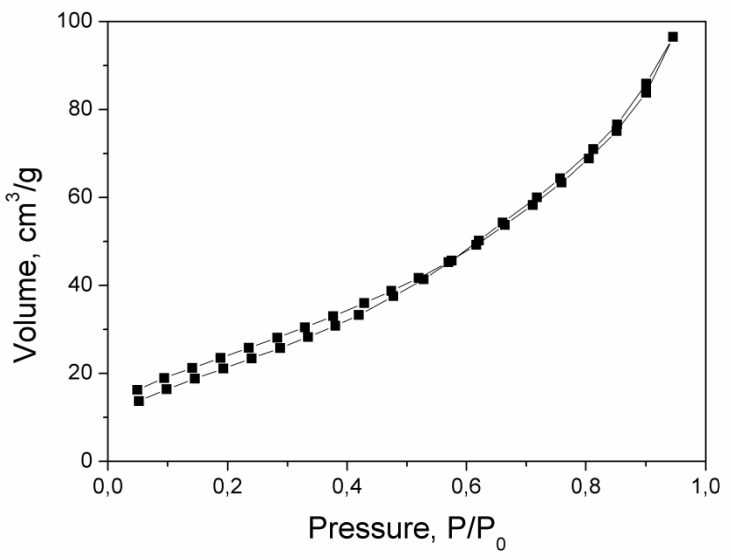

Fig. S2. Brunauer–Emmett–Teller (BET) isotherm for nitrogen adsorption/desorption on α-FeOOH.

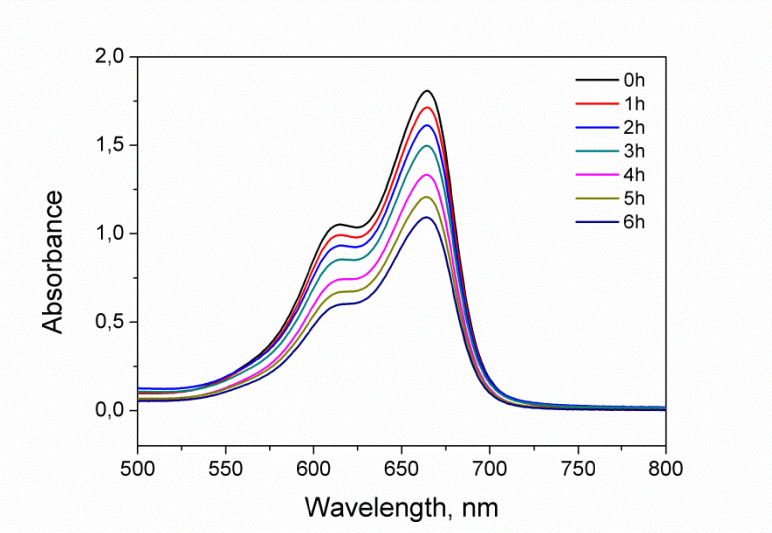

Fig. S3. Photocatalysis of MB by goethite under visible light at pH near the isoelectric point where weak MB adsorption is observed.The MB degradation in "photocatalysis" is the same as photolysis (Fig. S4). In both cases the relative concentration change C/C_0 in 5 hours is 0.66.

