Supporting Information

Gelification – an Effective Measure for Achieving Differently Sized Biocompatible Fe_3O_4 Nanocrystals through a Single Preparation Recipe

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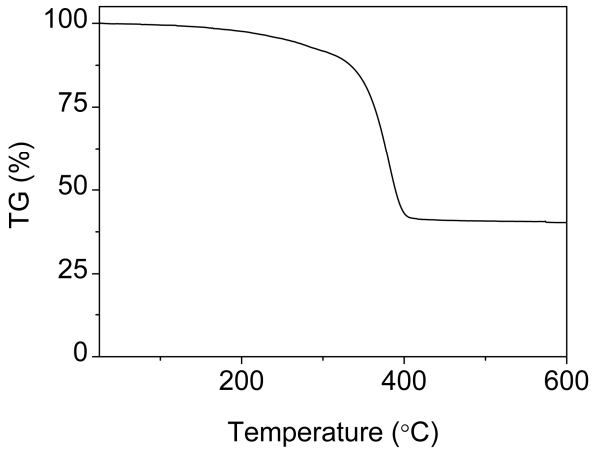

Figure S1. TGA curve of 11.3 nm Fe_3O_4 nanoparticles obtained by 30 min of reflux.

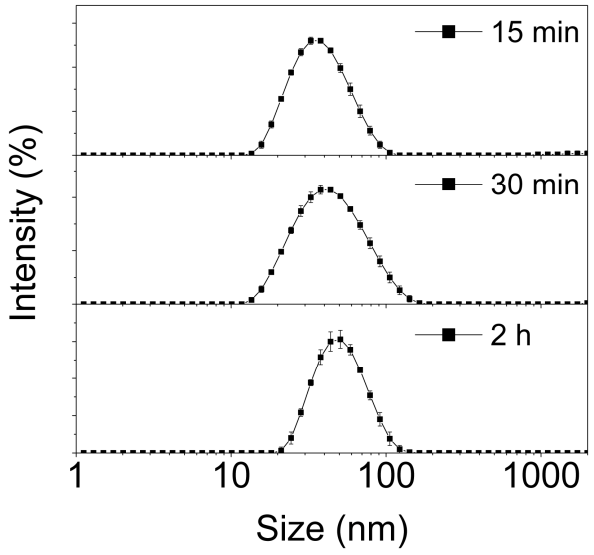

Figure S2. The hydrodynamic size distribution profiles of Fe_3O_4 particles obtained by different reflux time.

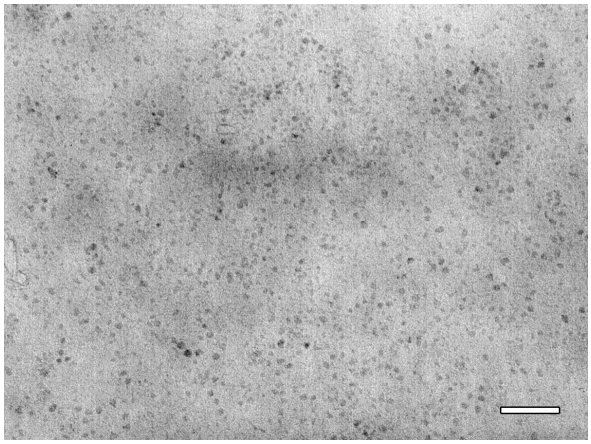

Figure S3. TEM image of Fe_3O_4 nanoparticles formed at the end of the first gelification process at round 224 ℃. The scale bar corresponds to 50 nm.

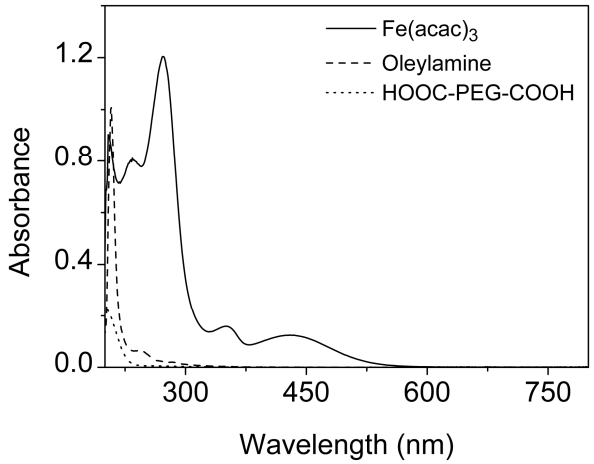

Figure S4. Absorption spectra of $Fe(acac)_3$, oleylamine, and HOOC-PEG-COOH.

