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Carboxyl-modified colloidal crystal templates for the synthesis of three-dimensionally ordered macroporous $SmMn_2O_5$ mullite and its application in NO_x-assisted soot combustion

Yongjie Chen‡[a], Chun Du‡[a], Yun Lang[a], Liwei Jia[b], Rong Chen[c] and Bin Shan*[a]

[a] State Key Laboratory of Material Processing and Die and Mould Technology and School of Materials Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China.

[b] Engineering Center, Wuxi Weifu Environmental Catalysts CO, LTD. NO. 9, Lingjiang Road, Wuxi, Jiangsu 214048, China.

[c] State Key Laboratory of Digital Manufacturing Equipment and Technology and School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China.

‡ These authors contributed equally to this work.

* Corresponding author: Bin Shan

Postal address:

State Key Laboratory of Material Processing and Die and Mould Technology and School of Materials Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People's Republic of China.

E-mail address: bshan@mail.hust.edu.cn.

S1. The preparation of SMO by Hydrothermal method

The catalyst of SMO with nanoparticle structure was synthesized by traditional hydrothermal (HT) method. Briefly, 5 mmol $Sm(NO_3)_3·6H_2O$ was dissolved in 40 ml deionized water and then 7 mmol $Mn(C_2H_3O_2)_2·4H_2O$ and 3 mmol $KMnO_4$ were added into the solution at the same time and constantly stirred for 30 min. Afterwards, 20 ml NaOH (4M) was slowly added into the solution and vigorously stirred for another 30 min. Then the mixed solution was transferred into a 100 ml stainless steel Teflon-lined autoclave with a filling capacity of 60%. Afterwards, the autoclave was put in an oven at a temperature of 250 °C for 24 h. After the system was cooled down to room temperature, the final products were washed with deionized water three times, and dried at 100 °C for 12 h. Finally, the SMO-HT was obtained by grinding.

S2. The preparation of polymer templates

The carboxyl-modified poly(methyl methacrylate) spheres with different contents of carboxyl groups were synthesized with emulsifier-free emulsion polymerization technique. The monomer precursor containing methyl methacrylate (MMA) as the main monomer and acrylic acid (AA) as the functional monomer was refined through reduced pressure distillation. A three-necked, 2000 ml round-bottomed flask was filled with the mixed solution of acetone (100 ml), water (400 ml) and the refined monomers (150 ml, The ratios of MMA: AA show in table S1). When the mixed solution in the flask was heated to 70 ^{o}C in water bath, 0.5 g of potassium persulfate (KPS, water-phase initiator), 0.9 g of azodiisobutyronitrile (AIBN, oil-phase initiator) and 300 ml water which had been preheated to 70 ^{o}C were added. A monodisperse CPMMA microsphere were obtained after two hour reaction under constant stirring (300 r/min) and N_2 protection. Then, the microspheres were hexagonal closest packed into colloidal crystals by centrifugation (4000 r/min, 10h) followed by drying at 60°C over night. These dried colloidal crystals were used as template in the synthesis of 3DOM catalysts.

Table S1 The monomer recipe used to synthesize reactants of different templates.

Sample	MMA	AA
PMMA	150.00ml	0
CPMMA-2.5%	146.25ml	3.75ml
CPMMA-5%	142.50ml	7.50ml
CPMMA-7.5%	138.75ml	11.25ml
CPMMA-10%	135.00ml	15.00ml

Fig. S1 shows the SEM images of the polymer template with different monomers. The result indicates that the microspheres used as templates are uniform in size. Besides, microspheres in Fig. S1a)-e) are slightly different in size. What's more, the regularity and arrangement of microsphere are good when the addition ratio of functional monomers is less than 5%. When the addition of functional monomers is 7.5%, the arrangement becomes a little bit worse, and it becomes even worse when the addition of functional monomers is around 10%. The result of Fig. S1e shows obvious adhesion between each microsphere. This result can be attribute to the fact that MMA is insoluble in water as an oily monomer, and monodisperse microspheres can be obtained by emulsifier-free emulsion polymerization technique. However, AA can be soluble in water, so the monodisperse microspheres of polyacrylic acid cannot be obtained by emulsifier-free emulsion polymerization technique when water is used as a dispersive medium. This allows the AA to be uniformly polymerized on the PMMA microspheres when the content of AA is less. However, when the content of AA is increasing, self-polymerization occurred in AA and adheres the CPMMA microspheres together.

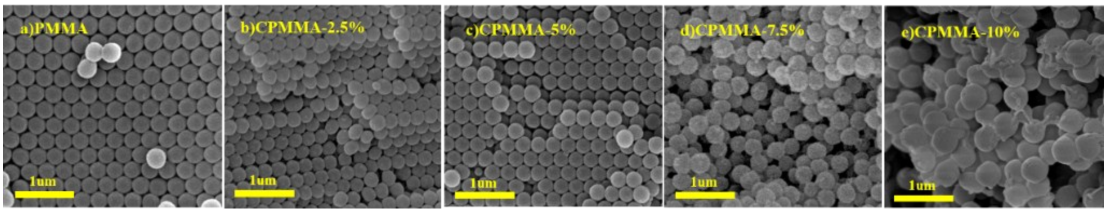

Fig. S1 The SEM images of polymer template; a) PMMA, b) CPPMA-2.5%, c) CPPMA-5%, d) CPPMA-7.5%, e) CPPMA-10%.

Fig. S2 shows the TG result of different polymer template under Argon atmosphere. It could be concluded that the decomposition temperature of polymer template increased with the content of additional AA augmenting. This can be attributed to the covalent bond formed by the addition of carboxyl groups into the polymer, which is conducive to the improvement of thermal stability of the polymer and the decomposition temperature of the polymer template.

