

Supplementary Information

A General Method for Mass and Template-Free Production of Hierarchical Metal Oxide Spheres at Room-Temperature

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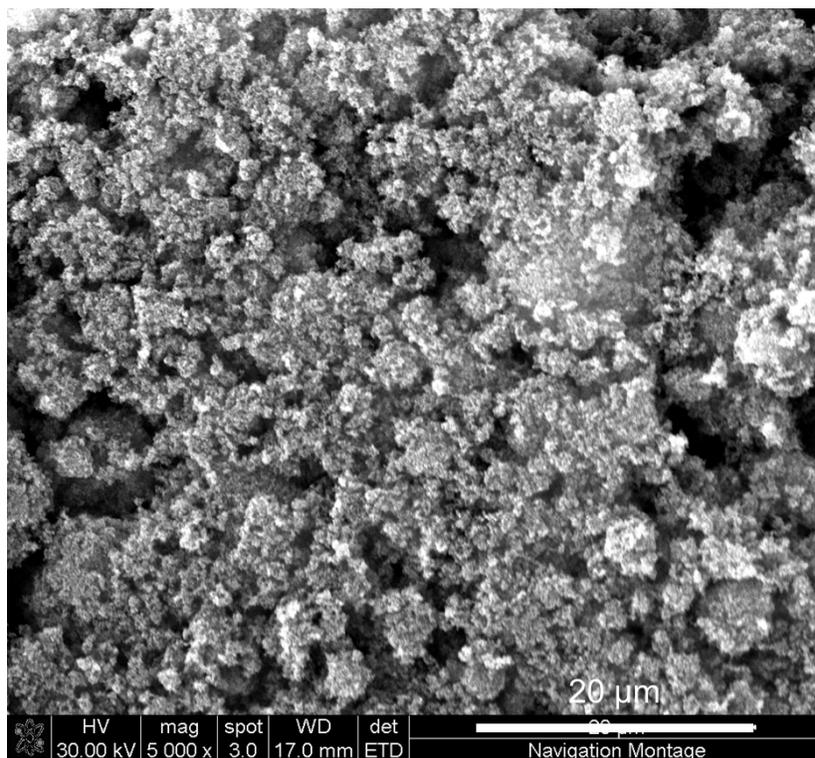


Fig. S1. SEM image of TiO₂ nanoparticles (Degussa P25).

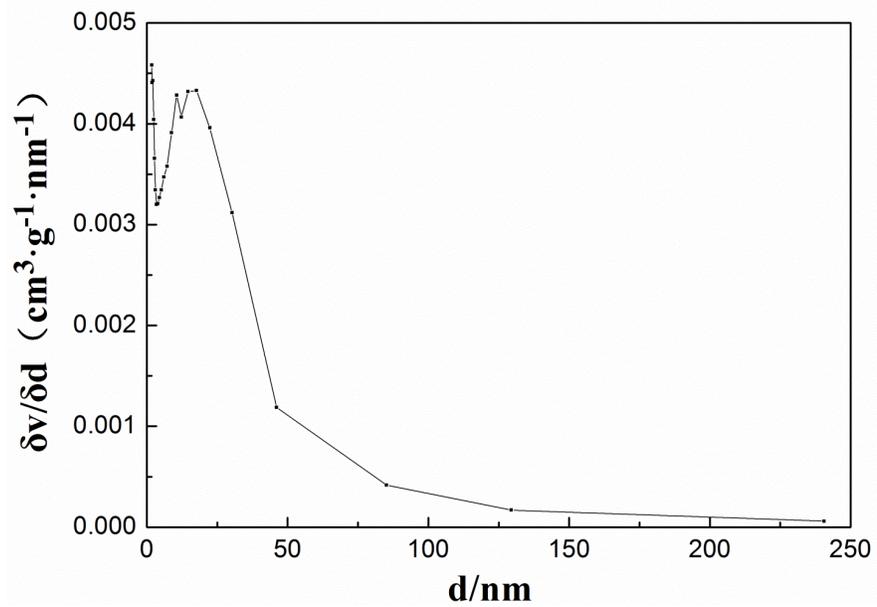


Fig. S2. The pore size distribution diagram of TiO₂ hierarchical spheres.

