Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Experimental Section

Chemical reagents include tetrabutyl orthotitanate (Sinopharm Chemical Reagent Co., Ltd., Shanghai Hushi), tetraethyl orthosilicate (Sinopharm Chemical Reagent Co., Ltd., Shanghai Hushi), HCl aqueous solution (Fuyu Fine Chemical Co., Ltd., Tianjin), tetrapropylammonium hydroxide (Cairui Chemical Technology Co., Ltd.), sodium aluminate (Fuyu Fine Chemical Co., Ltd., Tianjin) alkaline silica sol (Chengyu Chemical Co., Ltd., Qingdao), tetraethyl ammonium hydroxide (Guangfu Fine Chemical Co., Ltd.), zinc nitrate hexahydrate (Damao Chemical Co., Ltd., Tianjin) and ferric nitrate (Bodi Chemical Co., Ltd., Tianjin).

Synthesis of the samples

TS-1. Tetrabutyl orthotitanate (TBOT), HCl aqueous solution, tetraethyl orthosilicate (TEOS) and H_2O were mixed for 20 minutes at room temperature. The molar composition of the solution was $1.0SiO_2$: $0.0167TiO_2$: $20H_2O$: 0.135HCl. The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to form SiO_2-TiO_2 amorphous powder by 2-4 s of heating at 200℃. (Figure S1) The SiO_2-TiO_2 amorphous powder has been calcined at 500℃ for 5h. Then 1g SiO_2-TiO_2 amorphous powder and 0.674g or 0.540g 25% tetrapropylammonium hydroxide (TPAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 130 ℃ for 48 h under autogenous pressure. The solid were obtained by washing with distilled water and centrifuging several times. The product was dried at 100℃ and calcined at 540℃ for 6 h to remove the template.

Silicalite-1. HCl aqueous solution, tetraethyl orthosilicate (TEOS) and H_2O were mixed for 6h at room temperature. The molar composition of the solution was $1.0SiO_2$: $20H_2O$: 0.135HCl. The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to SiO_2 amorphous powder by 2-4 s of heating at 200℃. (Figure S1) The SiO_2 amorphous powder has been dried to remove H_2O at 500℃ for 5h. Then 1g SiO_2 amorphous powder and 0.674g tetrapropylammonium hydroxide (TPAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 130 ℃ for 48 h under autogenous pressure. The solid were obtained by washing with distilled water and centrifuging several times. The product was dried at 100℃ and calcined at 540℃ for 6 h to remove the template.

Beta. Sodium aluminate ($NaAlO_2$) and H_2O were mixed to form clear solution. Then alkaline silica sol was added and mixed for 2h at room temperature. The molar composition of the solution was $1.0SiO_2$: $0.02Al_2O_3$: $28H_2O$. The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to amorphous powder by 2-4 s of heating at 110℃. (Figure S1) Then 1g amorphous powder and 1.4125g 25% tetraethyl ammonium hydroxide (TEAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 145 ℃ for 96 h under autogenous pressure. The solid was obtained by washing with distilled water and centrifuging several times. The product was dried at 100℃ and calcined at

540℃ for 6 h to remove the template.

ZSM-5. Sodium aluminate ($NaAlO_2$) and H_2O were mixed to form clear solution. Then alkaline silica sol was added and mixed for 30 minutes at room temperature. The molar composition of the solution was $1.0SiO_2$: $0.02Al_2O_3$: $25H_2O$. The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to amorphous powder by 2-4 s of heating at 200℃. (Figure S1) Then 1g amorphous powder and 0.7g 25% tetrapropylammonium hydroxide (TPAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 130 ℃ for 48 h under autogenous pressure. The solid were obtained by washing with distilled water and centrifuging several times. The products was dried at 100℃ and calcined at 540℃ for 6 h to remove the template.

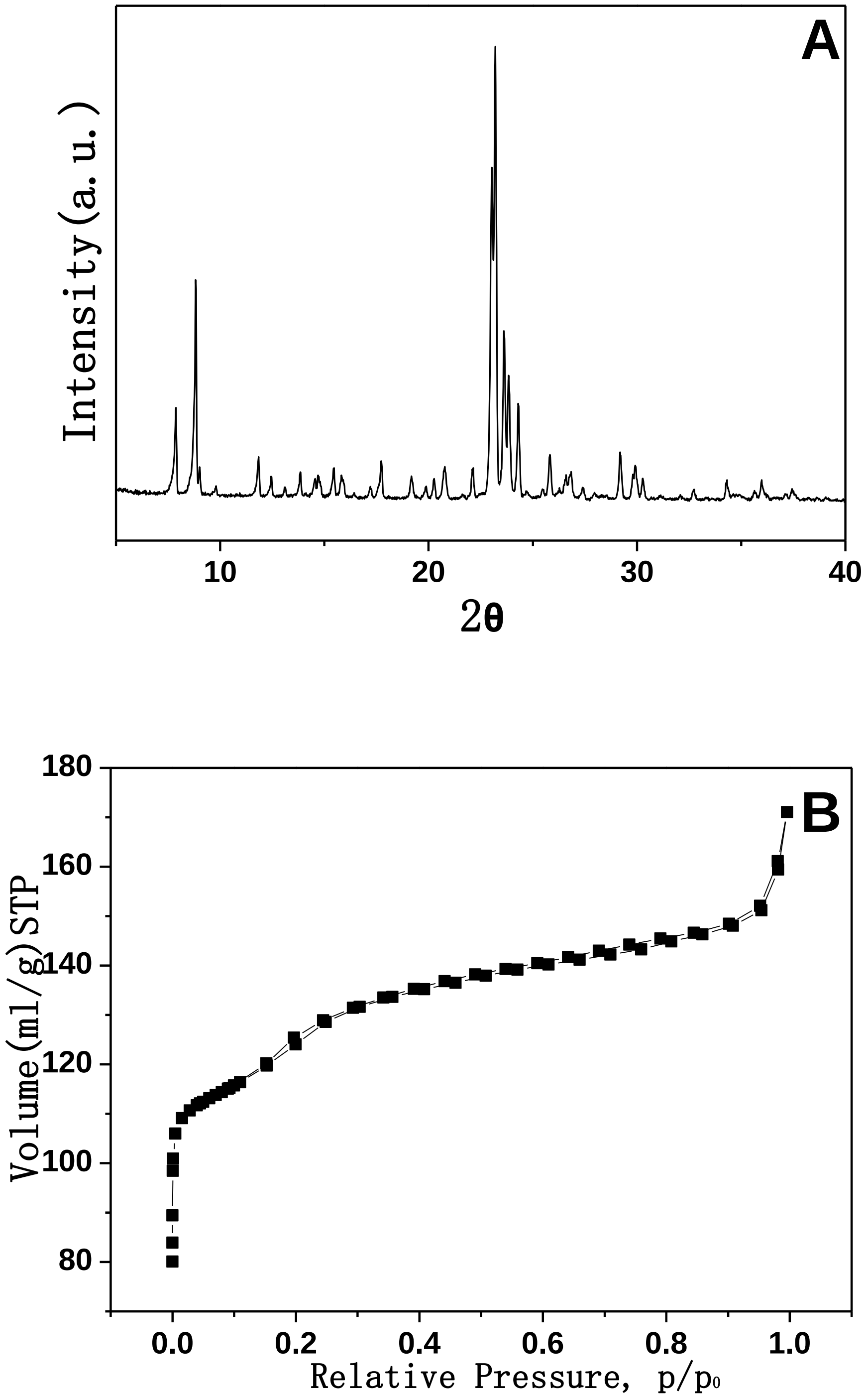
5%-Zn-ZSM-5. 0.8657g zinc nitrate hexahydrate, 0.5g HCl aqueous solution, 26.8g H_2O and 15.63g tetraethyl orthosilicate (TEOS) were mixed for 1h at 30℃.The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to SiO_2-ZnO amorphous powder by 2-4 s of heating at 110℃. Then 1g SiO_2-ZnO amorphous powder and 1.34g 25% tetrapropylammonium hydroxide (TPAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 170 ℃ for 72h under autogenous pressure. The solid was obtained by washing with distilled water and centrifuging several times. The products was dried at 110℃ and calcined at 540℃ for 6h to remove the template.

