

## Supplementary information

# Assembly of composites into core-shell structure using ultrasonic spray drying and catalytic application in the thermal decomposition of ammonium perchlorate

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## Experimental

### Preparations of composite 3,5-dinitrobenzoates micro-nano spheres

Table 1 The spray drying conditions and the equipment information.

Operation	Solvent (Aceton)	Dimension of tower	
T Heating chamber (°C)	100	Total height (m)	2
Precursor volumetric flow rate (ml/min)	3	Heating chamber (m)	1
Carrier gas	N <sub>2</sub>	Diameter (m)	0.9
N <sub>2</sub> output press (MPa)	0.02	Oil heating layer (m)	0.16
Vacuum pump (MPa)	-0.05		
Residence time (s)	1~2		
Preheating gas (°C)	30		

## Results and discussion

### The formation mechanism of the core-shell structure

A hypothesis, which moisture (solvent) and dissolved components migrate in the droplet caused by concentration difference, is introduced to explain core-shell formation in the drying process.<sup>29,30</sup> It is assumed that (3,5-DNB)<sub>3</sub>Fe, (3,5-DNB)<sub>2</sub>Co and (3,5-DNB)<sub>2</sub>Cu have similar solubility and surface activity ranged smaller concentration, which means their precipitate rate and precipitate size only depend on concentration. As the droplet evaporated, a meniscus region is formed. In this area, solvent (acetone) can no longer remain liquid phase and begins vaporizing into steam, and (3,5-DNB)<sub>3</sub>Fe and (3,5-DNB)<sub>2</sub>Co(Cu) precipitate into small particles with micro or nano size. Solvent evaporation causes capillary flow in the region. Diffusion rate of precipitate particles relies more on particle size. Because small particles have lower buoyancy force but higher Brownian motion effect than large particles, they move faster to the meniscus area. The precipitated particles with different size self-assemble into core-shell spheres under interparticle capillary force causes. With the meniscus region shrinks rapidly, the precipitated particles in meniscus region are trapped and limited movement.<sup>30</sup> Finally, large particles compose the core structure, and very small particles tend to go to surface assembling a core-shell structure.<sup>31</sup> From the view of thermodynamics, one would expect large particles with lower surface energy to be on the surface, and the small particles with higher surface energy encapsulated in the core. However, the large particles are not able to diffuse from the core to the surface at the short evaporation time. Therefore, the core-shell formation (droplet-to-particle) of the samples is a kinetically driven process rather than a thermodynamically driven phenomenon.<sup>28, 31-33</sup>

In this hypothesis phenomena, the diffusivity rate is dominated by precipitated particles size resulting in the self-assembly, which can be described by the Stokes–Einstein equation,<sup>28, 32, 34</sup> shown in **Eq.(1)**.

