

Electronic Supplementary Information

‘Colloidal cubes for the enhanced degradation of organic dyes’

Synthesis of hematite cubic colloids

The synthesis of hematite cubic colloids is based on the gel-sol method of Sugimoto *et al.*¹ The adjusted procedure described below leads to cubic colloids with a size, *i.e.*, an edge length, of approximately 1000 nm. The synthesis description is followed by recommendations on the procedure so as to ensure the reproducibility of the results. The size of the cubic colloids can be tuned by variation in the excess amount of ferric ions (Fe_x^{3+}), *i.e.*, by variation in the molar ratio of ferric ions and hydroxide ions. We varied Fe_x^{3+} by changing the concentration of the sodium hydroxide solution while keeping the amount of ferric ions constant as indicated in Table S1.

Experimental

Materials Iron(III) chloride hexahydrate (p.a., Sigma-Aldrich) and sodium hydroxide pellets (p.a., Emsure) were used as received. Both chemicals can be stored at room temperature and ambient pressure, but we only used previously unopened small pots containing iron(III) chloride hexahydrate. Freshly tapped Millipore water obtained from Synergy Ultrapure Water Systems was used as solvent (pH = 5-6). The used oven was a Memmert Type UE300 with a hardened glass window in the door and the air-circulation set to marker 2.

Methods Firstly, two stock salt solutions were prepared. A 5.04 M sodium hydroxide solution (pH 13-14) was prepared by dissolving 20.16 g sodium hydroxide in Millipore water using a 100 mL volumetric flask. The solution was left to cool to room temperature before filling the volumetric flask to 100 mL. For the iron(III) chloride solution, 50.02 g iron(III) chloride hexahydrate from a just opened, new container was weighed in a 250 mL Pyrex bottle as rapidly as possible while keeping the vessel containing the salt under a nitrogen flow to prevent the absorption of water by the iron(III) chloride hexahydrate. After adding 100 mL Millipore water using a 100 mL graduated cylinder, the iron(III) chloride solution was sonicated for 20 min. to ensure complete dissolution. Subsequently, the two salt solutions were mixed. The 100 mL sodium hydroxide solution was added by pouring in approximately 20 s directly to the iron(III) chloride solution while stirring magnetically at the maximum speed of the magnetic stirrer (1100 rpm for the used magnetic stirrers²). The volumetric flask was weighed before and after the addition in order to accurately calculate the amount of sodium hydroxide solution that was added³. The mixture was stirred at maximum speed for an additional 10 min. to ensure homogeneity. The magnetic stir bar was removed from the resulting gel using another clean magnet and the gel was placed into a pre-heated oven at 100 °C to age for eight days. During aging, the oven was kept closed at 100 °C and the gel was not agitated. Typically after a few days, the formation of a dark sediment below a clear yellow supernatant was observed through the door window. After the aging period, the bottle was removed from the oven and left to cool gradually to room temperature. The supernatant was removed using a Finn pipette. The supernatant had a pH of 0, measured with pH paper. The sol was washed several

¹T. Sugimoto *et al.*, J. Colloid Interface Sci., 1992, 152, 587-590; T. Sugimoto *et al.* J. Colloid Interface Sci., 1993, 159, 372-382; L. Rossi *et al.*, Soft Matter, 2011, 7, 4139-4142

²Set to the last marker; for the Ikamag Ret the marker > 1100 UpM and for the Ika-Werke RCT Basic marker 11

³The density of sodium hydroxide solutions at different concentrations is listed in R.H. Perry and D. Green. Perry's Chemical Engineers' Handbook. McGraw-Hill, 1984

times with Millipore water by centrifugation until the supernatant reached a steady pH value in the range pH 3-4. Clearly, the centrifugation speed and time depend on the size of the cubic particles. For cubic colloids with an edge length of approximately 1000 nm, centrifugation at 800 *g* for 30 min. is sufficient to collect the sol. During the washing procedure lighter particles did not sediment but formed a layer on top of the supernatant. This layer was removed with a Finn pipette. The cubic colloids were eventually stored in Millipore water in a Pyrex bottle at room temperature and ambient pressure.

