Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

New insights into size-controlled reproducible synthesis of anisotropic Fe_3O_4 nanoparticles: The importance of reaction environment

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Experimental method

Materials: Iron acetylacetonate ($Fe(acac)_3$) and oleic acid (OA, technical 80%) were purchased from Alfa Aesar. Benzyl ether (BE, 98%) was used as received from Sigma Aldrich.

Synthesis of different shaped Fe_3O_4 NPs : 0.706 g (2 mmol) of $Fe(acac)_3$, and 1.26 mL (3.6 mmol) of OA were added to 20 mL benzyl ether in 50 mL double neck round bottom flask. The reaction mixture was degassed at room temperature for 90 min under mild stirring on the standard schlenk line under different pressures in order to tune the amount of residual oxygen. After degassing, the solution was flushed with argon (Ar). The temperature of the reaction mixture was increased to 290°C at different heating rate under Ar atmosphere, and kept at this temperature for 30 min. During the reaction, the color of the solution was changed from dark orange to dark-brown indicating the formation of Fe_3O_4 NPs. After cooling down the solution to room temperature, 40 mL toluene was added, and the resultant solution was centrifuged at 2000 rpm for 5 min. The supernatant was discarded, and the precipitate was redispersed in 10 mL n-hexane and 20 mL acetone followed by centrifugation at 4000 rpm for 5 min. The collected Fe_3O_4 NPs were again washed with hexane and acetone. The precipitate was dried, and redisperse in 10 mL toluene in the presence of 50 µL OA.

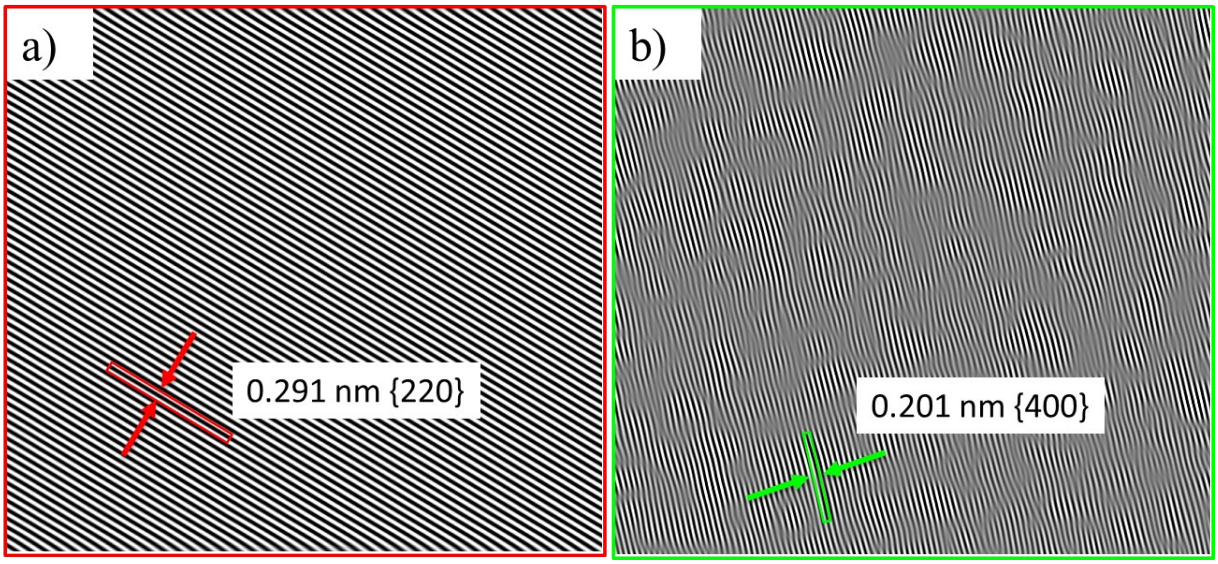

Fig. S1 Determination of lattice spacing based on inverse FFT image produced from the reflections marked by red and green circles in Fig. 1.