6.2%-Fe-ZSM-5. 0.769g ferric nitrate nonahydrate, 27.0g H_2O and 15.63g tetraethyl orthosilicate (TEOS) were mixed for 6 h at 30℃. The aerosol particles were generated by an aerosol apparatus (Model 9306 TSI) with an air pressure of 10Psi and dried to amorphous powder by 2-4 s of heating at 200℃. Then 1g amorphous powder and 0.674g 25% tetrapropylammonium hydroxide (TPAOH) aqueous solution were loaded into Teflon-lined autoclave and crystallized at 130 ℃ for 48h under autogenous pressure. The solid was obtained by washing with distilled water and centrifuging several times. The product was dried at 100℃ and calcined at 540℃ for 6h to remove the template.

Epoxidation of Propylene. The reaction was carried out in a stainless-steel reactor. 0.2 g catalyst, 34 mL of methanol, and hydrogen peroxide (30wt %) were mixed. The concentration of hydrogen peroxide was 1 mol/L. Propylene was charged to the reactor to reach pressure of 0.4 MPa. The solution was stirred at 60℃ for 1 h. The products were analyzed on a 9790Fuli gas chromatograph with a hydrogen flame ionization detector (FID) and a PEG-20 M capillary column (50 m*0.32 mm*0.5 μm). The residual H_2O_2 was checked by a standard iodometric titration. The H_2O_2 conversion ($X_{H_2O_2}$), selectivity of propylene oxide (S_{PO}), and utilization of H_2O_2 ($U_{H_2O_2}$) were defined as follows: $X_{H_2O_2}=(n_{0(H_2O_2)}-n_{(H_2O_2)})/n_{0(H_2O_2)}$

$S_{PO}=n_{PO}/(n_{PO}+n_{MME}+n_{PG})$ $U_{H_2O_2} = (n_{PO}+n_{MME}+n_{PG}) / n_{0(H_2O_2)} \bullet X_{H_2O_2}$

The $n_{0(H_2O_2)}$ and $n_{(H_2O_2)}$ stand for the initial and final mole content of H_2O_2, respectively. The n_{PO}, n_{MME}, and n_{PG} stand the number of moles of PO, MME, and PG, respectively.


A
Intensity(a.u.)
10
20
30
40
2θ
B
Volume(ml/g) STP
180
160
140
120
100
80
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure, p/p0

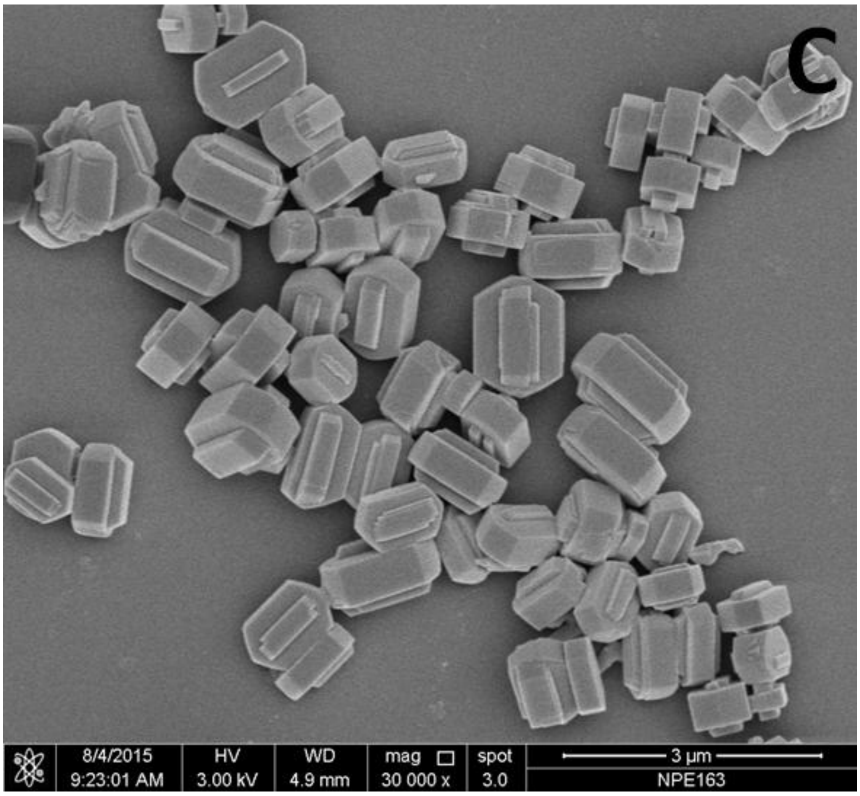
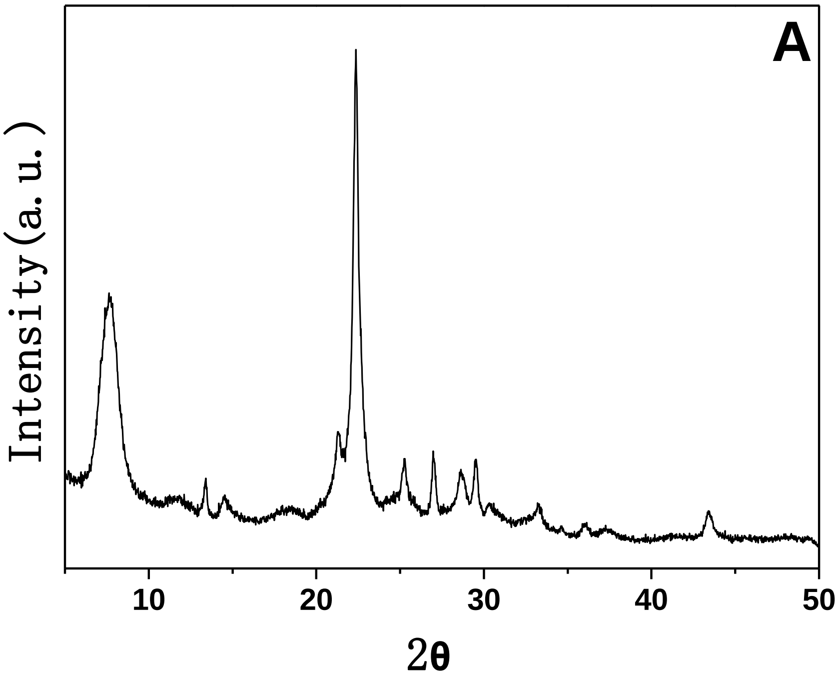


Figure S1 Analytical data for silicalite-1. A) XRD pattern, B) N_2 sorption isotherm, C) SEM image.