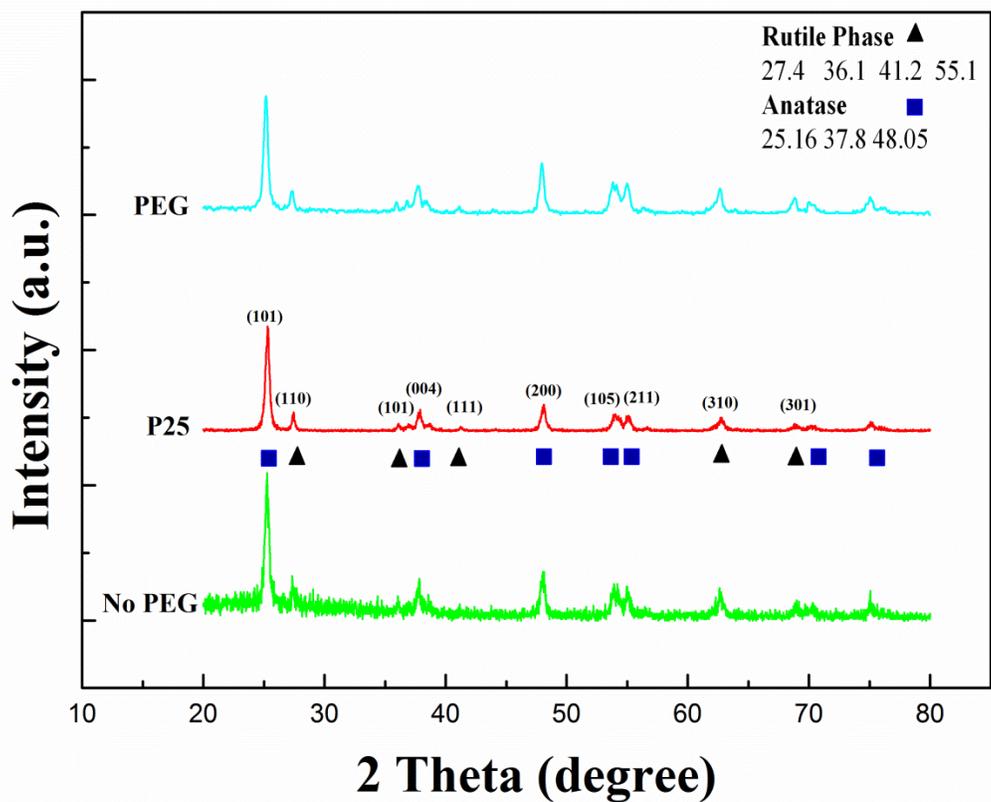


Fig. S3. The XRD patterns of TiO₂ HMOS, Degussa P25 and P25 treated by PMSA process without PEG.

There is no distinct difference in crystalline structures of TiO₂ HMOS, Degussa P25 and TiO₂.treated by PMSA process without PEG, which indicates that the PEG removal process by sintering does not change their crystalline structures.

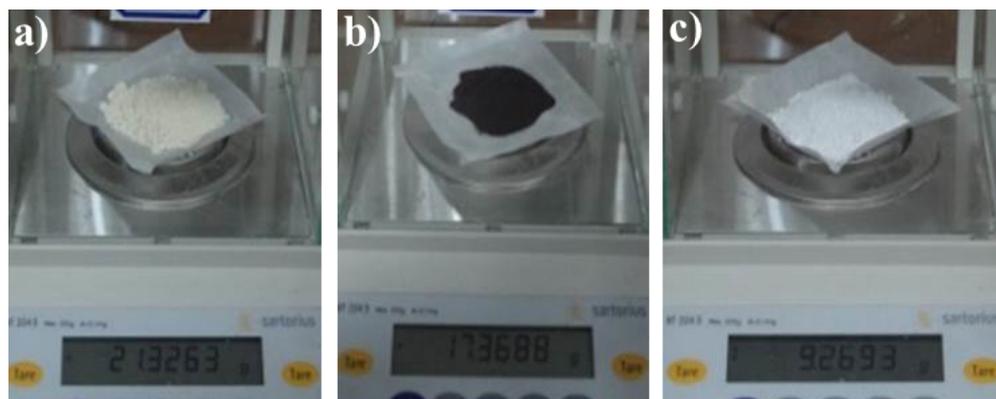


Fig. S4. The appearances and weights of the HMOS of TiO_2 (a), Fe_2O_3 (b) and ZrO_2 (c) fabricated by the PMSA method.