Recommendations It is essential to perform the hematite cubes synthesis in a quantitative fashion, because the synthesis results were found to be very sensitive to the precise ratio between ferric ions and hydroxide ions. Since iron(III) chloride hexahydrate is highly hygroscopic, the actual water content determines the effective molar mass of the substance, which in turn determines the precise amount of ferric ions in the 50 g iron(III) chloride hexahydrate. Iron(III) chloride hexahydrate stored in previously opened vessels contains an unknown amount of water. It is therefore advisable to use unopened 50 g vessels, which can conveniently be used up entirely for one synthesis.

The iron(III) chloride solution should be prepared just before use, since it was previously observed that small iron oxide (β -FeOOH) colloids form from the solution after some time⁴.

Since sodium hydroxide pellets are less hygroscopic than iron(III) chloride hexahydrate, the preparation of the sodium hydroxide solution can be done at ambient conditions. However, the dissolution of sodium hydroxide in water is an exothermic reaction causing the solution to become very warm. Volumetric flasks are calibrated to room temperature and for that reason it is necessary to let the solution cool down before filling the volumetric flask to 100 mL.

The last step of the procedure is washing the sol. In this step, the size polydispersity can be reduced by sedimenting the particles by means of gravitational sedimentation instead of centrifugation. Cubic colloids of approximately one micrometer in size sediment overnight whereas smaller particles require more time and consequently remain in the supernatant.

Table S1: Experimental details of the hematite cubes used in this research or as seed particles for silica coated hematite cubes. The sample codes correspond to the letter used in Table 1. Fe_x^{3+} is the excess amount of ferric ions. The size is the average edge length and pd% is the polydispersity

Sample	Fe_x^{3+} (mol)	Size (nm)	pd% (%)
H1	0.017	374	14
H2	0.020	663	7
H3	0.019	800	5
H4	0.020	920	7