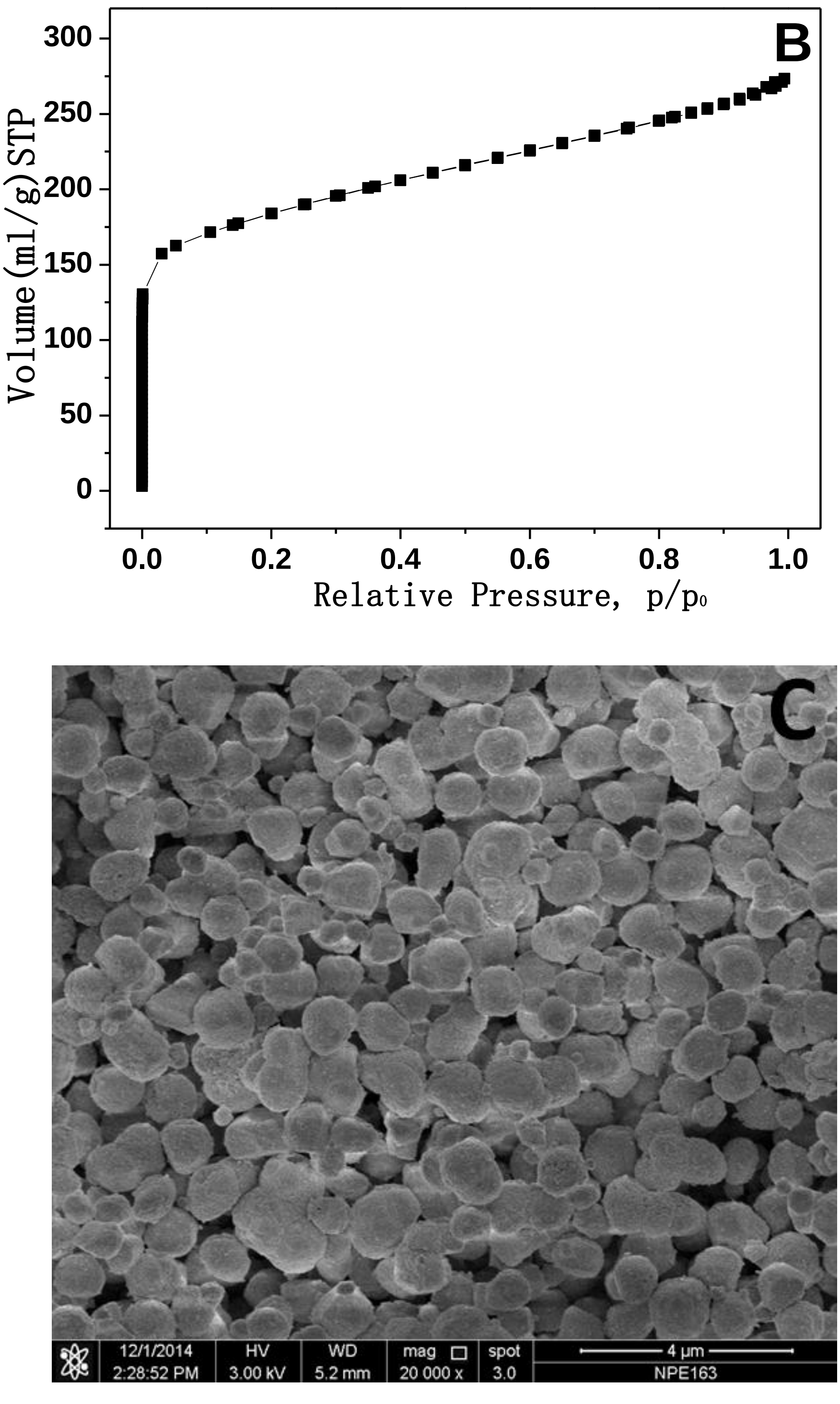
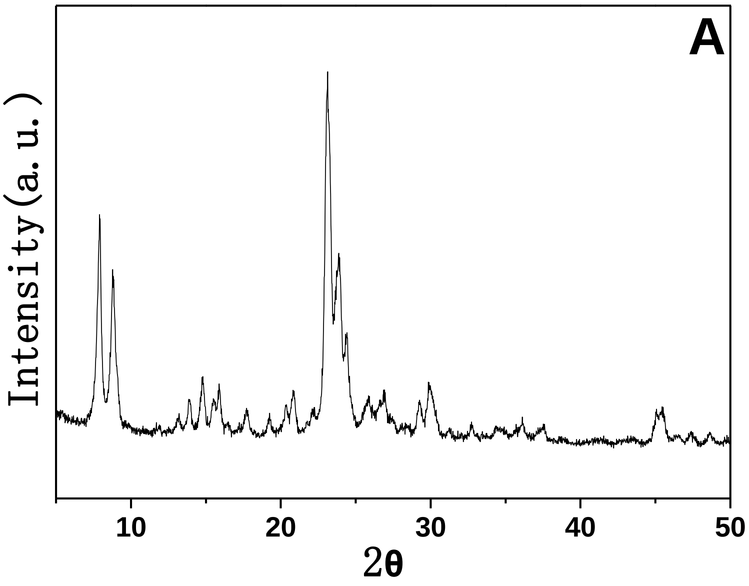
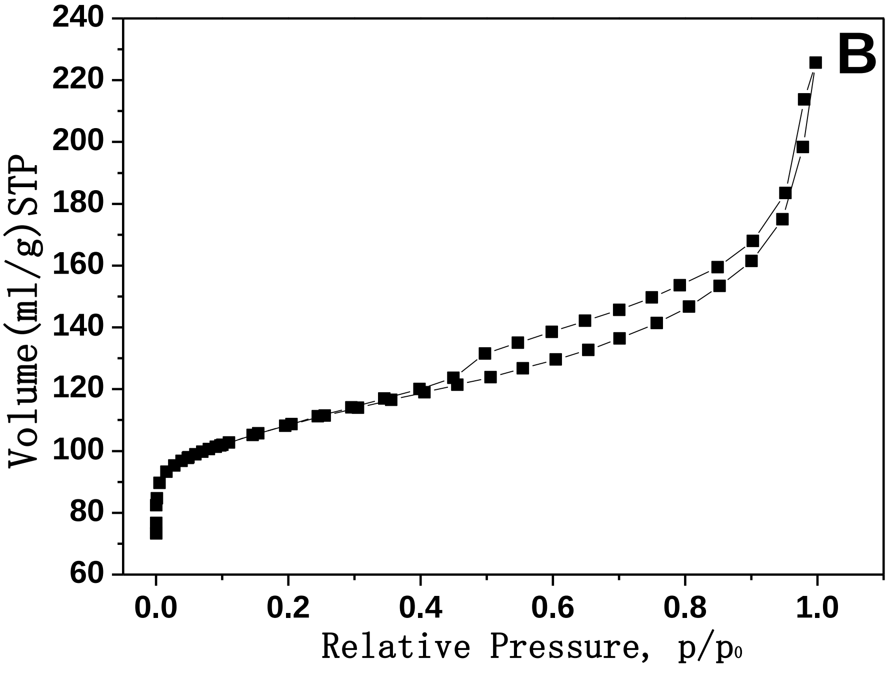


Figure S2 Analytical data for Beta. A) XRD pattern, B) N_2 sorption isotherm, C) SEM image.


