

Supporting Information for

Facile and template-free synthesis of robust, highly active and easily recyclable submicrometer-sized hierarchical TS-1 aggregates composed of ultra-small nanocrystalline (< 50 nm)

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Experimental Section

Materials

All chemicals were obtained from commercial suppliers and used without further purification: tetrapropylammonium hydroxide (TPAOH, Yixing Dahua Chemical, 25% in water), tetraethyl orthosilicate (TEOS, Shanghai Lingfeng Chemical Reagent, AR), tetrabutyl titanate (TBOT, Sinopharm Chemical Reagent, AR), isopropanol (Shanghai Lingfeng Chemical Reagent, AR), acetonitrile (Genereal-Reagent, AR), thiophene (Th, J&K Chemical, AR), benzothiophene (BT, J&K Chemical, AR), dibenzothiophene (DBT, J&K Chemical, AR), 4-methyldibenzothiophene (4-MDBT, J&K Chemical, AR), 4,6-dimethyldibenzothiophene (4,6-DMDBT, J&K Chemical, AR), hydrogen peroxide aqueous solution (H₂O₂, SCR, AR).

Synthesis of submicrometer-sized hierarchical TS-1 aggregates

In a typical run for preparation of *aggTS-1*, 10.98 g of TPAOH solution was added dropwise into a mixture of 10.42 g TEOS and 18.0 g of deionized water and continuously stirred for 4 h at 40 °C (Solution I). Meanwhile, 0.43 g TBOT was dissolved in 6.0 g of isopropanol (*i*-PrOH) in an ice-water bath of 0 °C and kept stirring for 4 h (Solution II). Next, Solution I was cooled down to 4 °C in an ice-water bath firstly and then Solution II was added dropwise into it under stirring. The molar composition of sol precursor was SiO₂: 0.025 TiO₂: 0.27 TPAOH: 29.2 H₂O: 2 *i*-PrOH. The resulting mixture was kept stirring at 4 °C for another 4 h and concentrated at 40 °C for 24 h. The obtained gel was then transferred in a freeze-drying machine and further dehydrated at -50 °C for 10 h to remove the residual moisture and get the fully dried gel precursors. To carry out the SAC treatment, 3.6 g of freeze-dried gel precursors were put into a smaller Teflon container which was then sealed in a 100 ml Teflon-lined stainless steel autoclave. 0.7 g of deionized water was added into the bottom of Teflon liner of the autoclave, avoiding the direct contact with the gel precursors. The SAC process was conducted at 180 °C for 10 h. After that, it was cooled to room temperature. The powder product was filtered, washed repeatedly with deionized water and dried at 80 °C overnight. Finally, it was calcined in a muffle furnace at 550 °C for 6 h. The resultant materials were denoted as *aggTS-1*(*x*), in which *x* refer to the TPAOH/SiO₂ molar ratio of the sol compositions, e.g. *aggTS-1*(0.27). Correspondingly, the control samples were named as TS-1(*x*), e.g. TS-1(0.27), which were synthesized according to the similar procedure but without the freeze-drying step before

SAC treatment.

Material characterization

SEM images were obtained on a field-emission scanning electron microscopy of Hitachi SU8220. HRTEM images and selected area electron diffraction patterns were recorded on a JEM-2100F electron microscope. DLS measurements were recorded on a Malvern Panalytical-Zetasizer Nano-ZS90. XRD patterns were recorded on a Rigaku D/Max 2200PC powder X-ray diffractometer with Cu K α radiation (40 kV, 40 mA) in the 2 θ range from 5° to 50°. The relative crystallinity of synthesized materials was calculated from the peak area of five strong peaks in the 2 θ range of 22-25°. UV-Vis diffuse reflectance spectra were recorded in the range of 190 – 800 nm on a Shimadzu UV-310PC spectrometer with an integrating sphere accessory and BaSO₄ as the reference. Nitrogen sorption isotherms were obtained on a Micromeritics TriStar 3020 porosimeter at 77 K. All samples were degassed at 150 °C for 12 h under flowing nitrogen before the measurement. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method basing on the adsorption branches of the isotherms. The micropore volumes and external surface areas were derived from the t-plot method calculation. Elemental content analysis was recorded on an inductively coupled plasma optical emission spectrometer (ICP-OES) of Agilent 725. XPS results were obtained on an ESCALab250.