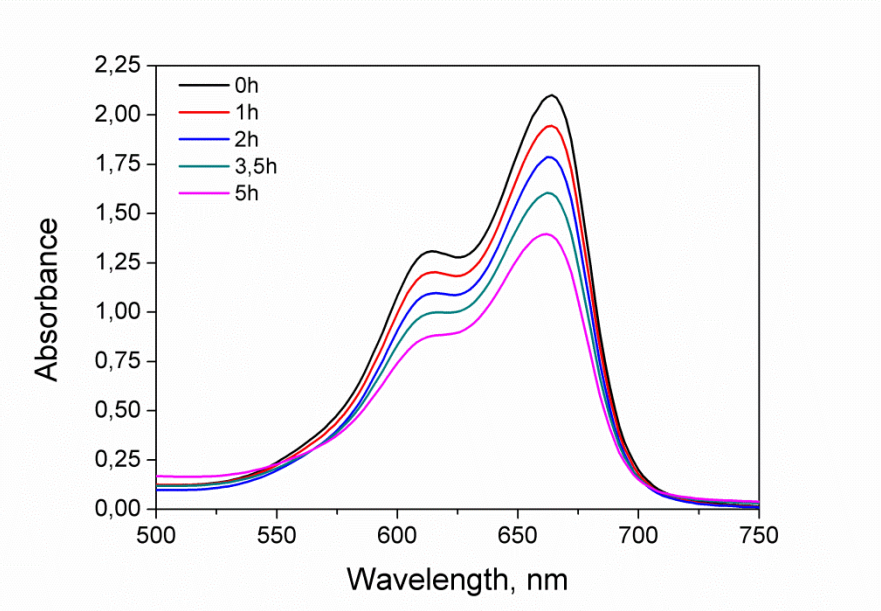

Fig. S4. Photolysis of MB in water during the irradiation under light using for desorption tests. The relative concentration change C/C_0 in 5 hours is 0.66.

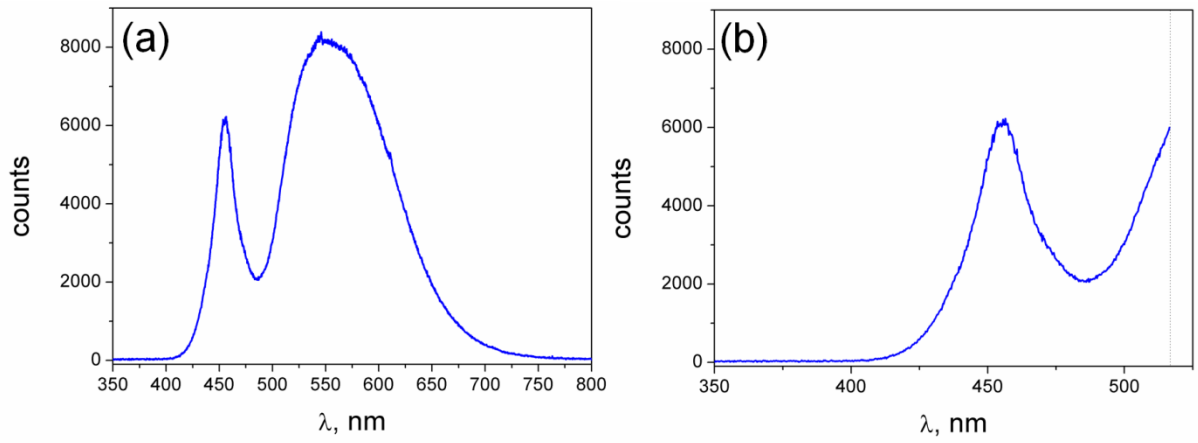

Fig.S5. Emission spectra of LED light source used for desorption experiments (left) and spectral part adsorbed by goethite (right).

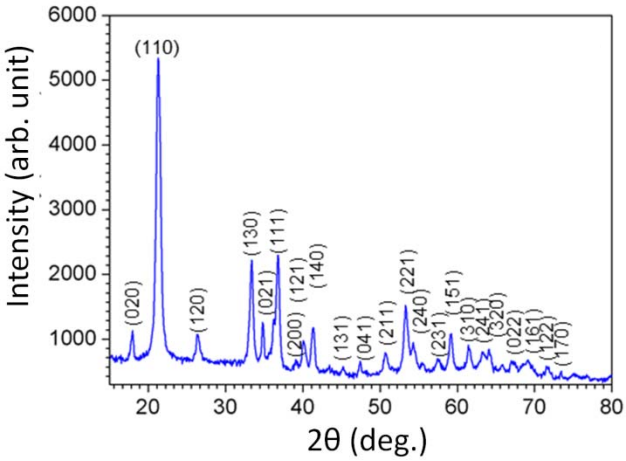

Fig. S6. XRD spectrum of α-FeOOH.