A
Intensity(a.u.)
10
20
30
40
50
2θ


B
Volume(ml/g)STP
60
80
100
120
140
160
180
200
220
240
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure, p/p0

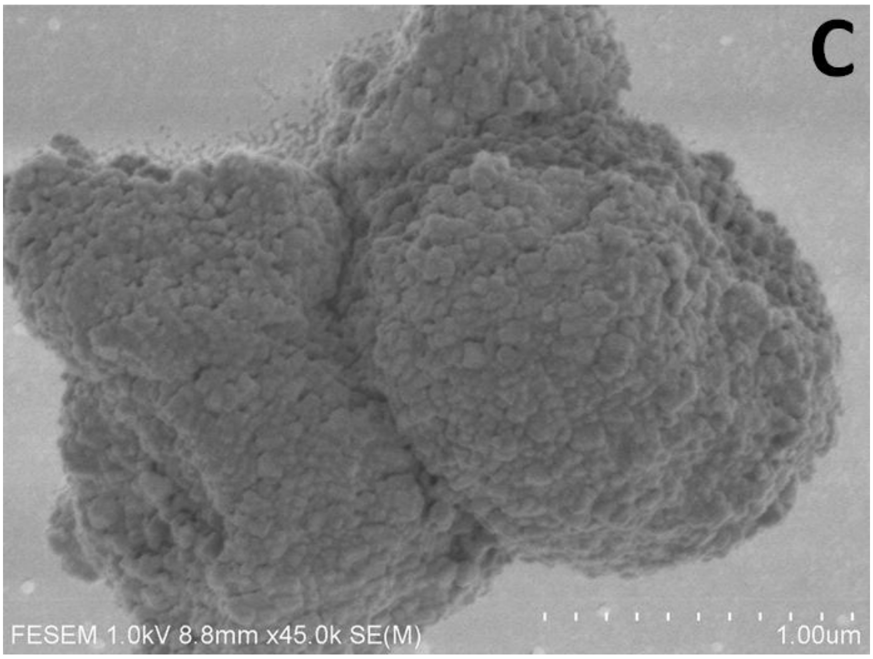
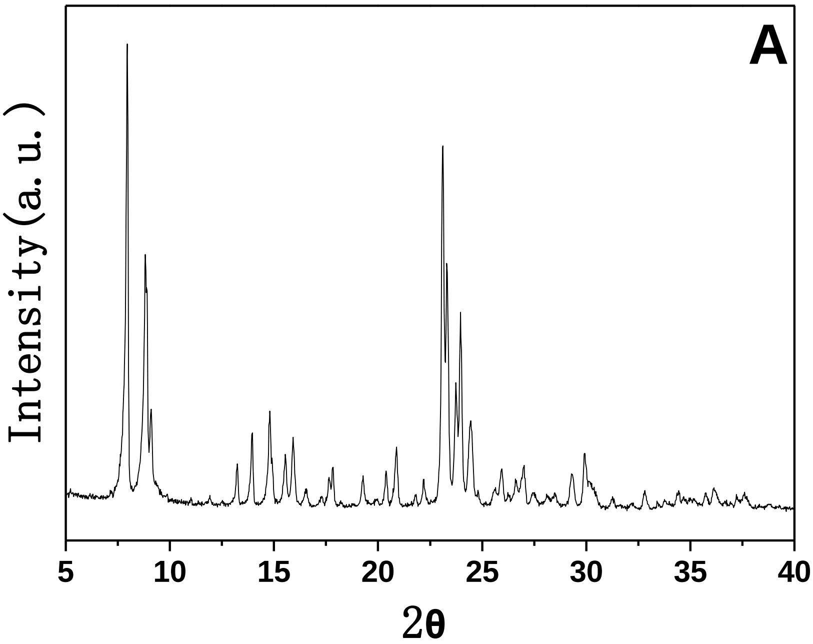
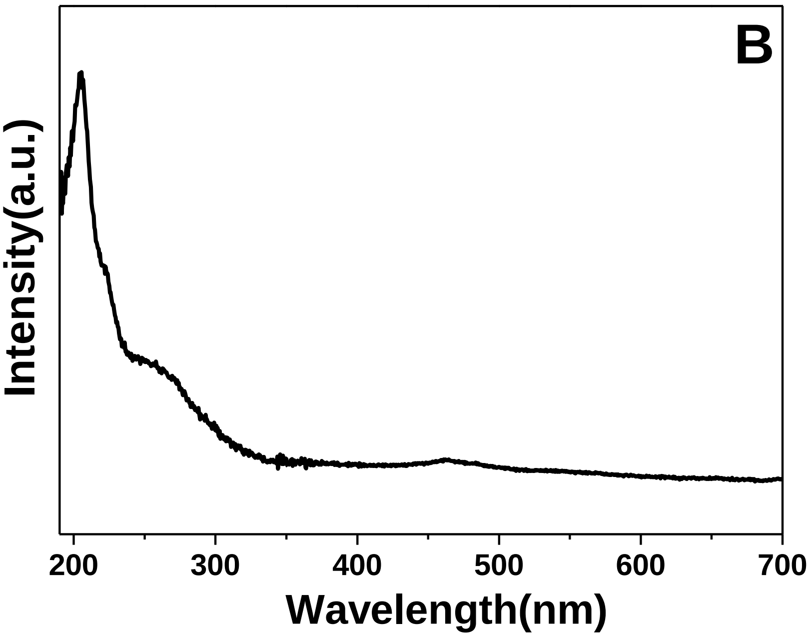
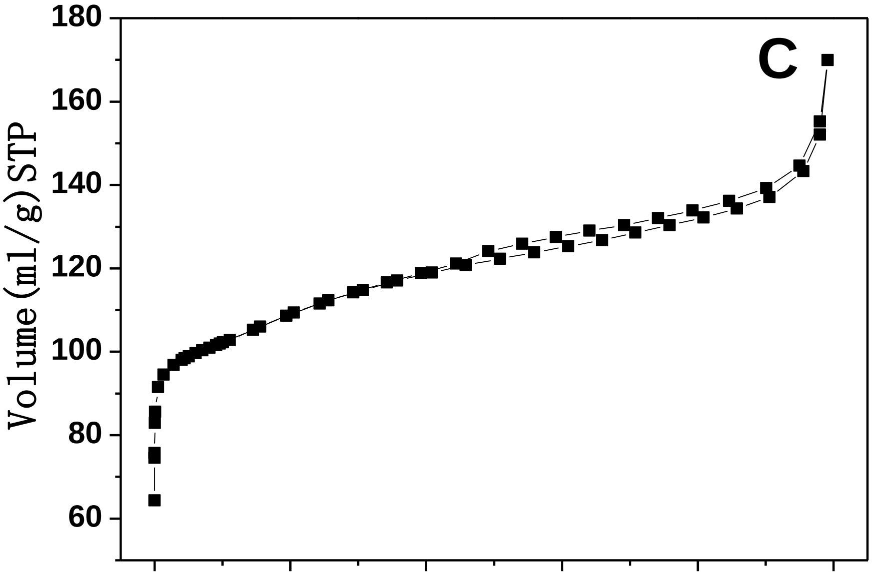


Figure S3 Analytical data for ZSM-5. A) XRD pattern, B) N_2 sorption isotherm, C) SEM image.




B
Intensity(a.u.)
200
300
400
500
600
700
Wavelength(nm)


C
Volume(ml/g)STP
180
160
140
120
100
80
60
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure, p/p0

m).