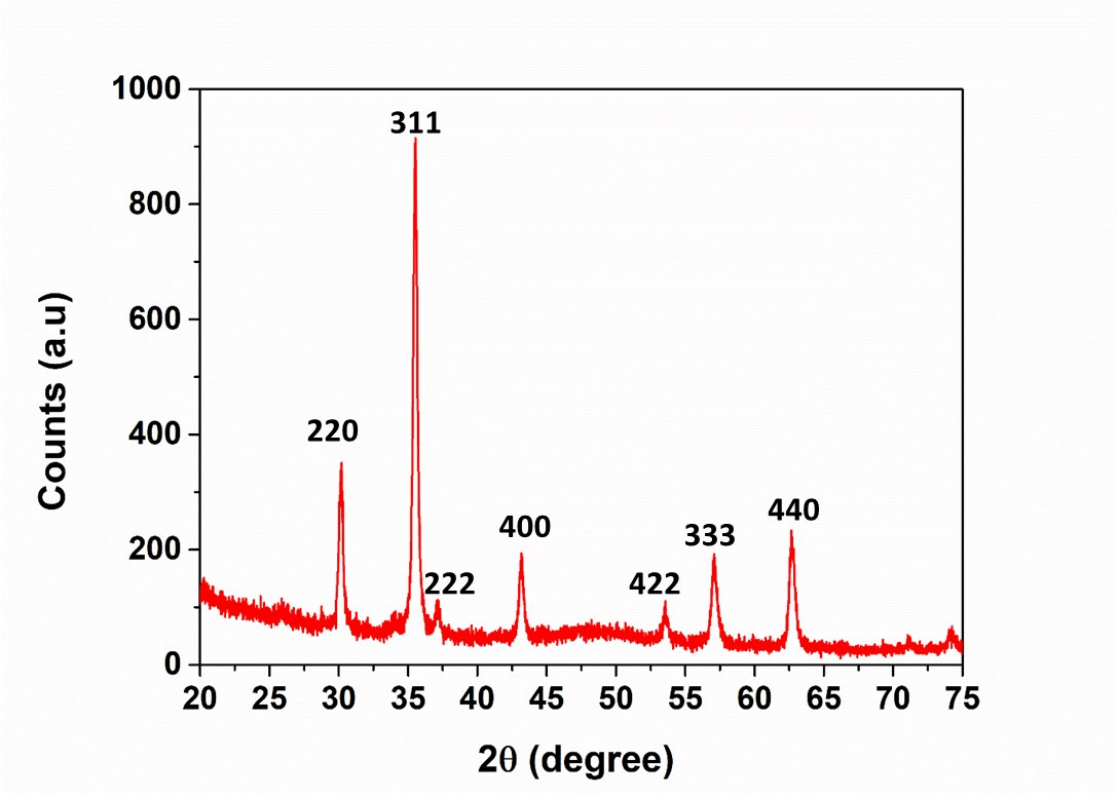

Fig. S2 X-ray diffraction (XRD) pattern of Fe_3O_4 nanocubes.

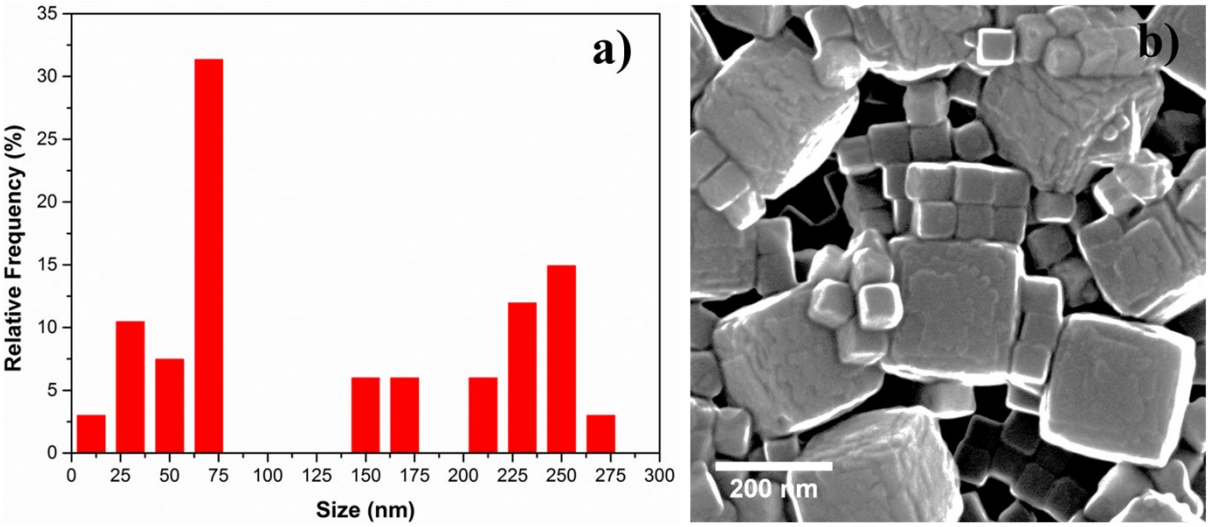

Fig. S3 a) Histogram and b) SEM image show two different populations (~72 nm and ~240 nm) of Fe_3O_4 nanocubes grown at the heating rate of 1°C/min (SD~ 18%, where SD refers to standard deviation)