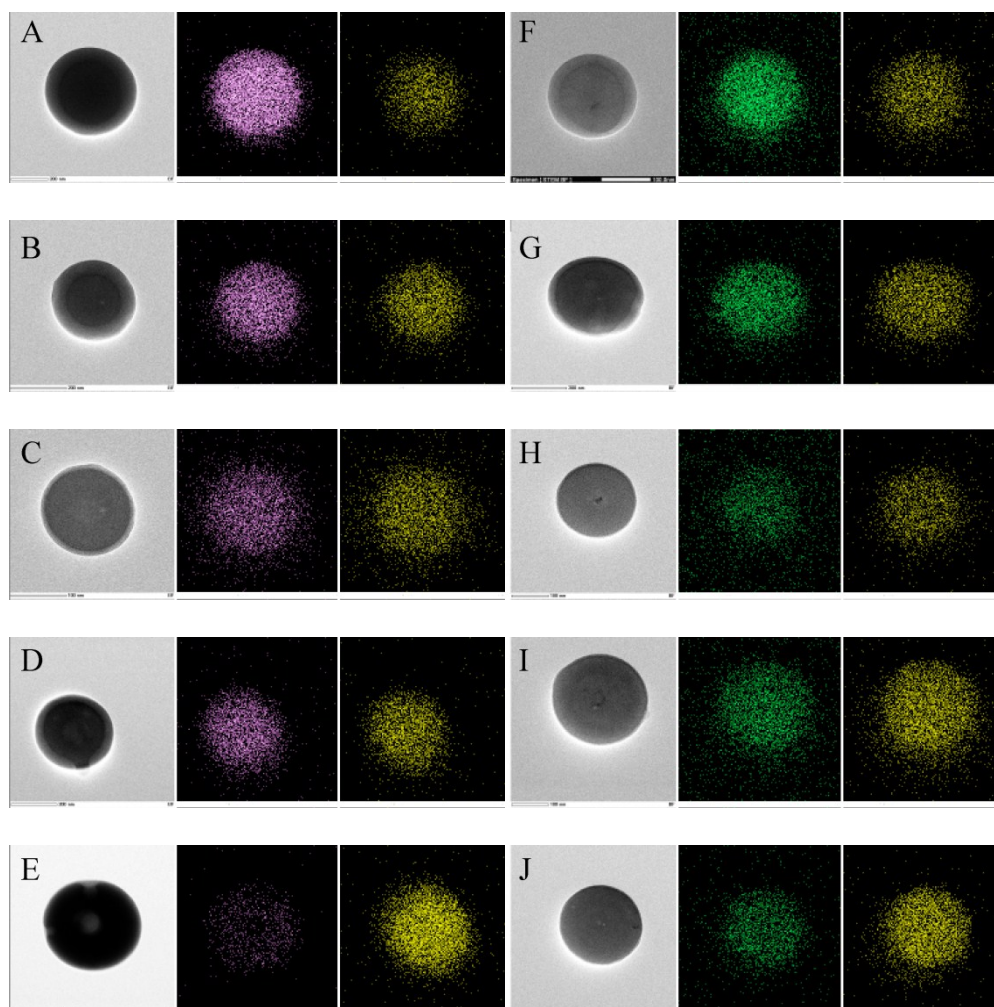
$$D = \frac{K_B \cdot T}{6\pi\mu R_0} \quad (\backslash * \text{MERGEFORMAT}(1))$$

Where  $D$  is the diffusion coefficient ( $\text{m}^2/\text{s}$ );  $K_B$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ );  $T$  is the temperature (K);  $\mu$  is the viscosity of the solvent ( $\text{kg m}^{-1} \text{ s}^{-1}$ );  $R_0$  is the component particle size (m). Because the diffusion coefficient is a representative of the component particle movement rate,<sup>33</sup> this equation also suggests that the particle movement has a negative correlation with component size, in which small particles much more easily diffuses to droplet surface.

### The catalysis effect of (3,5-DNB)FeCo and (3,5-DNB)FeCu on decomposition of AP

The (3,5-DNB)M•M's micro-nano spheres with different component ratios are prepared by ultrasonic spray drying technology, and the results are shown in Fig. 1. As shown in a series of TEM images, the (3,5-DNB)FeCo and (3,5-DNB)FeCu spheres in the range of 400~600 nm are smooth and preserved core-shell shape. Especially, the core-shell structure became unapparent when Fe/Cu ratio increased gradually (Fig. 1, H~J).

The compositions of the samples are characterized further by energy dispersive spectroscopy of TEM (TEM-EDS) (Fig. 1). Elemental mapping analysis of TEM-EDS exhibit that metal elements (Fe, Cu, Co) uniformly distributed on the whole sphere surface (Fig. 1, EDS). Co element intensity (pink color) mixed in Fe element (yellow color) is changed with component ratios (Fig. 1, A-E, EDS). Cu element (green color) mixed with Fe element (yellow color) is varied to different color intensities (Fig. 1, F-J, EDS). Therefore, only making some tiny changes of component ratio of CPS can achieve different catalytic effects. The catalysis effects of (3,5-DNB)M•M's micro-nano spheres on thermal decomposition of AP further demonstrates this concerted catalysis. The uniform mixture of the components {(3,5-DNB)<sub>3</sub>Fe, (3,5-DNB)<sub>2</sub>Cu, (3,5-DNB)<sub>2</sub>Co} would promote concerted catalysis of (3,5-DNB)M•M's micro-nano particles.



**Fig. 1** TEM and elemental mapping images of the spray-dried particles: (A)-(E) (3,5-DNB)FeCo with (3,5-DNB)Fe/(3,5-DNB)Co ratios of 2:8, 4:6, 5:5, 6:4, 8:2; (F)-(G) (3,5-DNB)FeCu with (3,5-DNB)Fe/(3,5-DNB)Cu ratios of 2:8, 4:6, 5:5, 6:4, 8:2.