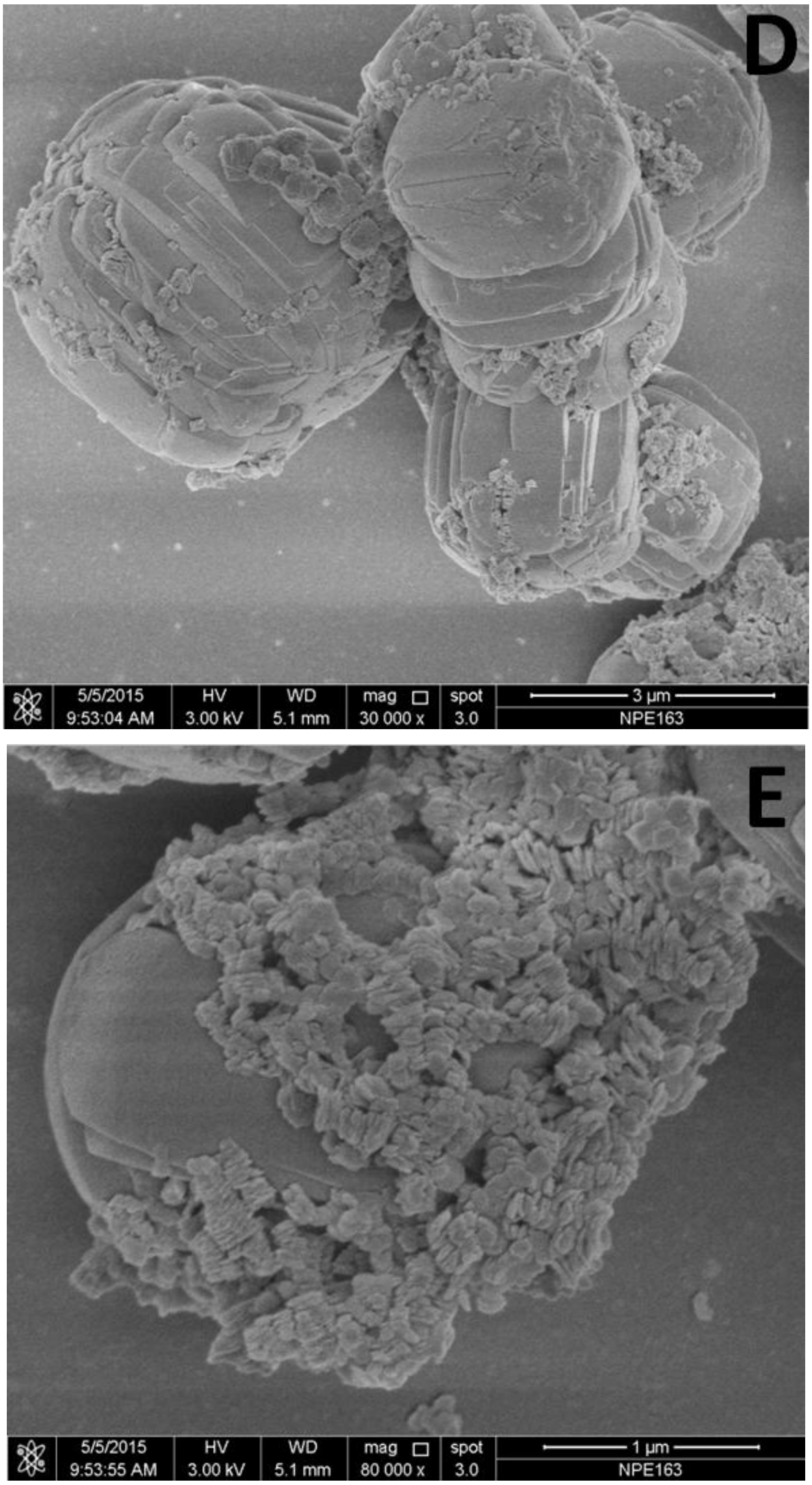
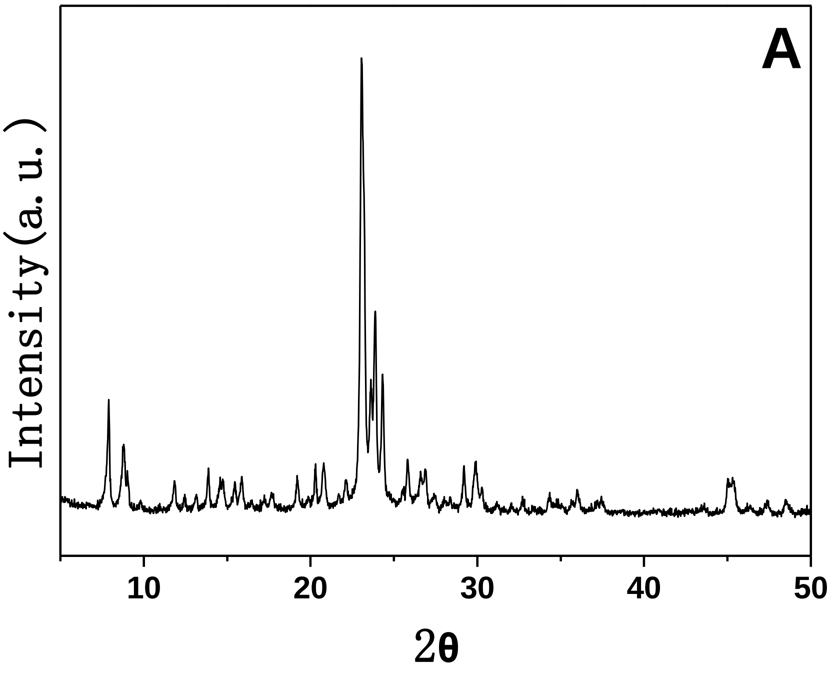
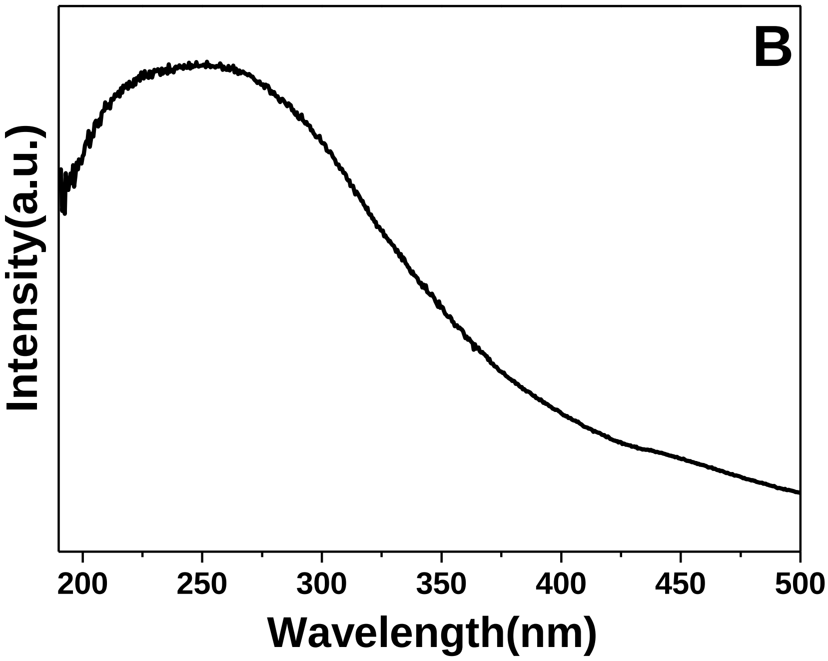


Figure S4 Analytical data for Zn-ZSM-5. A) XRD pattern, B) UV-vis spectrum, C) N_2 sorption isotherm, D) SEM image (scale bar 3 μm), E) SEM image (scale bar 1 μm).


A
Intensity(a. u.)
10
20
30
40
50
2θ


B
Intensity(a.u.)
200
250
300
350
400
450
500
Wavelength(nm)