Catalytic reaction

The comprehensive oxidative desulfurization behavior was evaluated using thiophene (Th), benzothiophene (BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) as model sulfur compounds. Typically, 10 mL of model fuel oil (500 ppm sulphur content in *n*-octane), 10 mL of acetonitrile or water as solvent, 63.75 μ L of H₂O₂ (30 wt%), 50 mg catalyst were stirred at 333 K for 6 h. During this period of time, the products were sampled per hour, diluted in 1 mL ethanol and analyzed on Shimadzu GC-2010 Plus equipped with an autosampler, two 30 m Rxi-5Sil MS capillary columns, a flame ionization detector and a mass detector. For the recycling-regeneration of catalysts, the spent catalysts in the DBT reaction media were filtered and washed several times with acetonitrile. After dried at 60 °C for 12 h, the catalysts were transferred to a muffle furnace and calcined at 550 °C for 6 h. The regenerated catalyst is used for the new DBT catalytic oxidation reaction, and the recycling-regeneration test

was conducted 5 times.

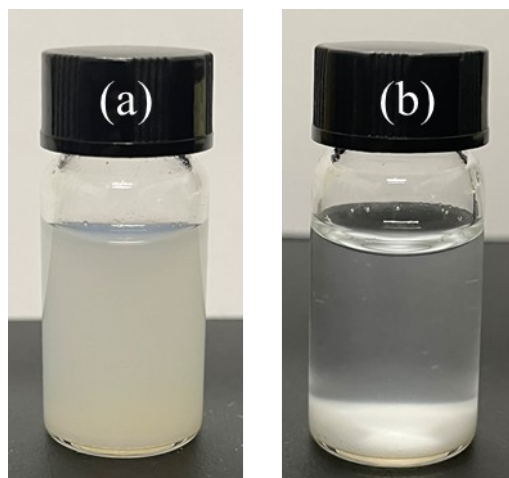
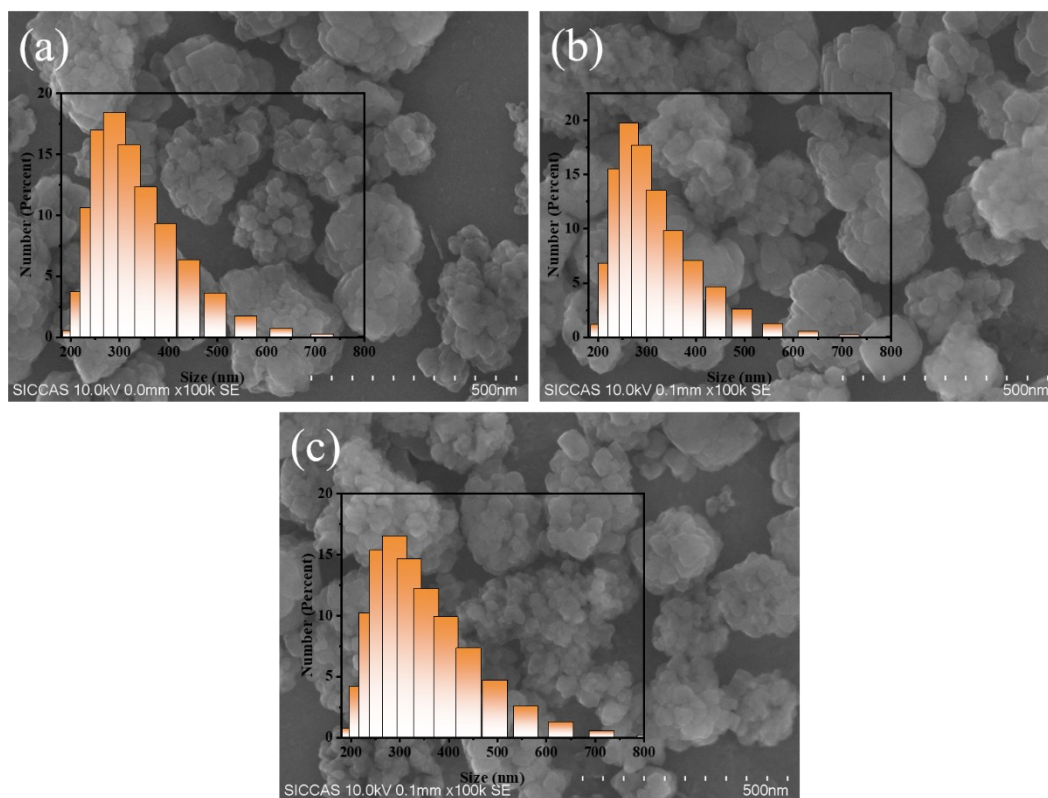


Figure S1. Digital photographs of synthesized (a) TS-1(0.27), (b) *agg*TS-1(0.27) dispersed in water.