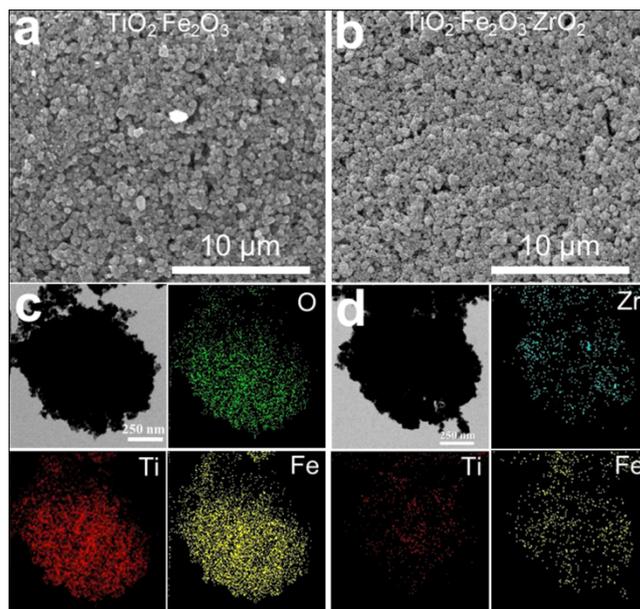


Fig.S5. SEM images of hierarchical spheres of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ (a), $\text{TiO}_2\text{-Fe}_2\text{O}_3\text{-ZrO}_2$ composites (b) and their corresponding TEM/EDX O-K, Ti-K, Fe-K, Zr-K maps.

The designed mass ratio of TiO_2 to Fe_2O_3 is 1:1 and mass ratio of TiO_2 to Fe_2O_3 to ZrO_2 is 2:2:1. The adopted mass ratio of metal oxide nanoparticles to PEG (20000) is 3:1.

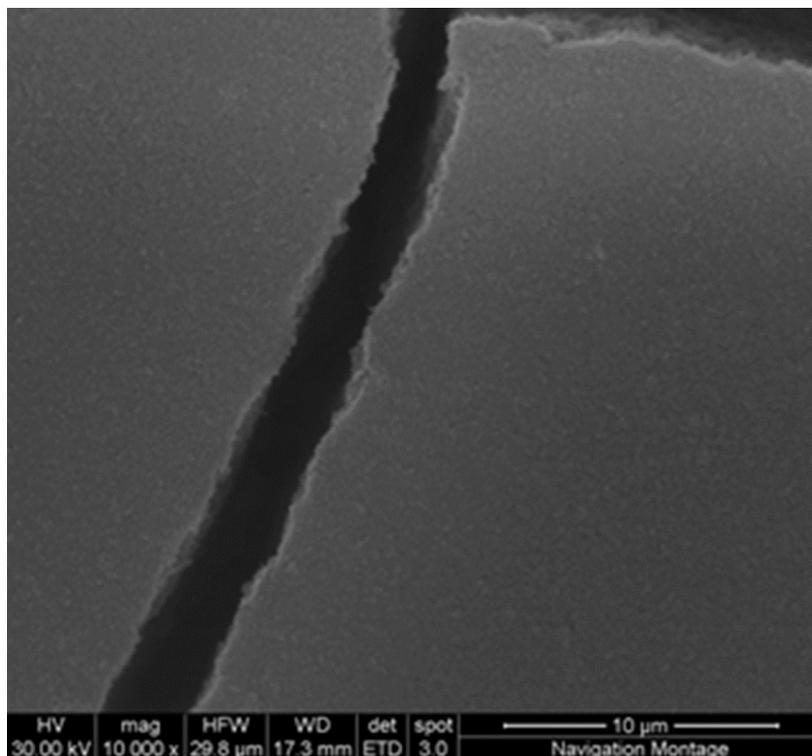


Fig.S6. SEM image of TiO₂ film shows no hierarchical spheres form by wet grinding fabrication process.

During the fabrication of TiO₂ hierarchical spheres, TiO₂ nanoparticles are dry grinded with PEG and this is an important process. However, if water is added during the grinding process, no hierarchical spheres appear. This experimental result indicates that the "lying" configuration of PEG cannot form if water is added.