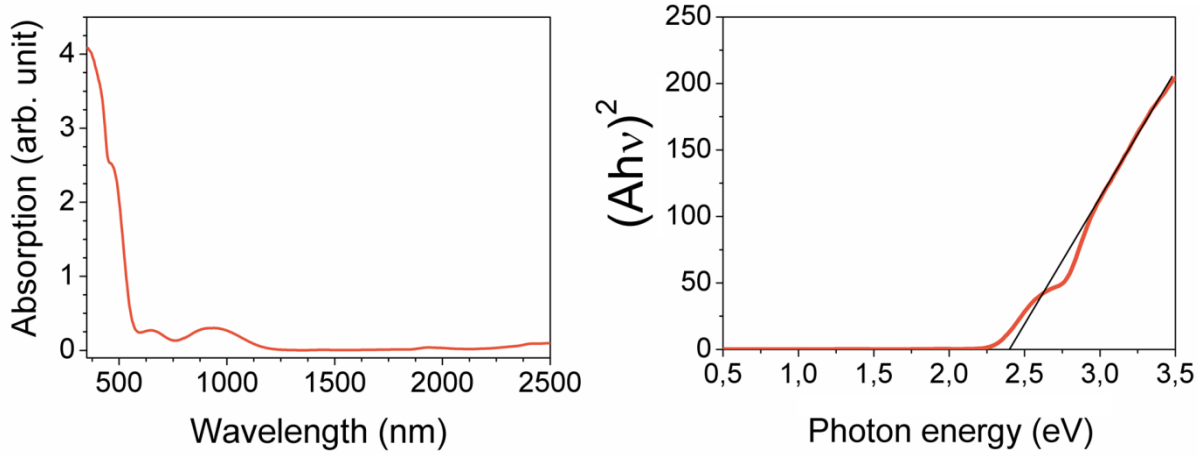

Fig. S7. Kubelka-Munk optical absorption spectrum of α-FeOOH (left) and b) optical absorption $(ah\nu)^2$ versus photon energy plot of synthesized α-FeOOH.

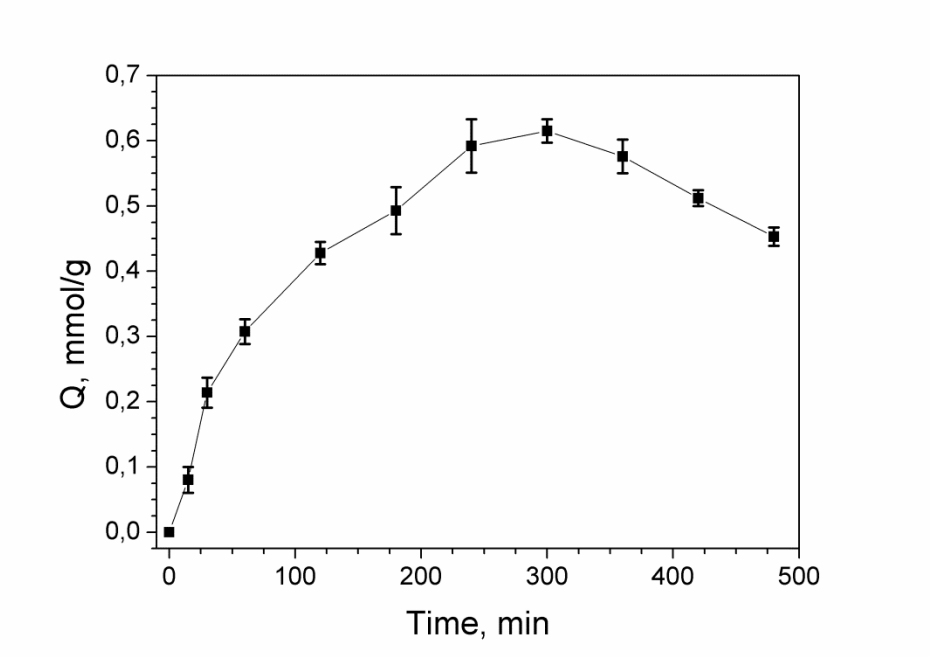

Fig. S8. The desorbed amount of MB from goethite nanowires at pH 8 as a function of the irradiation time.After certain time the concentration of desorbed goethite decreases which may be attributed to photolysis (please see next Fig. S9).