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Figure S2. SEM images and DLS particle size distribution of sample *aggTS-1(0.27)* experienced (a) 1 h, (b) 3 h, and (c) 6 h ultrasonic treatment.

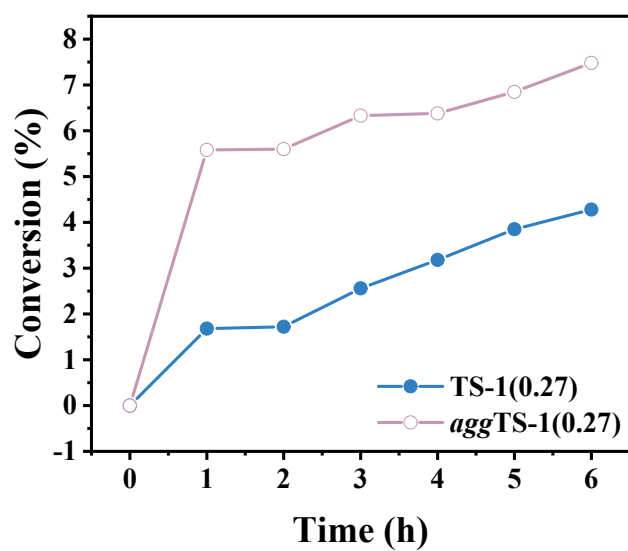
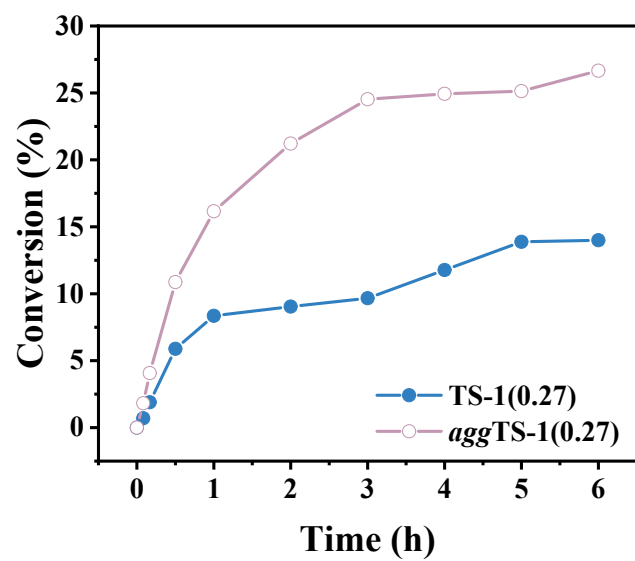


Figure S3. Conversion of 4-MDBT and 4,6-DMDBT as a function of reaction time over synthesized catalysts.

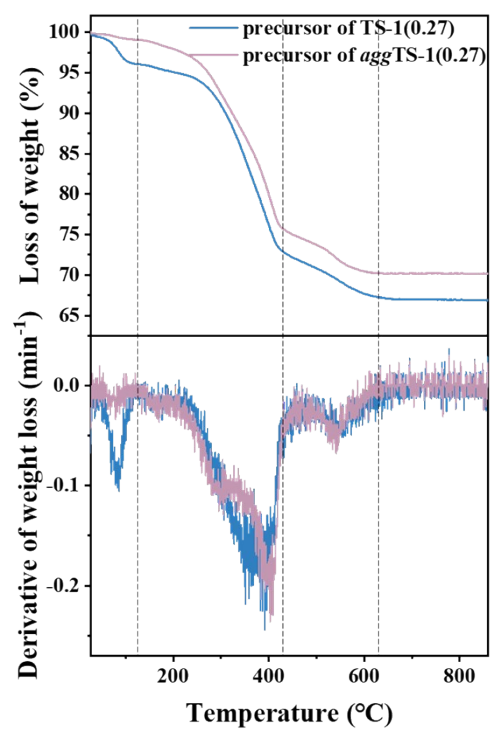


Figure S4. Thermogravimetric analysis curve of precursor of TS-1(0.27) and *agg*TS-1(0.27).