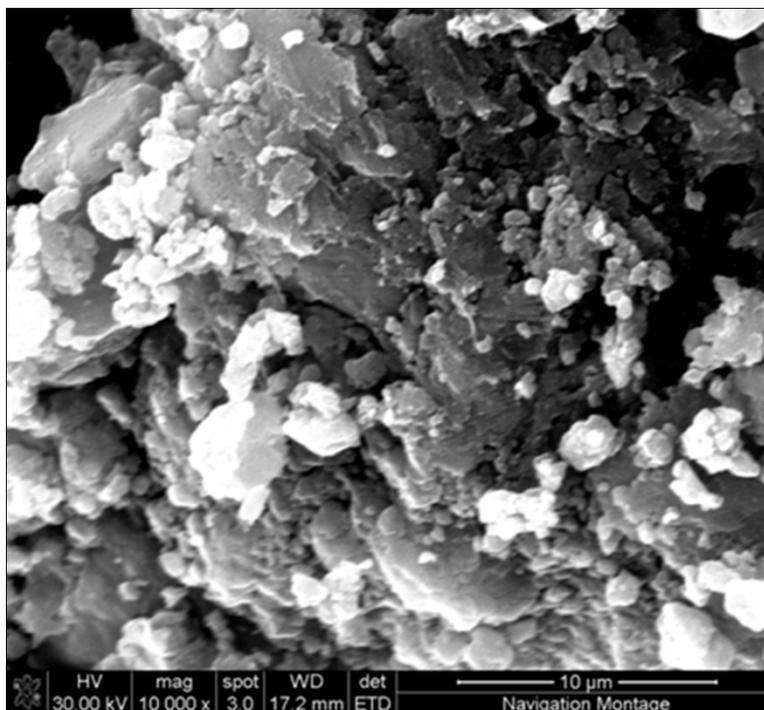


Fig.S7. SEM image of TiO_2 powders after grinding with PEG-20000 without dispersing. The mass ratio of TiO_2 to PEG is 3:1.

This experimental result indicates that the hierarchical spheres do not form during the grinding process, they will appear in the next water dispersing process by self-assembly.

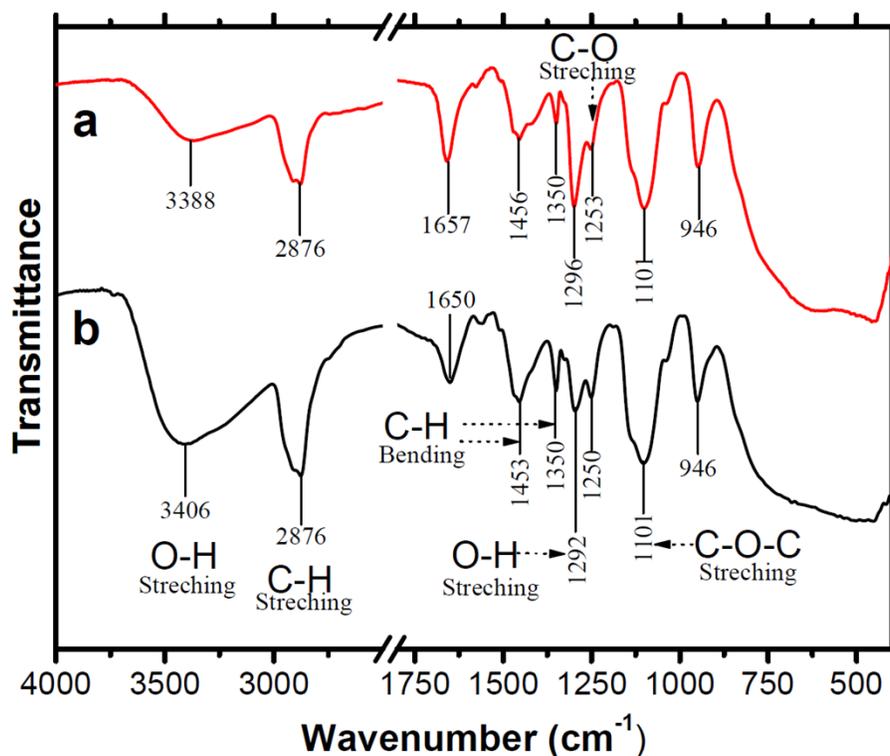


Fig.S8. The infrared transmittance spectra. (a)the mixture of TiO₂ and PEG-20000 without dry grinding treatment, (b) TiO₂ HMOS with dry grinding treatment.