⁴D.M.E. Thies-Weesie *et al.*, J. Colloid Interface Sci., 1995, 174, 211-223

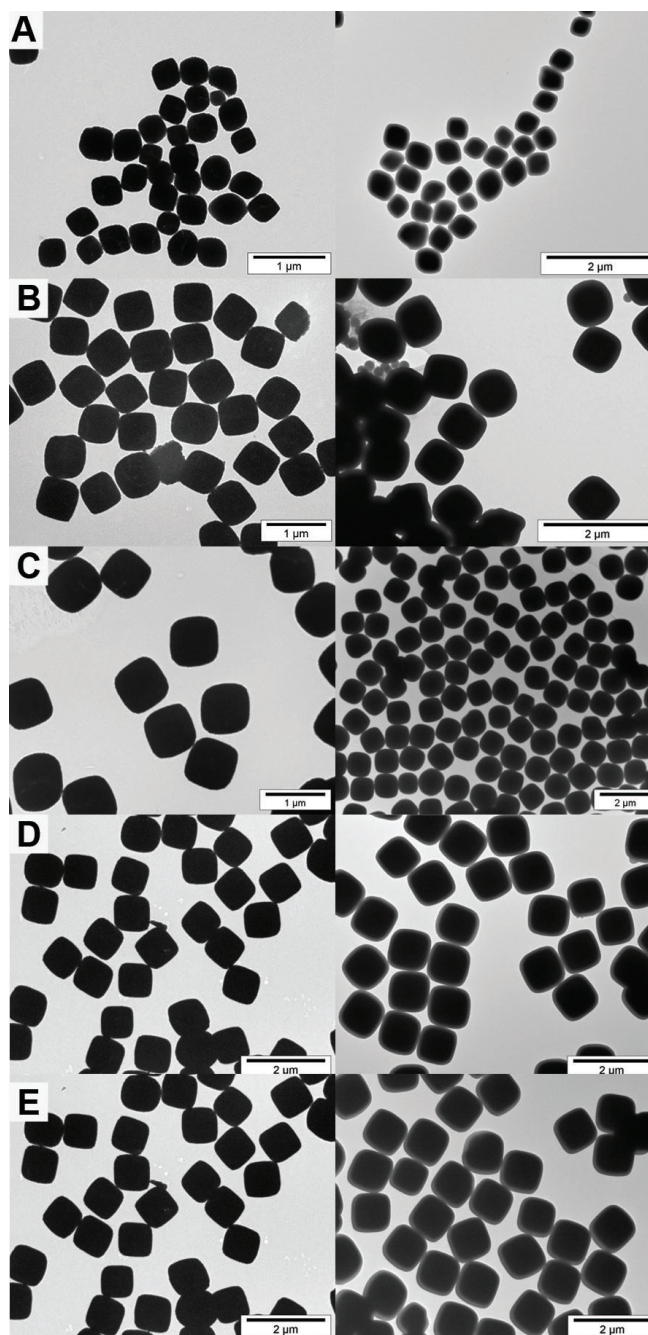


Figure S2: Typical TEM images of the silica coated hematite cubes used in this research (right) and their corresponding seed particles (left). The particles are displayed in the same order as they are listed in Table 1 (S1-S4b). All silica coatings were smooth and uniform.

Infrared spectroscopy

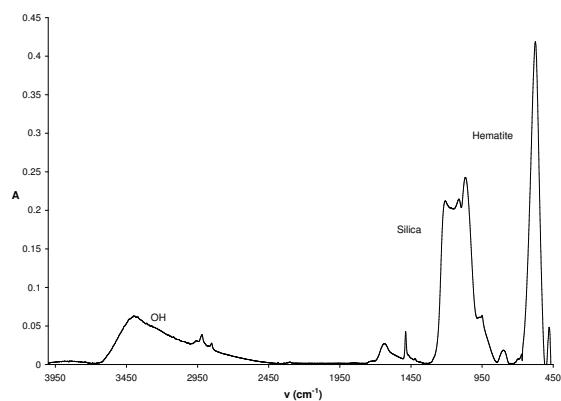


Figure S3: Infrared spectrum of silica coated hematite cubes. The peak of hematite can be found at $\sim 550 \text{ cm}^{-1}$ and the peak of silica at $\sim 1100 \text{ cm}^{-1}$. At $2500\text{-}3000 \text{ cm}^{-1}$, a large band of OH can be seen.

Hematite etching

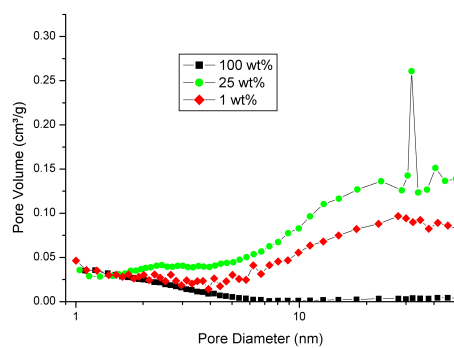


Figure S4: Pore size distributions measured with nitrogen physisorption of hematite etched hematite cubes for different wt% of remaining hematite.

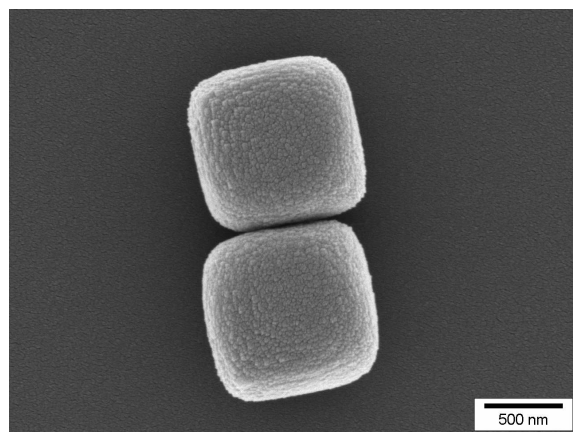


Figure S5: High magnification SEM image of hematite cubes showing the rough surface.