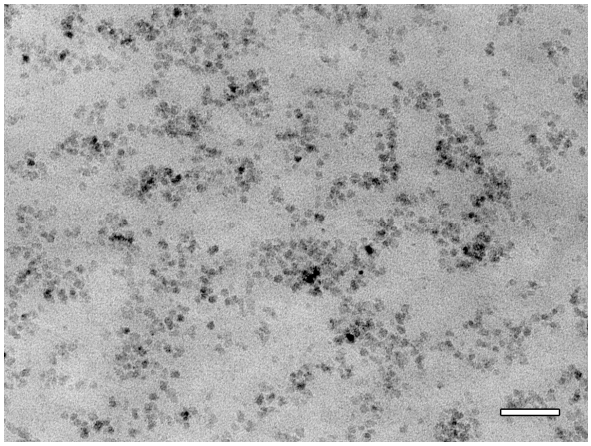

Figure S5. TEM image of the Fe_3O_4 nanoparticles obtained in the absence of oleylamine by reflux time of 2 h. The scale bar corresponds to 50 nm. The average particle size is of 5.4 nm

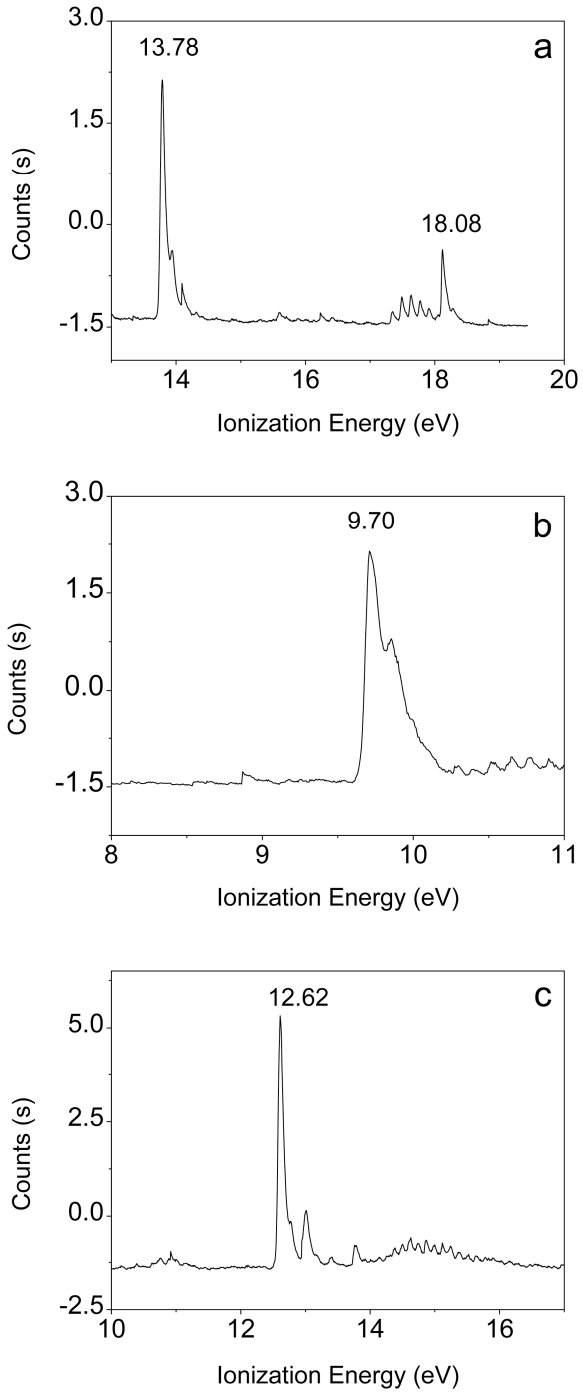

Figure S6. The photoelectron spectra of the small molecules collected during the preparation. Spectra shown in frame a-c were recorded successively while the U-tube containing the frozen molecules was warmed up.

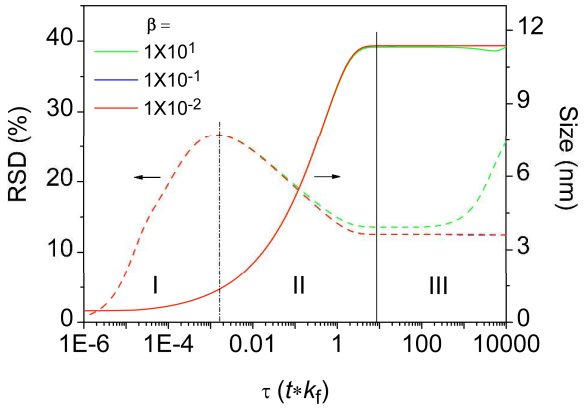

Figure S7. The simulation results on the particle size (solid line) and size distribution (dashed line) obtained by varying β values with α value fixed as 1.0×10^{9}. Note: the blue and the red RSD lines are completely overlapped.