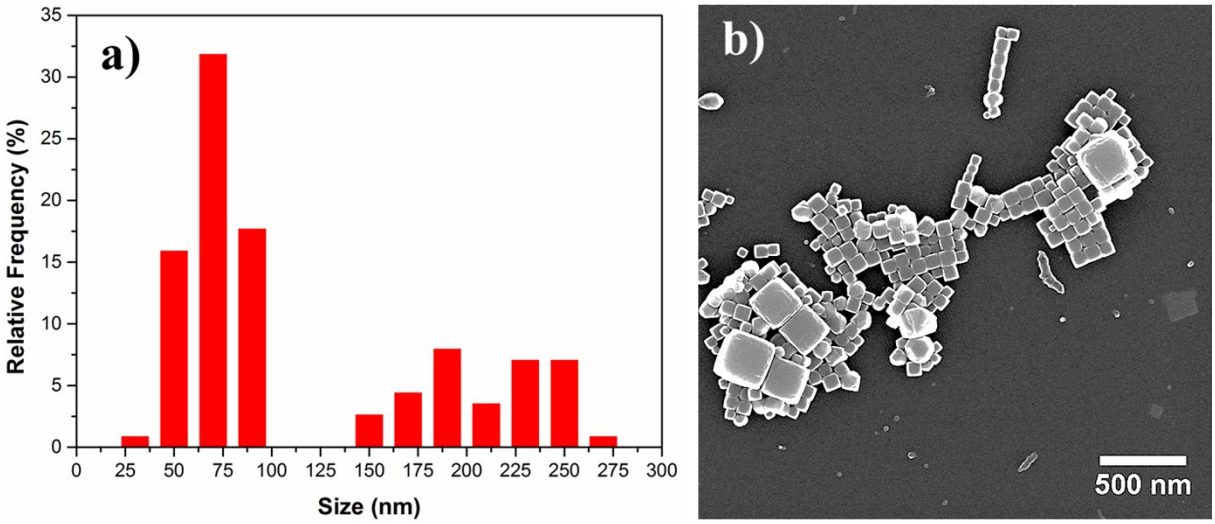

Fig. S4 a) Histogram and b) SEM image show two different populations (~70 nm and ~220 nm) of Fe_3O_4 nanocubes grown at the heating rate of 2°C/min (SD~16%).