The absorption peak at 3406 cm⁻¹ (attributed to the vibrations of -OH) in spectrum (a) is relatively broader and deeper than that in spectrum (b), indicating that there exists more hydrogen bonds in TiO₂ HMOS. Also, the OH stretching peak at 1292 cm⁻¹ is relatively lower in spectrum (b), which indicates that more hydroxyl groups at terminals of PEG molecules are bonded with the nanoparticles. However, the details are very complicated and needs the systematic studies.

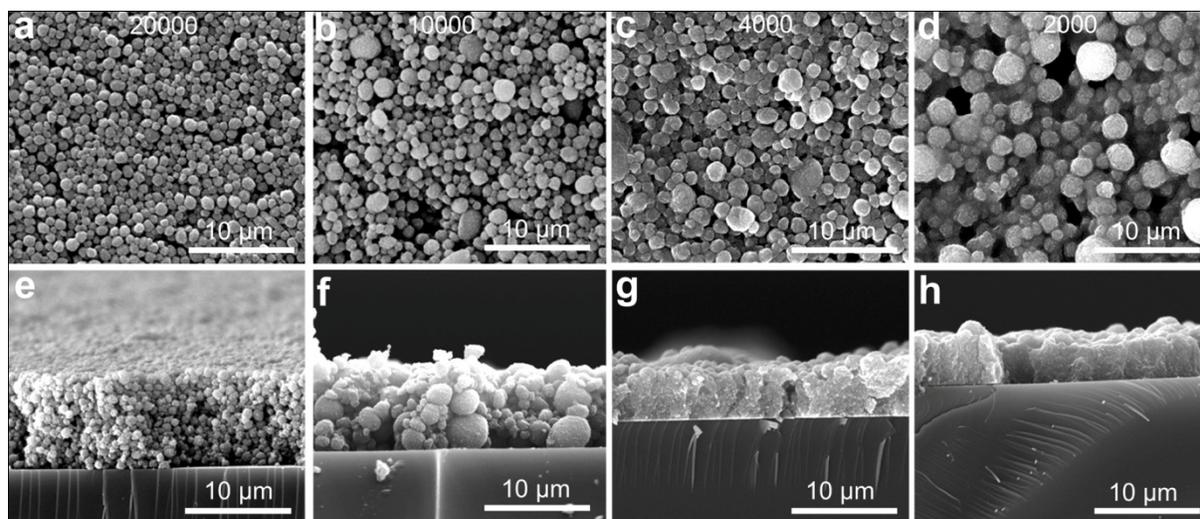


Fig.S9. Surface and cross-section SEM images of TiO_2 film with the fixed mass ratio of TiO_2 NPs to PEG is 3:1. The adopted PEG molecular weights are 20000 (a, e), 10000 (b, f), 4000 (c, g) and 2000(d, h).

With the molecular weight of PEG decreased from 20000, 10000, 4000, to 2000, the hierarchical spheres tend to be larger and the size dispersions increase greatly (Figure a-d). The cross-section observations (Figure e-h) show much distinct changes in morphology. For sample PEG-20000, the resulted TiO_2 film is composed of hierarchical spheres completely. With the PEG molecular weight decreases from 20000 to 10000, some larger spheres form framework and the smaller ones filled in their apertures. But the morphology of the particles is spherical and distinct boundaries can be seen among the particles. When the PEG molecular weights come to 4000 and 2000, hierarchical spheres can be only observed on the surface of the film.