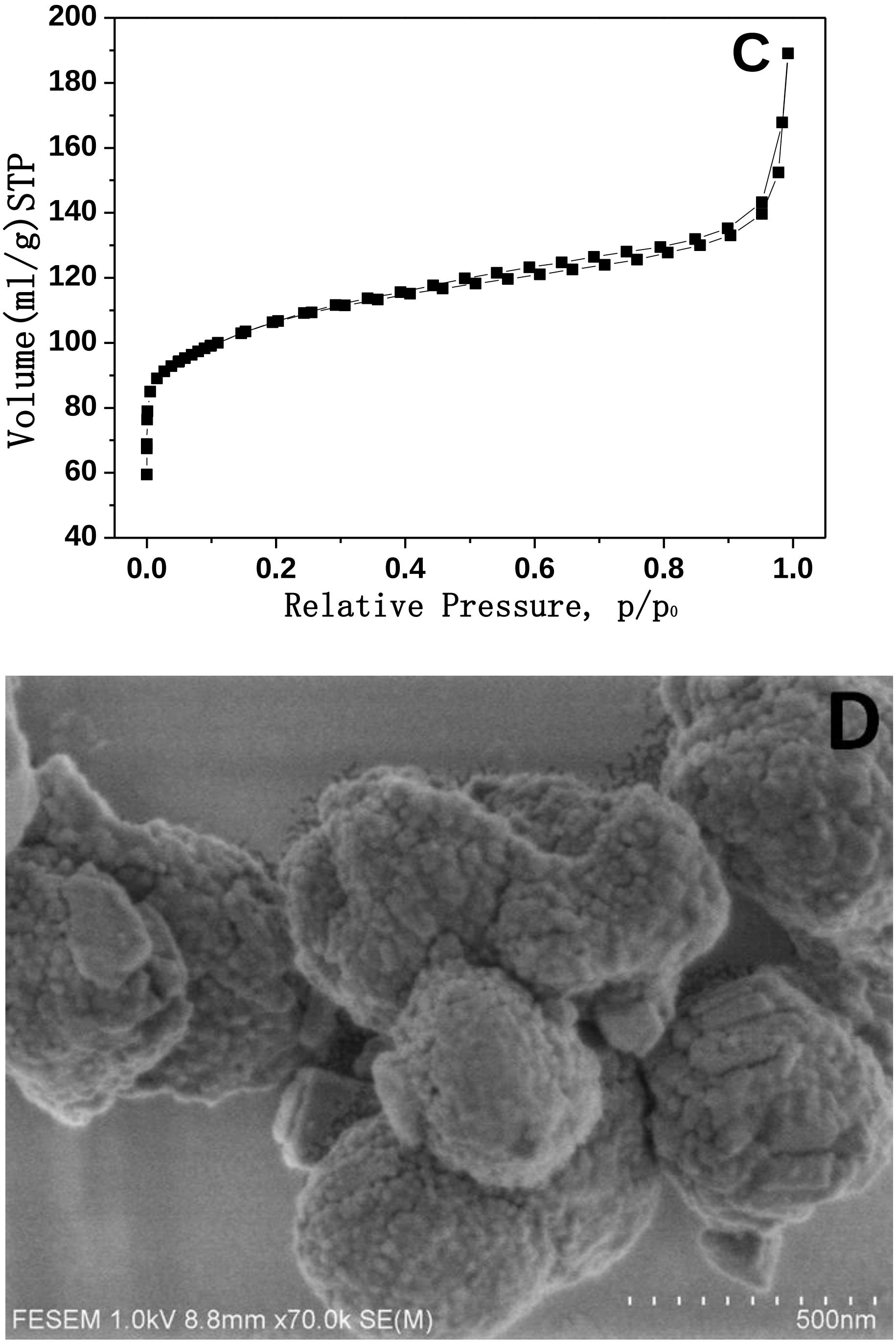


Figure S5 Analytical data for Fe-ZSM-5. A) XRD pattern, B) UV-vis spectrum, C) N_2 sorption isotherm, D) SEM image.

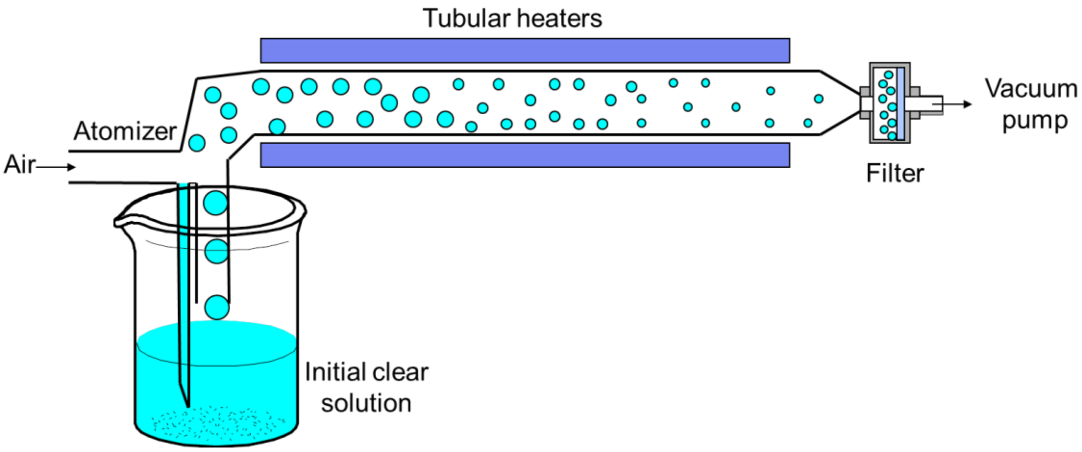


Figure S6 Aerosol-dry apparatus

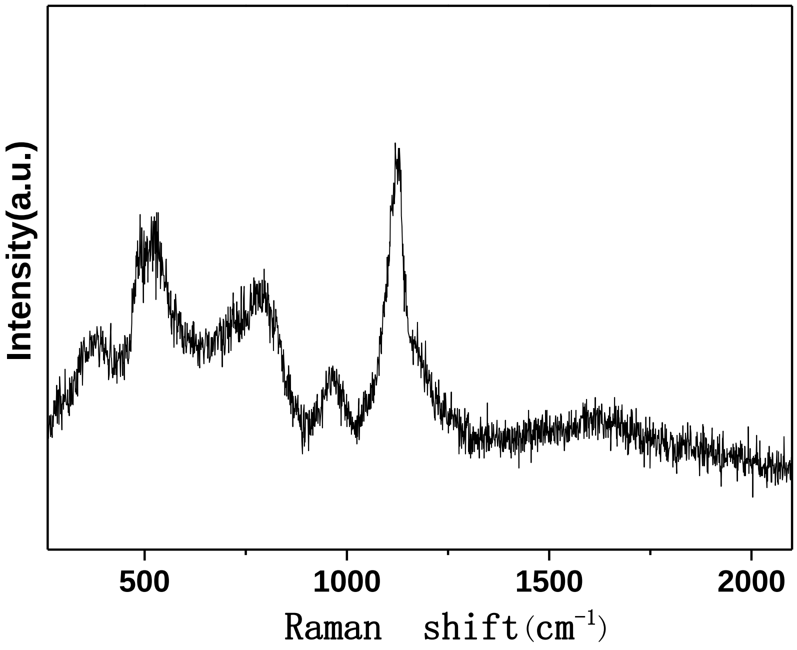


Figure S7 UV Raman spectrum of the TS-1-0.05 excited with the laser line at 244nm.

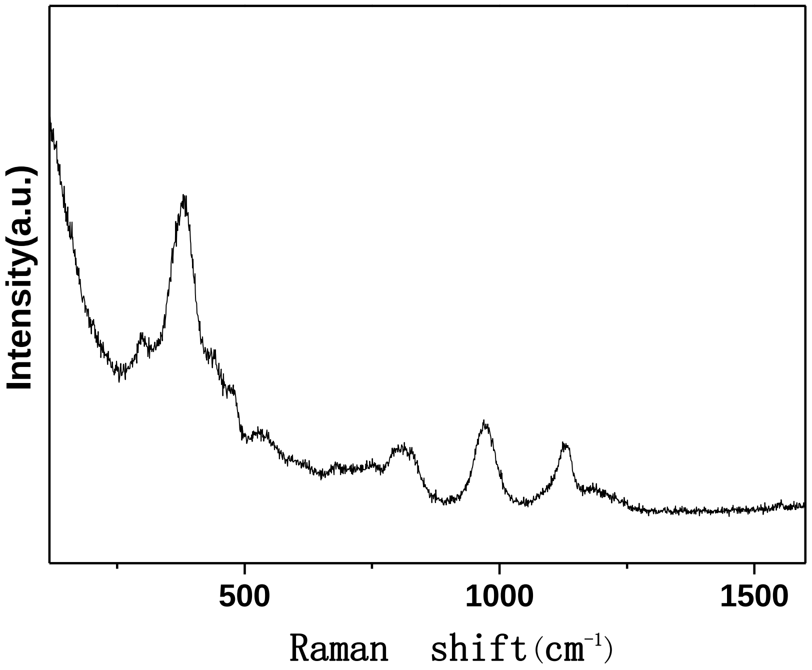


Figure S8 UV Raman spectrum of the TS-1-0.05 excited with the laser line at 325nm.