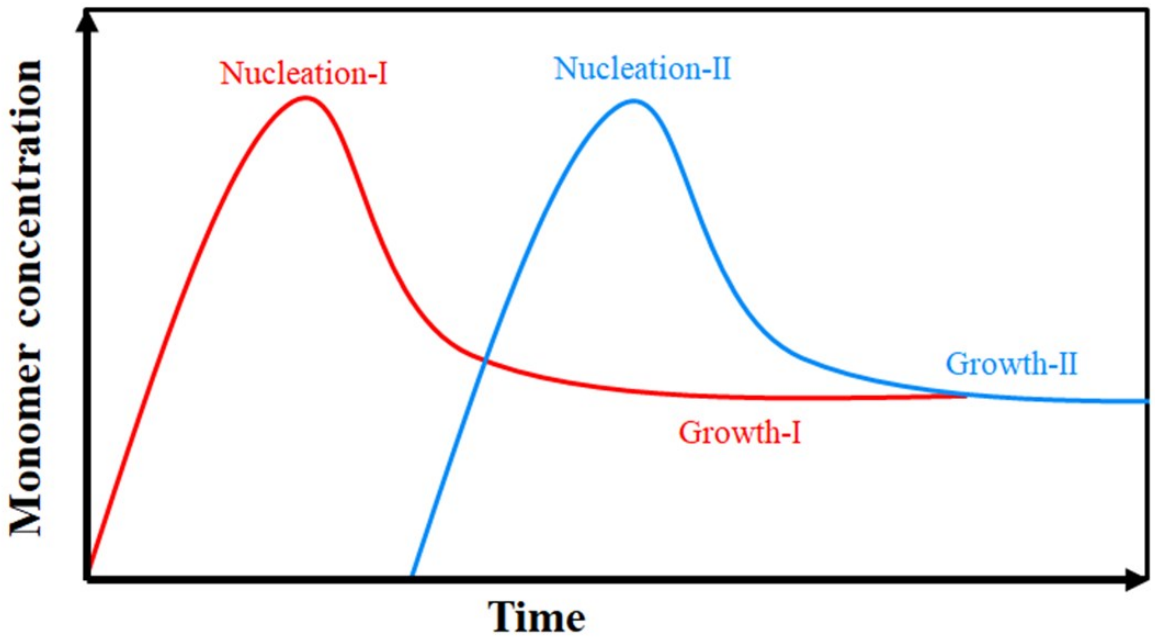

Fig. S5 Multiple nucleation and growth events in the formation of Fe_3O_4 nanocube at low heating rates (1°C and 2°C).