Degradation of methylene blue

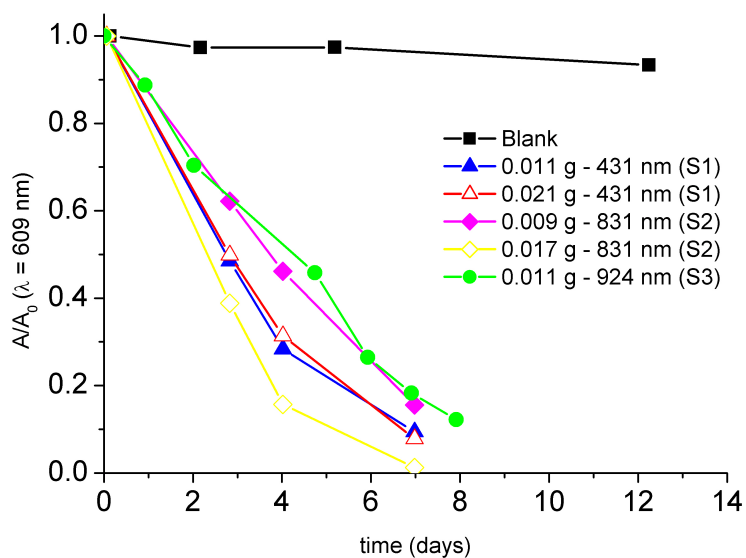


Figure S6: Normalized absorbance of methylene blue at $\lambda = 609$ nm as a function of reaction time. The degradation of methylene blue is promoted by silica coated hematite cubes compared to the blank (only hydrogen peroxide and methylene blue). The drawn lines are to guide the eye. Despite the difference in size and amount of cubes, the degradation rates are all quite similar.

Degradation of rhodamine B

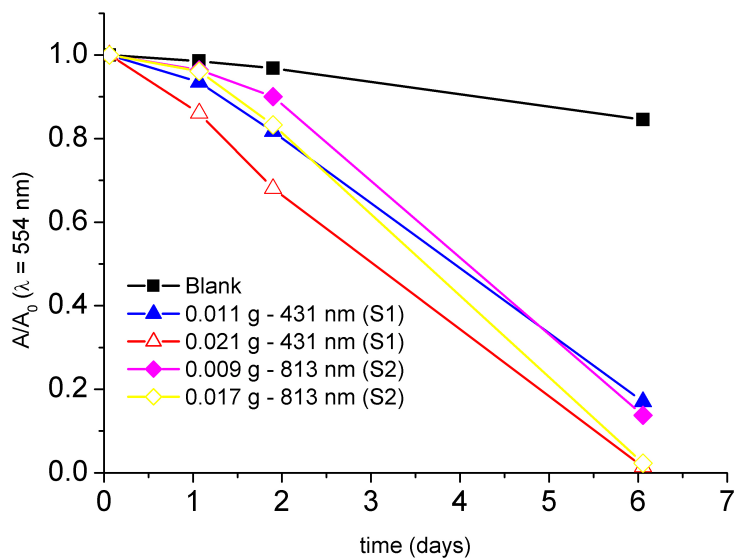


Figure S7: Normalized absorbance of rhodamine B at $\lambda = 554$ nm as a function of reaction time. The degradation of rhodamine B is promoted by silica coated hematite cubes compared to the blank (only hydrogen peroxide and rhodamine B). The drawn lines are to guide the eye. Despite the difference in size and amount of cubes, the degradation rates are all quite similar. Experimental conditions: 5 mL rhodamine B aqueous stock solution (1.82×10^{-4} M) and 5 mL H_2O_2 (35 wt%).