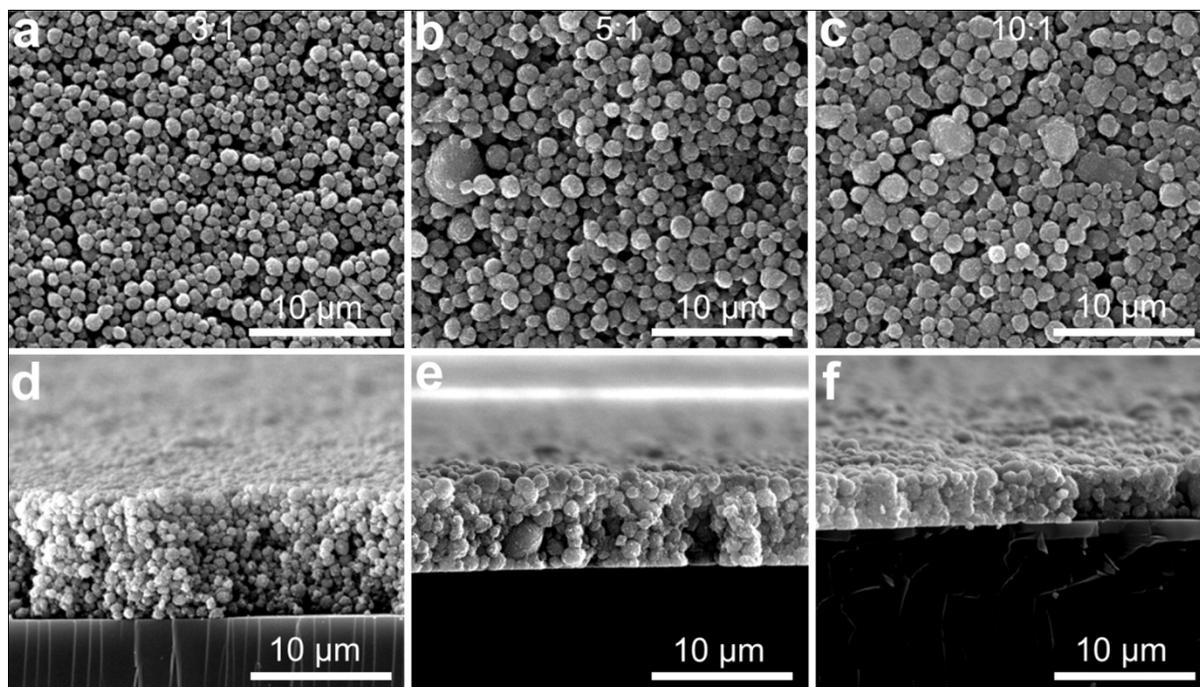


Fig.S10. Surface and cross-section SEM images of TiO_2 HMOS at fixed molecular weight 20000 with different mass ratio of TiO_2 to PEG is 3:1 (a, d), 5:1 (b, e) and 10:1 (c, f).

Different with the obvious configuration changes accompanied with the different PEG molecular weight, the mass ratio changes seem to have less important impact on the formation of hierarchical structures. All the films are totally composed of hierarchical spheres shown in the surface and cross-section SEM images. Only the size dispersion of the hierarchical spheres increases with the mass ratios increase from 3:1, 5:1, to 10:1.

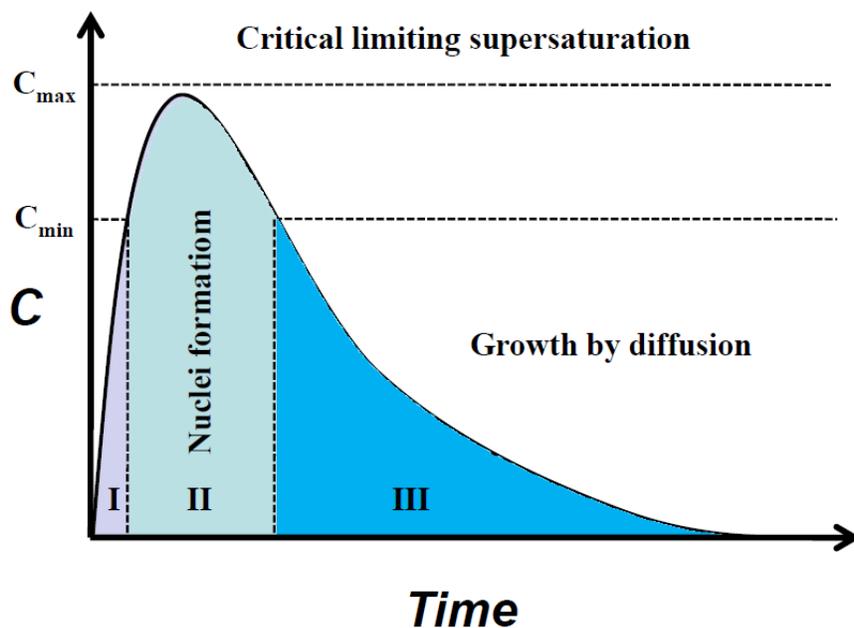


Fig.S11. Interpretation of the mono-dispersion of HMOS using the LaMer model. ^[32]In part I, the PEG linked nanoparticles are dispersed in solution and their number density increases rapidly. When the number density increases to the minimum supersaturating, many tiny nuclei form within relatively very short time (part II). Then, they slowly grow up by incorporation of the surrounding individual particles and form monodispersed HMOS (part III).