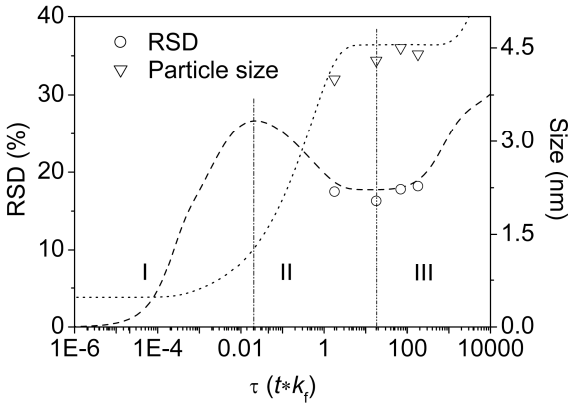

Figure S8. The best simulation results on particle size (dotted line) and size distribution (RSD, dashed line) of the nanocrystals obtained by replacing HOOC-PEG-COOH by equal mole of mPEG-COOH, overlaid with the corresponding experimental data from Figure 10. The parameter values for α and β are 4.0×10^{6} and 2.0×10^{0}, respectively.

The expressions of simulated quantities, method, and parameters.

When the nondimensional concentration and time are introduced by $c_n = C_n/P_0$, $p = P/P_0$, $\tau = k_f t$, the nondimensionalized rate equations are given as follows

$$\frac{\mathrm{d}\,p}{\mathrm{d}\,\tau} = -p \tag{S1}$$

$$\frac{\mathrm{d}\,c_1}{\mathrm{d}\,\tau} = p - \alpha c_1^2 - \alpha\sum_{n=1}^{N-1}(n)^{2/3}c_n c_1 + \beta\ (2)^{2/3}c_2 + \beta\sum_{n=2}^{N}(n)^{2/3}c_n \tag{S2}$$

$$\frac{\mathrm{d}\,c_n}{\mathrm{d}\,\tau} = \alpha(n-1)^{2/3}c_{n-1}c_1 - \beta(n)^{2/3}c_n - \alpha(n)^{2/3}c_n c_1 + \beta(n+1)^{2/3}c_{n+1} \tag{S3}$$

The experimental quantities computed based on the concentration profile including the mean size (D), radial variance (σ_R^2), relative standard deviation (RSD) and reaction conversion rate (Y) are expressed by equations given below

$$D = 2\langle R\rangle = 2\left(\frac{3}{4\pi\rho}\right)^{1/3}\left\langle n^{1/3}\right\rangle = 2\left(\frac{3}{4\pi\rho}\right)^{1/3}\frac{\int n^{1/3}c_n\,\mathrm{d}n}{\int c_n\,\mathrm{d}n} \tag{S4}$$

$$\sigma_{\mathrm{R}}^2 = \left(\frac{3}{4\pi\rho}\right)^{2/3}\frac{\int (n^{1/3}-\left\langle n^{1/3}\right\rangle)^2 c_n\,\mathrm{d}n}{\int c_n\,\mathrm{d}n} \tag{S5}$$

$$\mathrm{RSD} = \frac{\sigma_{\mathrm{R}}}{\langle R\rangle} \tag{S6}$$

$$Y = 1 - p \tag{S7}$$

The discrete rate equations 12-14 presented in discussion section were integrated numerically by using the same method as described by Bawendi and coworkers.[1,2] In brief, the discrete rate equations were approximated by a continuous Fokker-Planck partial differential equation (FPE). With respect to the concentration profile of *n*-sized particles, a taylor series expansion to the second order is adopted for small particles ($n<n_{\mathrm{match}}$) and the FPE is used for large particles (n_{match} is the matching point). To discretize the *n*-dependent part of the FPE, the Chang-Cooper (CC70) weighted finite difference scheme was applied. The initial values of the scaled precursor concentration and the scaled particle concentration were set to unity and zero, respectively. The simulation results presented in the Figure 11, Figure 12, Figure S4, and Figure S5 were obtained by setting the maximum cluster size *n* to 100,000, and the matching point to n_{match} = 10. Consequently, the number of the discrete rate equations equals to 550 and λ (the meshing space of the FPE for the large particles) equals 0.01345779773. Lattice parameter for the cubic crystallized Fe_3O_4 is 8.384 Å, and a unit cell is composed of eight Fe_3O_4 molecules, thus the number density for Fe_3O_4 is calculated to be 13.6 nm^{-3}. Integration in scaled time was performed using variable-coefficient ordinary differential equation solver (VODE) through the ODEPACK Fortran library.[3] The software version of MATLAB for visualizing the simulation results is MATLAB R2009b.

References:

(1) Rempel, J. Y.; Bawendi, M. G.; Jensen, K. F. *J. Am. Chem. Soc.* **2009**, *131*, 4479.

(2) Rempel, J. Y. Insights into Formation of Semiconductor Nanocrystals: from First Principles Calculations to Kinetic Models of Nucleation and Growth. Ph.D. Thesis, Massachusetts Institute of Technology, Boston, January 2008.

(3) Brown, P. N.; Byrne, G. D.; Hindmarsh, A. C. *SIAM J. Sci. and Stat. Comput.* **1989**, *10*, 1038.