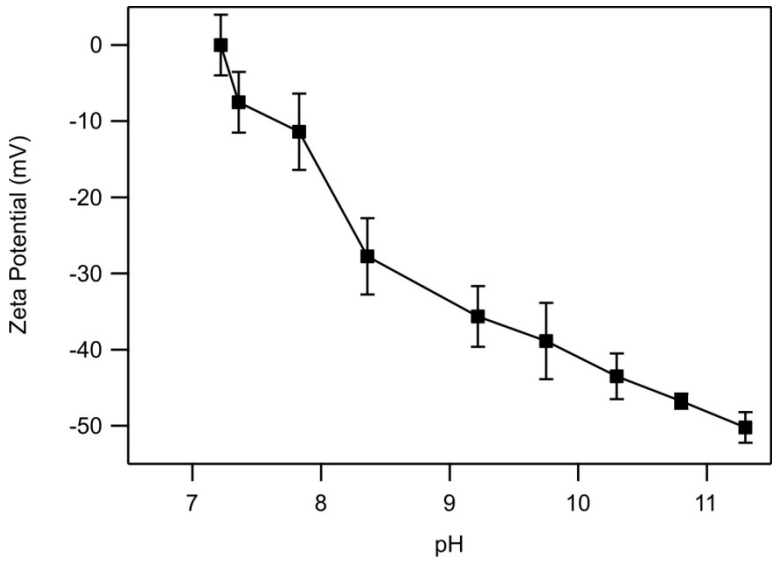

Fig. S9. Zeta potential of goethite suspensionsas a function of pH. Lines are only used as eye-guides.

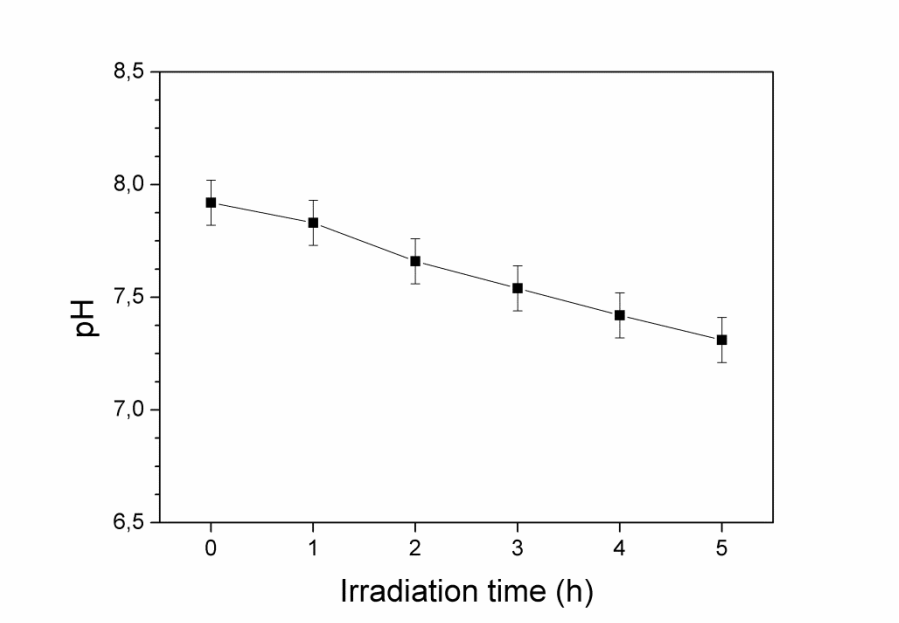

Fig. S10. pH changes during desorption under light irradiation for MB and goethite suspension at starting pH value 8.