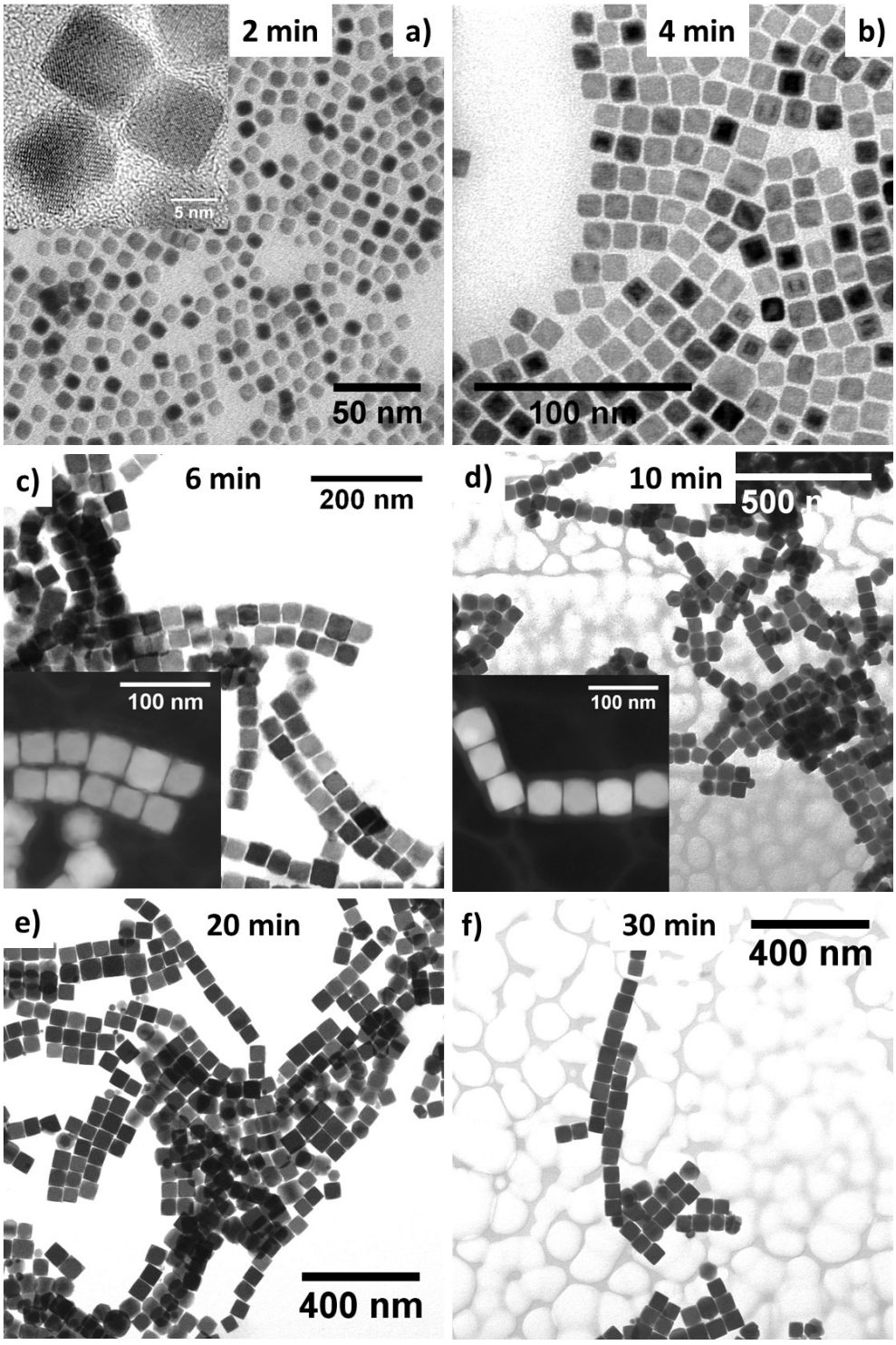

Fig. S6 BF STEM images show the intermediate reaction products collected at different time intervals in growth of Fe_3O_4 nanocubes at slow heating rate (5˚C/min). Inset in panel (a) is HRTEM image. Insets in panels (c) and (d) are dark field STEM images.

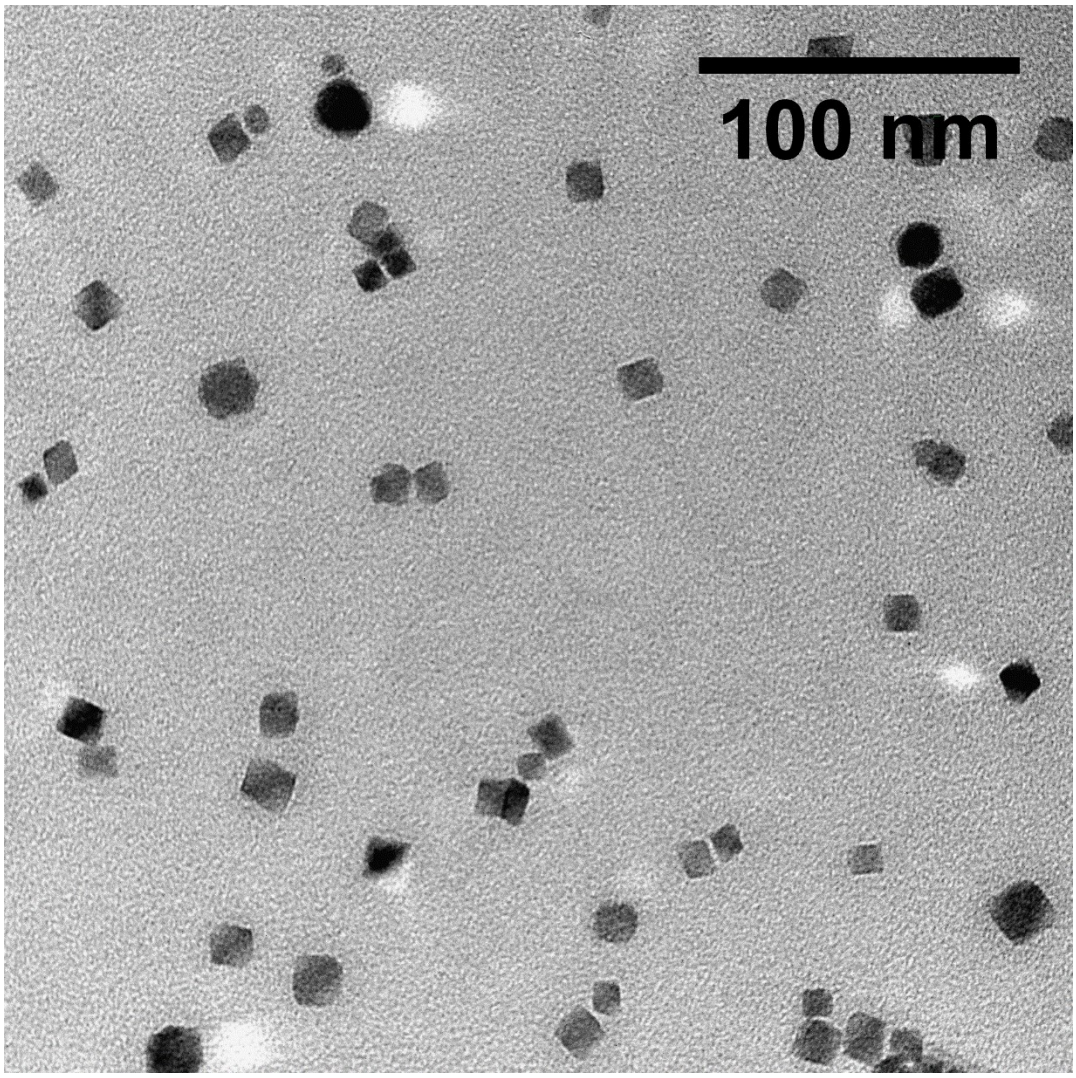

Fig. S7 TEM image show the intermediate reaction product collected after 2 min during the growth of Fe_3O_4 nanocubes at faster heating rate (10°C/min).