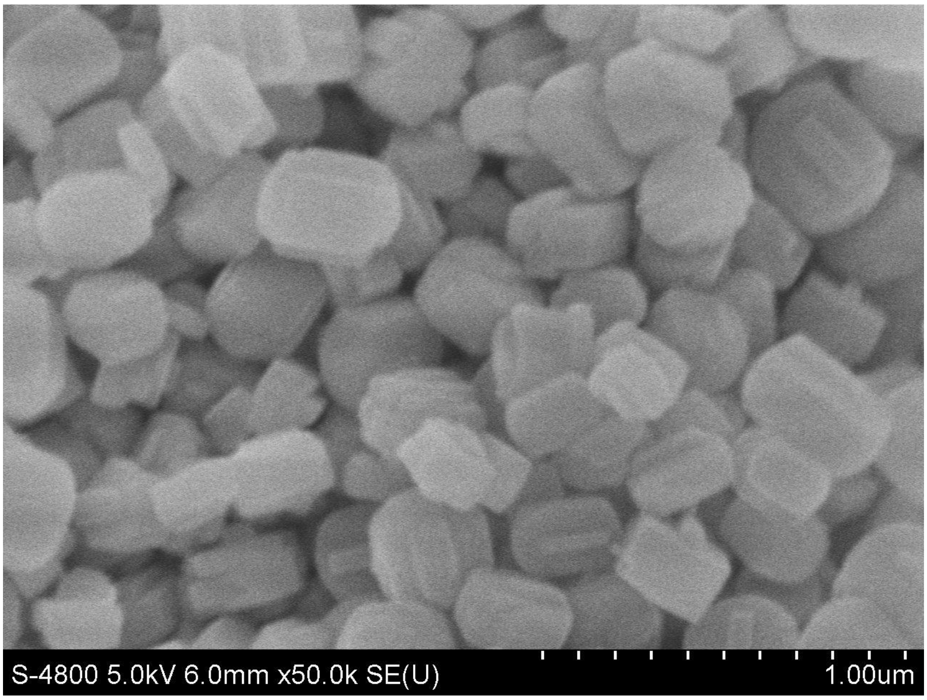
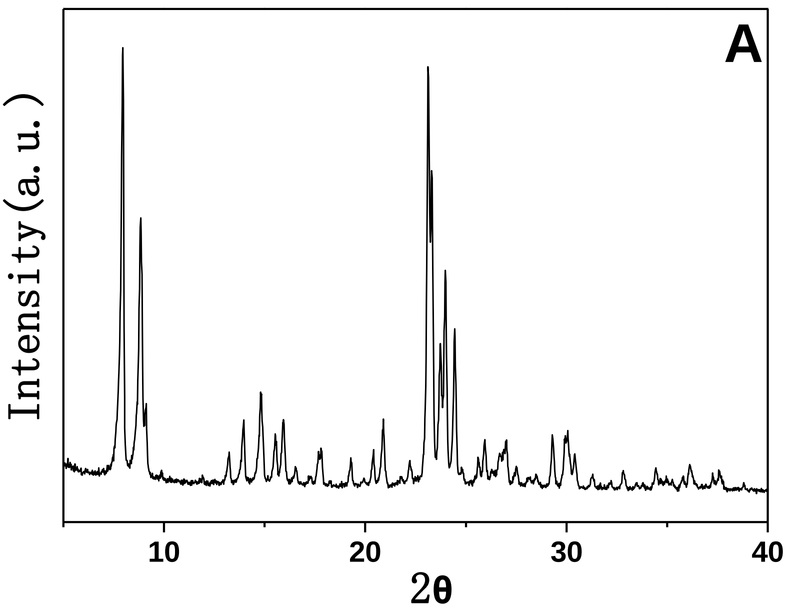
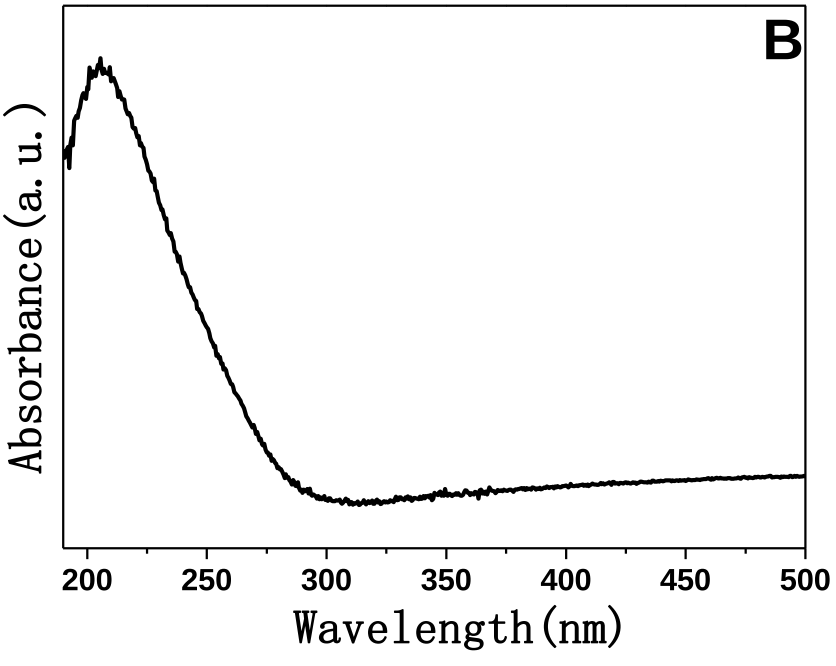


Figure S9 SEM image of the TS-1 crystallized at 110℃ for 48h.


A
Intensity(a. u.)
10
20
30
40
2θ


B
Absorbance(a. u.)
200
250
300
350
400
450
500
Wavelength(nm)

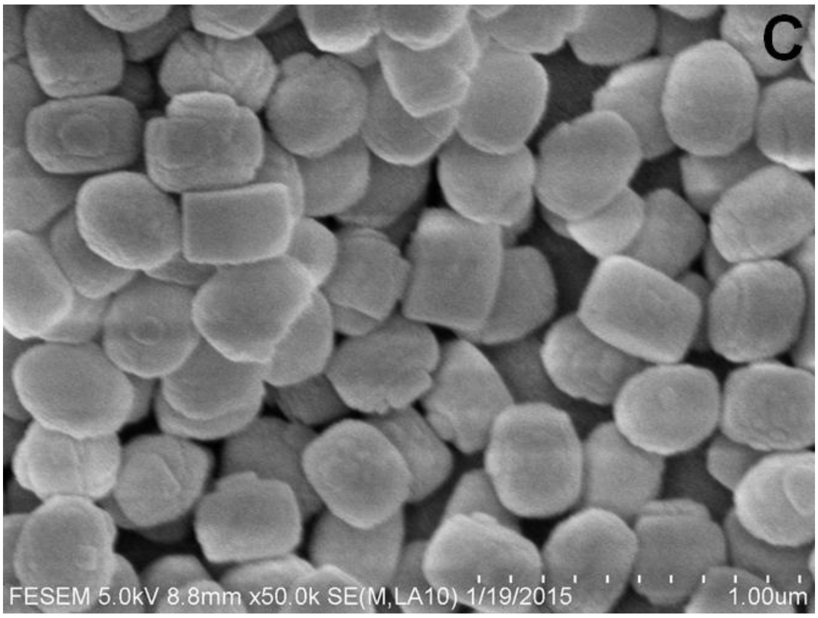


Figure S10 Analytical data for the TS-1(convention). A) XRD patterns, B) UV-vis spectrum, C) SEM image.