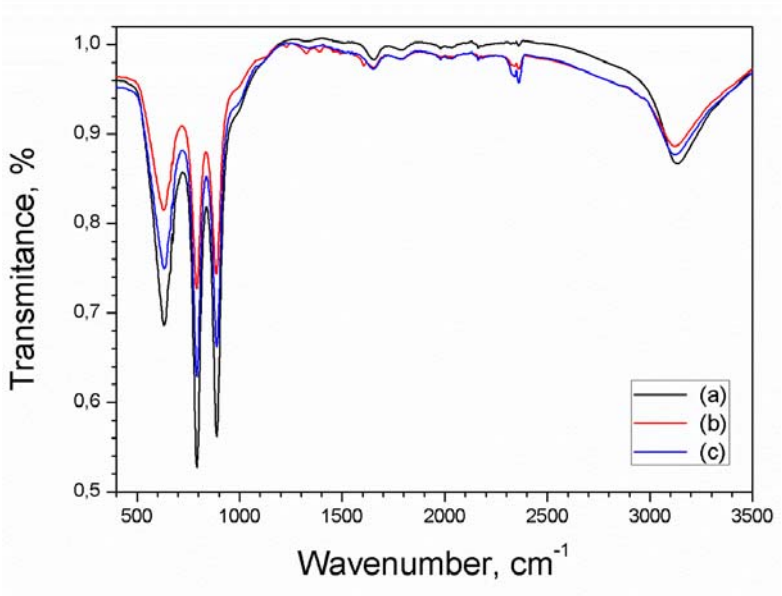

Fig. S11. ATR-FTIR spectra of of FeOOH (a); after MB adsorption onto FeOOH (b) and after desorption after irritation of light (c).

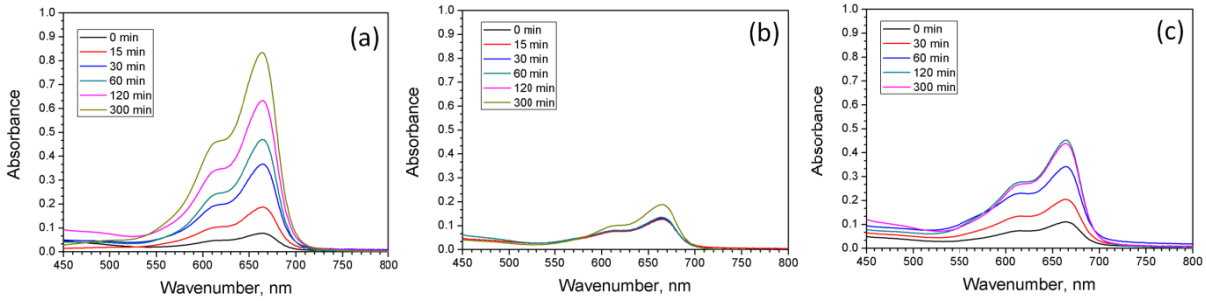

Fig. S12. Desorption of MB from goethite (a) under light irradiation at 30°C,(b) in dark at 30°C (b) and in dark at 70°C.

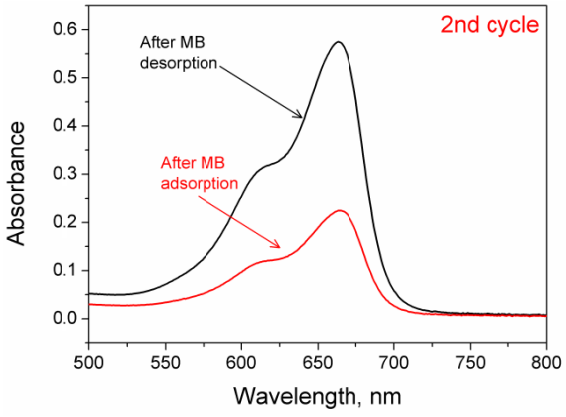

Fig. S13. MB adsorption and desorption under light irradiation for 5 hours over regenerated α-FeOOH nanowires.