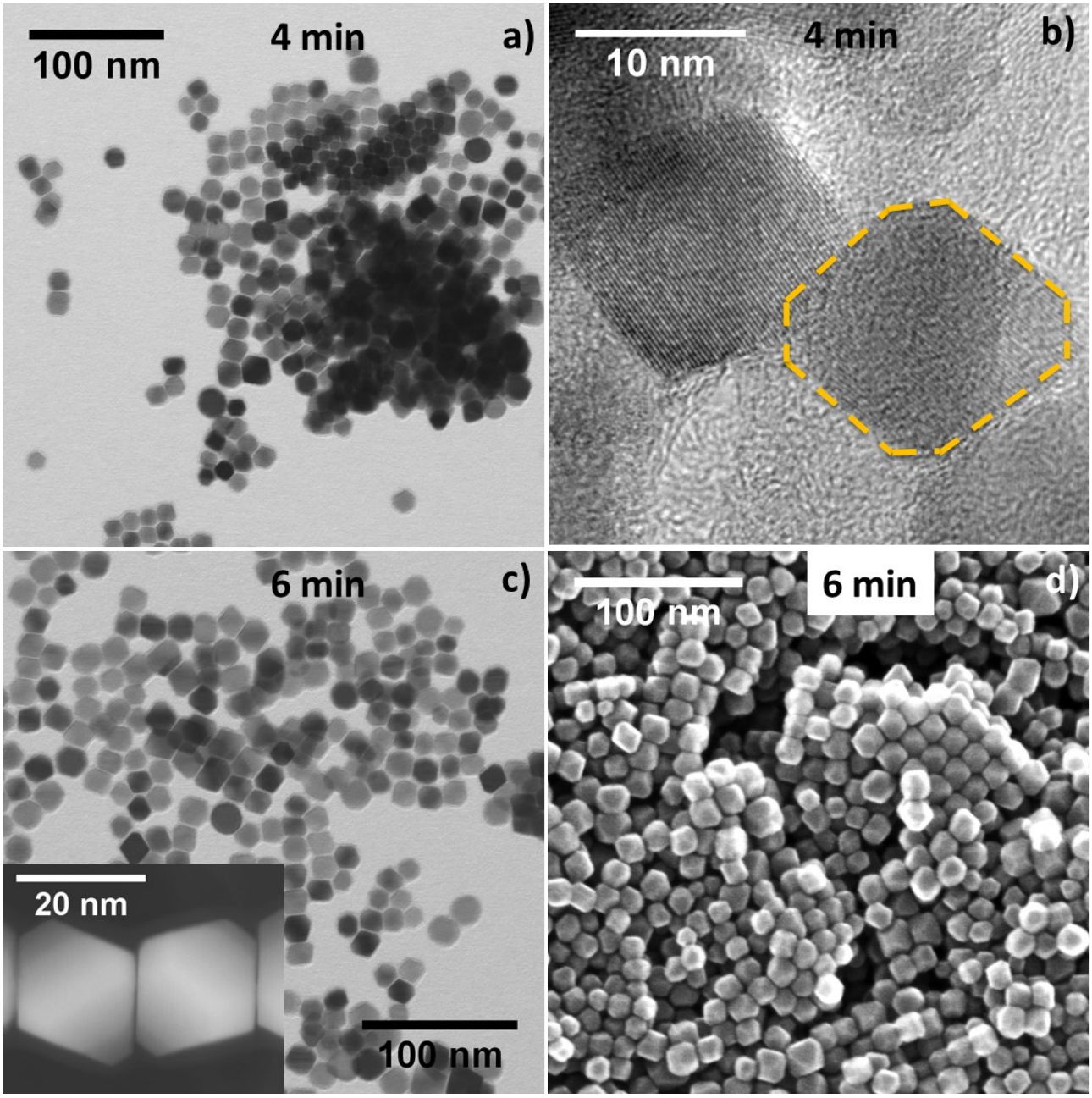

Fig. S8 Intermediate reaction products during the growth of Fe_3O_4 nanocubes at faster heating rate (10°C/min). a) BF STEM image of truncated octahedra after 2 min of the reaction. b) HRTEM image of NP shown in panel (a). c) BF STEM image of truncated octahedra NPs (inset is dark field STEM image) after 6 min of the reaction and d) SEM image.