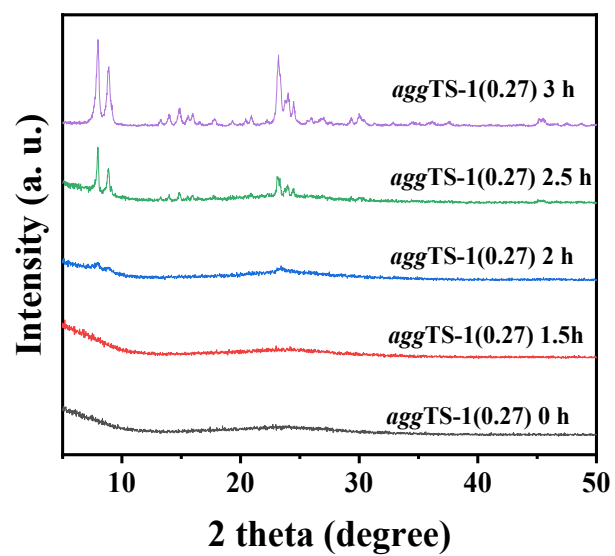


Figure S5 Powder XRD patterns of synthesized *aggTS-1(0.27)* with varied SAC treating times.

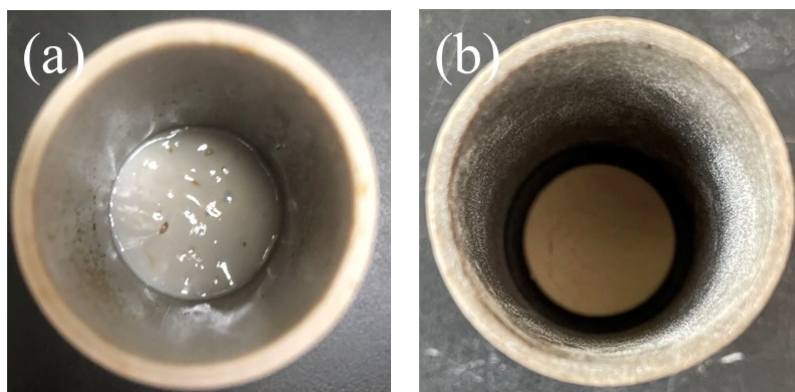


Figure S6 Digital photographs of synthesized (a) TS-1(0.27) and (b) *agg*TS-1(0.27) by SAC procedure.

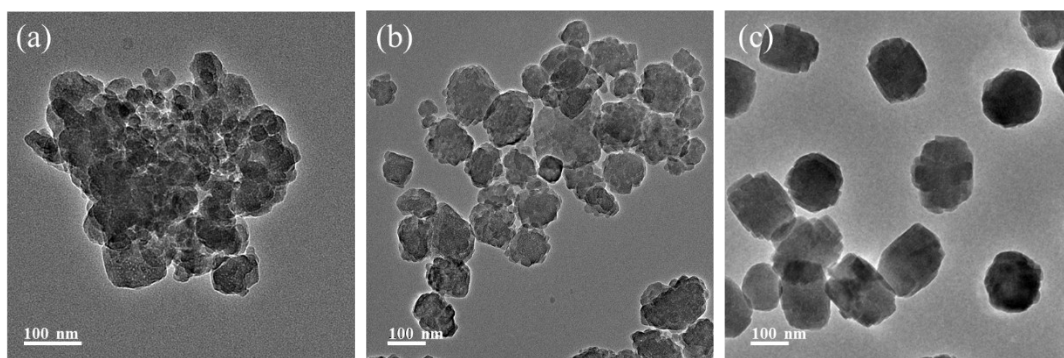


Figure S7 SEM images of synthesized catalysts with different water content (a) 0 wt%, (b) 3 wt%, (c) 5 wt%.

Table S1 Catalytic performance comparison between the *aggTS-1* and the literature-reported TS-1 zeolites

Sample	S-substrate	Time (h)	Catal. amount (mg)	Solvent	Temp. (K)	H ₂ O ₂ /S	Conv. (%)	Ref.
HTS-1(0.35)	BT	6	100	MeOH	333	-	100	1
TS-1 H2	BT	6	100	MeOH	333	4	100	2
	Th	6	100	Water	333	4	90	
HTS-1	Th	4	100	Water	333	4	100	3
	BT	4	100	MeOH	333	4	100	
	DBT	4	100	MeOH	333	4	100	
TS-1 meso	BT	3	50	--	323	10	87	4
TS-1 nanoplates	DBT	2	100	None	333	2	12	5
<i>aggTS-1</i>(0.27)	Th	2	50	Water	333	4	100	This work
	BT	6	50	ACN	333	4	89.9 ^a	
	DBT	6	50	ACN	333	4	91.6 ^a	

^a The extraction contribution of solvent is included, i.e. 66.0% and 60.0% extraction efficiency for BT and DBT, respectively.

Reference

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