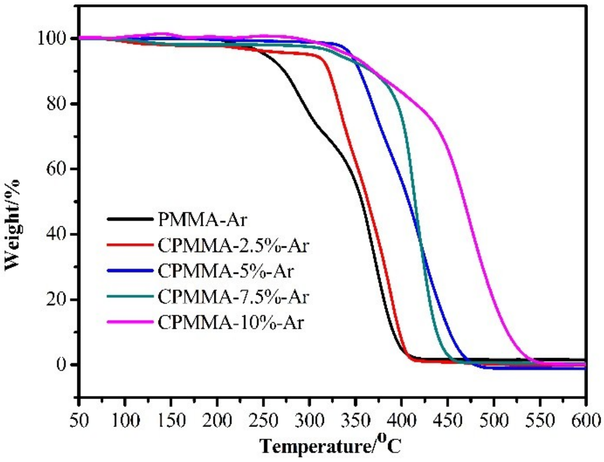

Fig. S2 The TG result of different polymer template.

S3. Reproducibility and stability of 3DOM SMO catalysts

We take the 3DOM SMO as representative specimen to testify the catalytic activity reproducibility. The testing results are included in Fig. S3a. Each sample was tested for three times, and we can see that the soot conversion curve is reproducible for fresh 3DOM SMO sample. Moreover, the stability of 3DOM SMO sample was also evaluated in Fig. S3b. After each test, the catalyst was taken to remix with soot and used to test again for another cycle. The results showed that though the activity slightly decreased after first cycle, especially at high temperature range. Generally speaking, it still maintained high catalytic performance for soot combustion under NO+O_2 atmosphere.

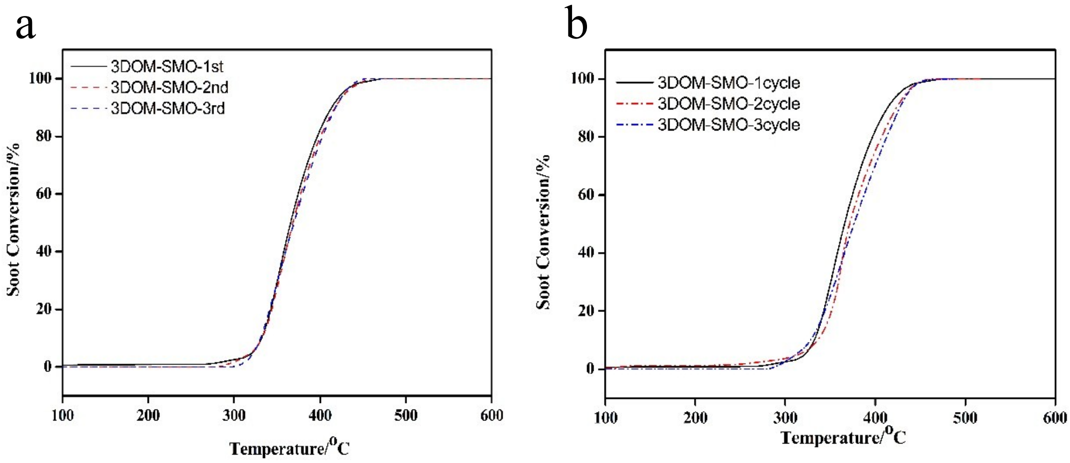

Fig. S3 a: Reproducibility of 3DOM SMO sample; b: Stability of 3DOM SMO sample. 400 ppm NO, 10% O_2 and N_2 as balance.

S4. The structures of SMO catalysts with different synthetic methods

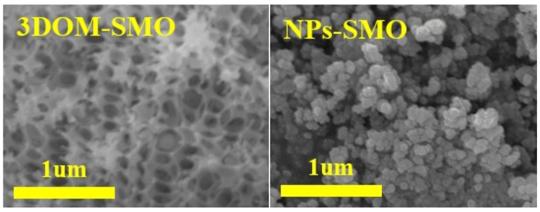

Fig. S4 The SEM results of SMO with different structure: a) 3DOM SMO synthetized by CCTM with CPMMA-5% as template; b) NPs-SMO synthetized by HT.

S5. The XRD result of SMO precursors after calcination at different temperatures

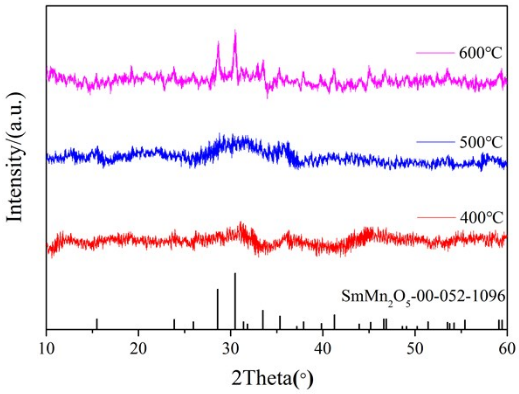

Fig. S5 The XRD pattern of calcined SMO precursors at different temperatures

Fig. S5 shows the XRD results of calcined SMO precursors, which were calcined at different temperatures for 4 hours. The XRD pattern indicates that there is not obvious characteristic peak for sample calcined at 400℃, and an amorphous peak appears in 25°~35° for sample calcined at 500℃, while the sample calcined at 600℃ shows characteristic peaks of SMO. The result can be attributed to the fact that the precursor did not form SMO when calcined at 400℃, while SMO has been forming at the sample calcined at 500℃, which means the formation temperature of SMO was within this temperature range.