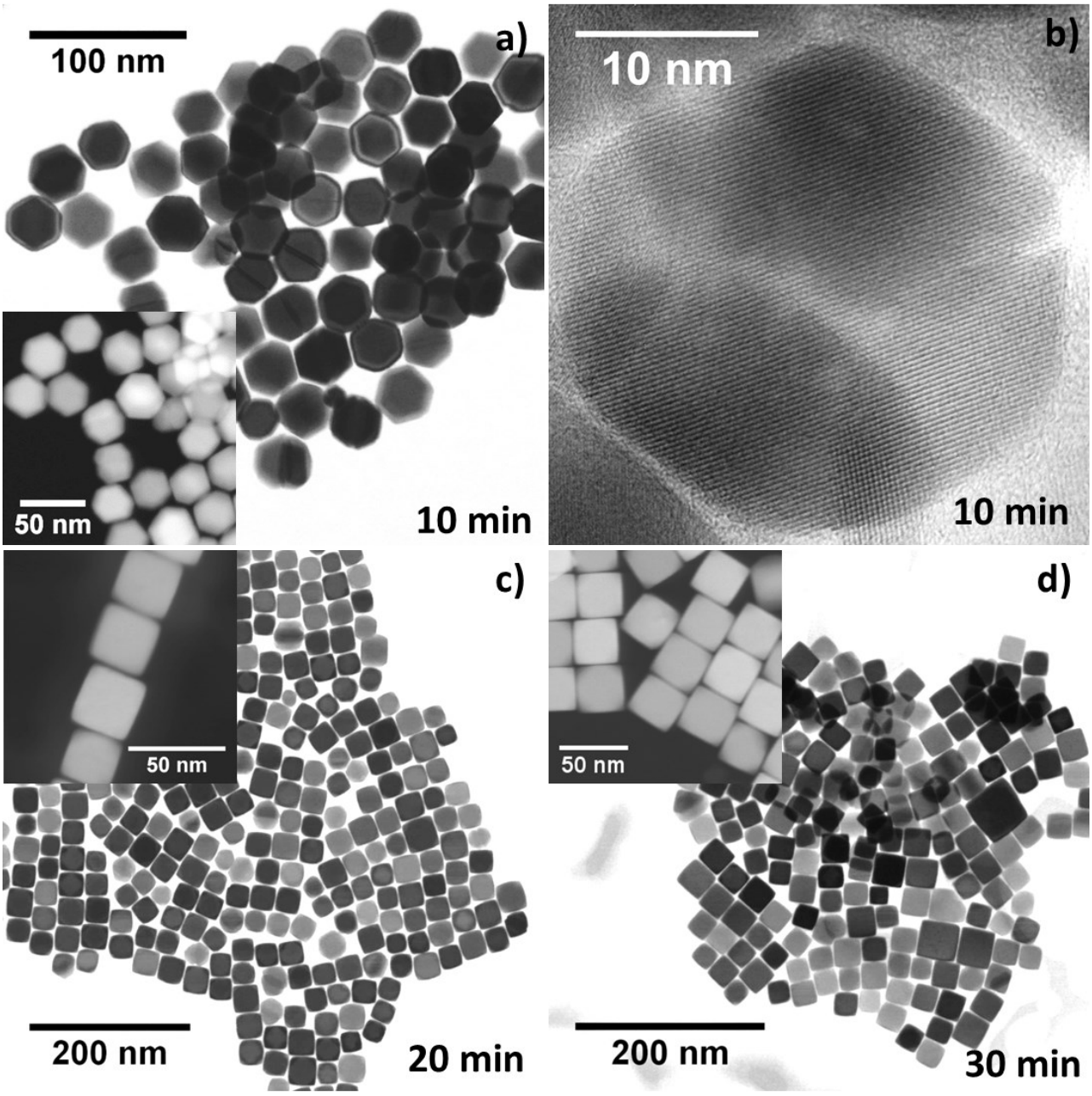

Fig. S9 Intermediate reaction products during the growth of Fe_3O_4 nanocubes at faster heating rate (10°C/min). a) BF STEM image of cuboctahedra after 10 min of the reaction. b) HRTEM image of NP shown in panel (a). c) BF STEM image of cubic NPs after 20 min of the reaction. d) c) BF STEM image of cubic NPs after 30 min of the reaction. Insets in panels (a), (c) and (d) are dark field STEM images.