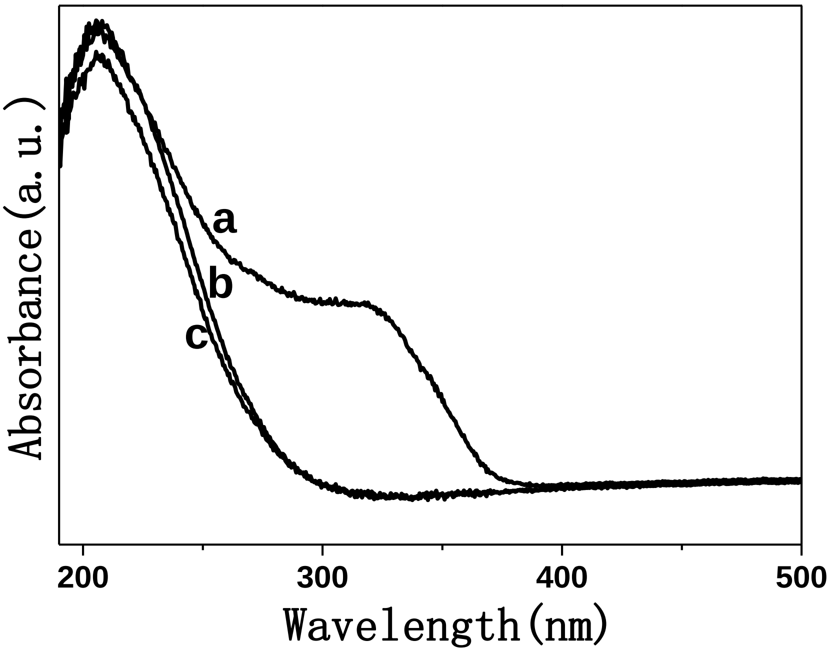
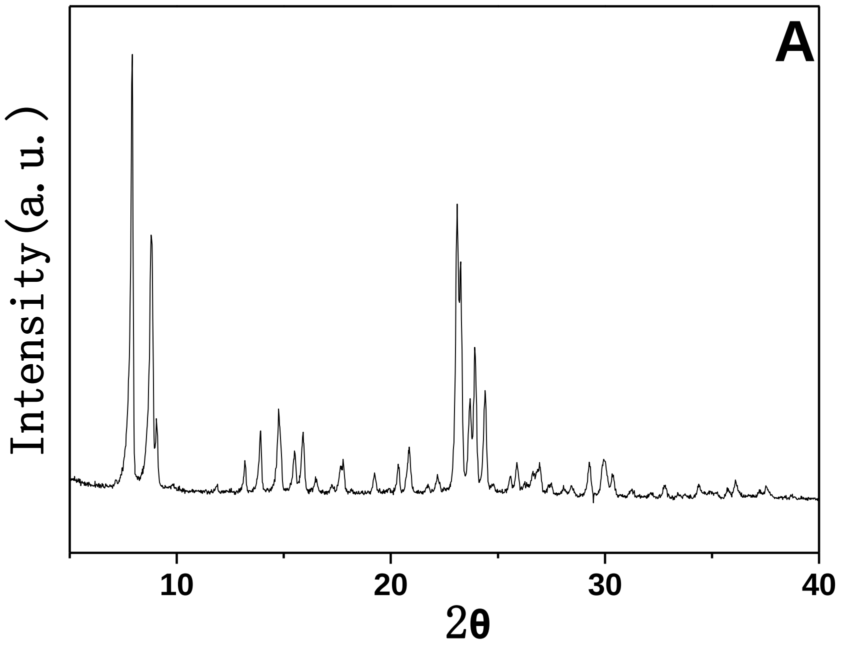
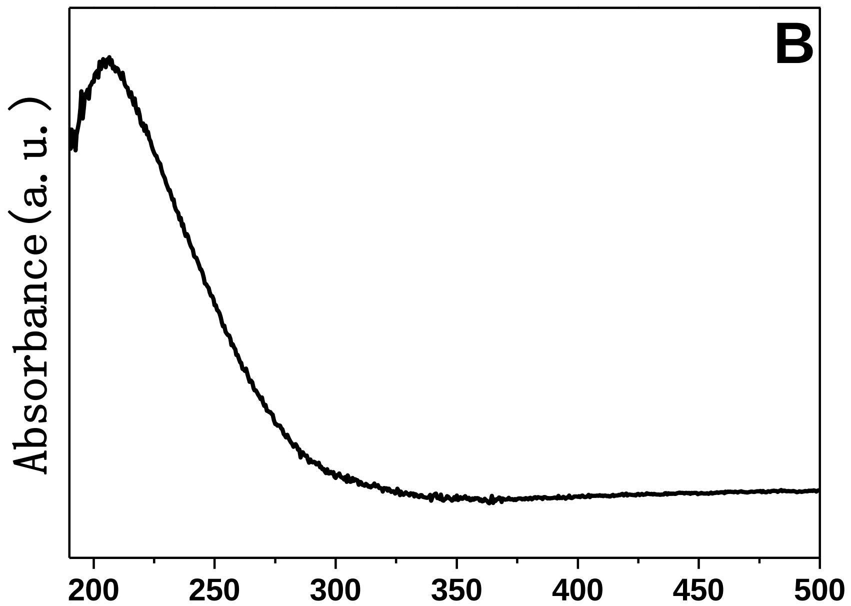


Figure S11 UV-vis spectra of the TS-1. a) Si/Ti= 30, b) Si/Ti= 40, c) Si/Ti= 50.


A
Intensity(a.u.)
10
20
30
40
2θ


B
Absorbance(a.u.)
200
250
300
350
400
450
500
Wavelength(nm)

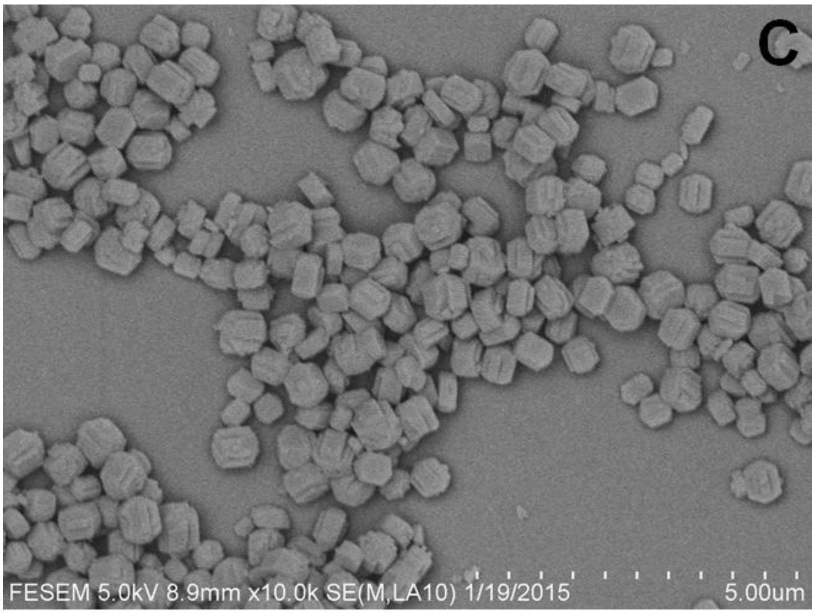


Figure S12 Analytical data for the TS-1-0.04. A) XRD pattern, B) UV-vis spectrum, C) SEM image.