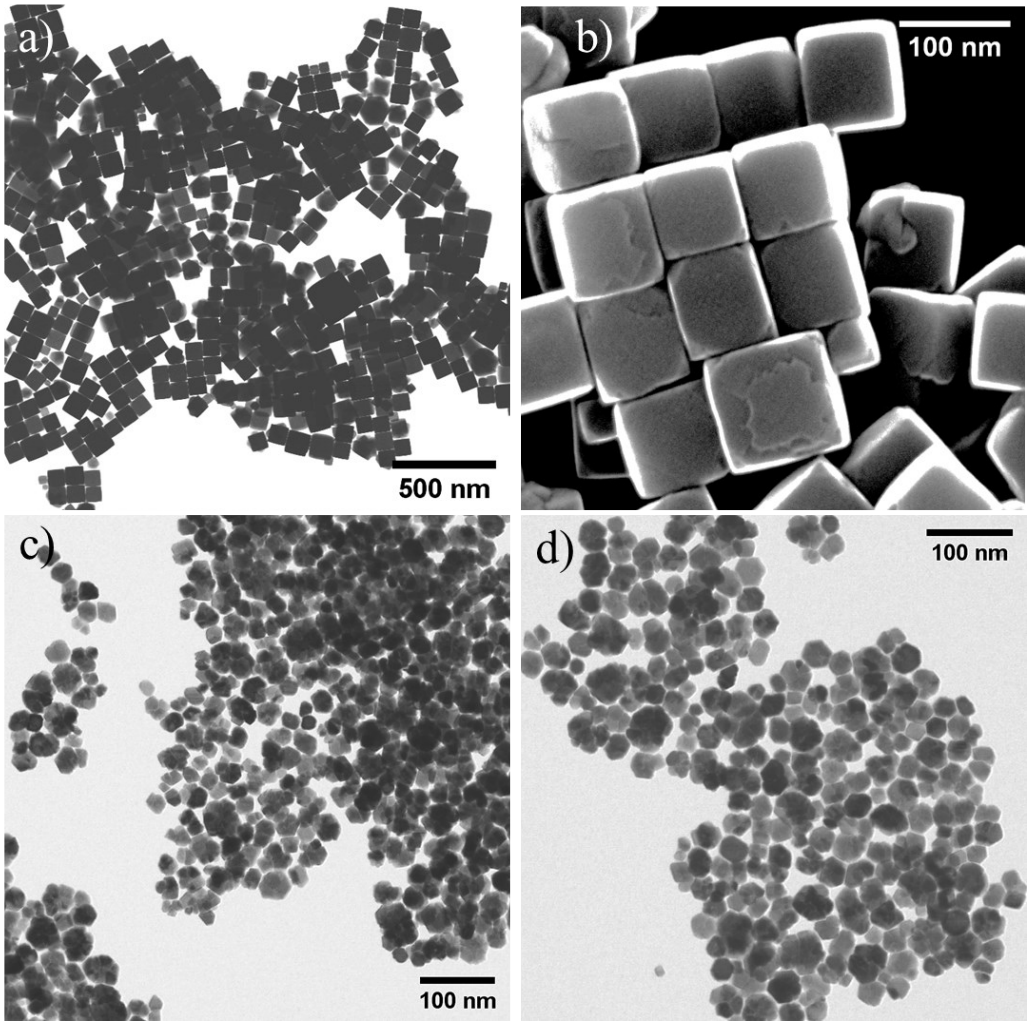

Fig. S10 The influence of solvent on the shape of Fe_3O_4 NPs; a) BF STEM and b) SEM image of nanocube of size ~86.3 nm (SD~6%), solvent (BE) volume: 10 mL, c, d) BF STEM images of flower shaped (single or multiply twinned) NPs of size ~30.9 nm (SD~10%), solvent (BE) volume: 50 mL.