Electronic Supplementary Information for Dalton Transactions

Supporting information

Improvement of cytotoxicity of titanocene-functionalized mesoporous materials by the increase of the titanium content

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This supporting information contains:

1. Solid-state ^{1}H MAS NMR spectra of **S1**–**S3**
2. ^{13}C MAS NMR spectrum of **S1**
3. ^{29}Si MAS NMR spectrum of **S1**
4. UV-vis spectra of **S1**–**S3**
5. FT-IR of **S1**, **S2** and **S3**
6. Pore distribution of **S1**–**S3**
7. Thermogravimetric curve of **S1**
8. Full details and figures of the DFT calculations of titanocene derivatives **2** and **3**
9. TEM images of S1, S2 and S3

1. Solid-state ^{1}H MAS NMR spectra of S1–S3

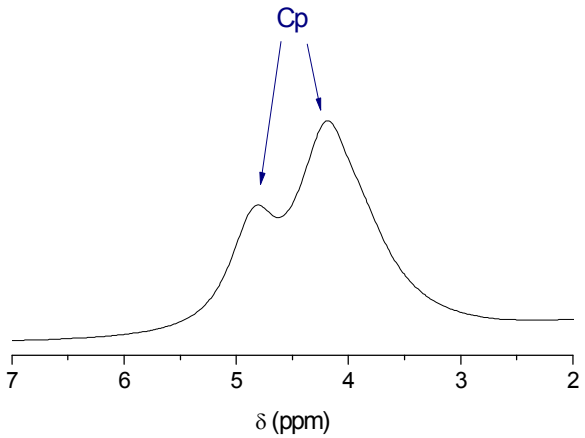

Figure 1. Solid-state ^{1}H NMR spectrum of **S1**

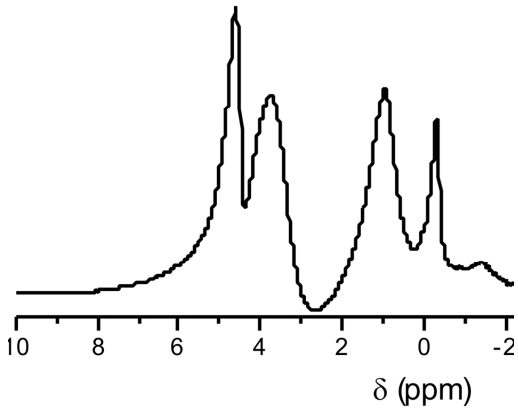

Figure 2. Solid-state ^{1}H NMR spectrum of **S2**

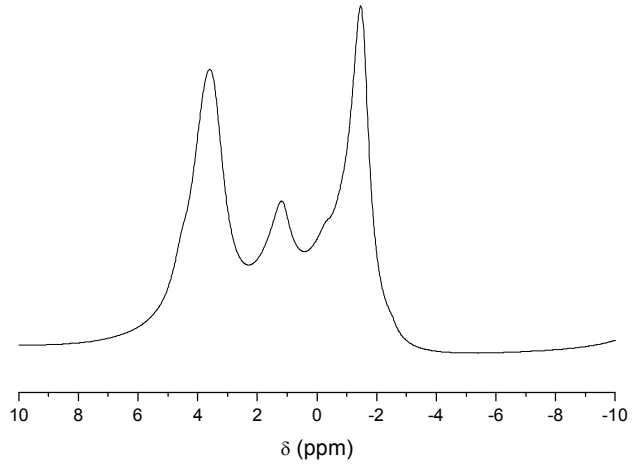

Figure 3. Solid-state ^{1}H NMR spectrum of **S3**

2. ^{13}C MAS NMR spectrum of S1

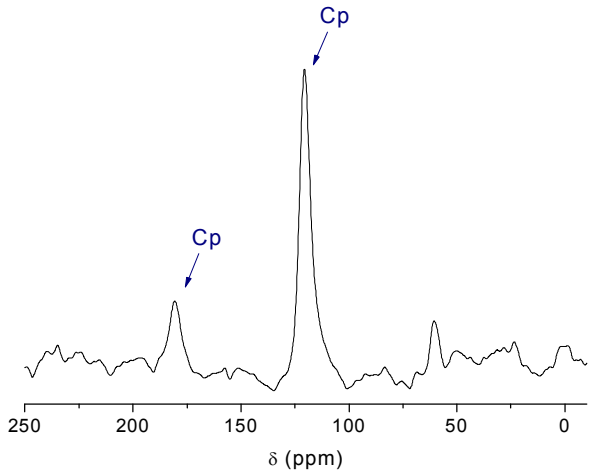

Figure 4. Solid-state ^{13}C NMR spectrum of **S1**

3. ^{29}Si MAS NMR spectrum of S1

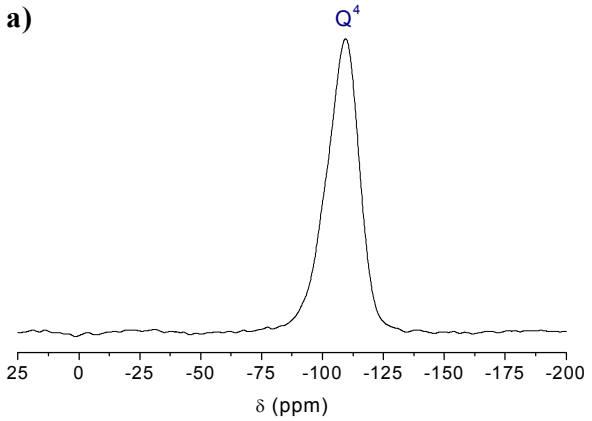

Figure 5. Solid-state ^{29}Si NMR spectrum of **S1**

4. UV-vis spectra of S1–S3

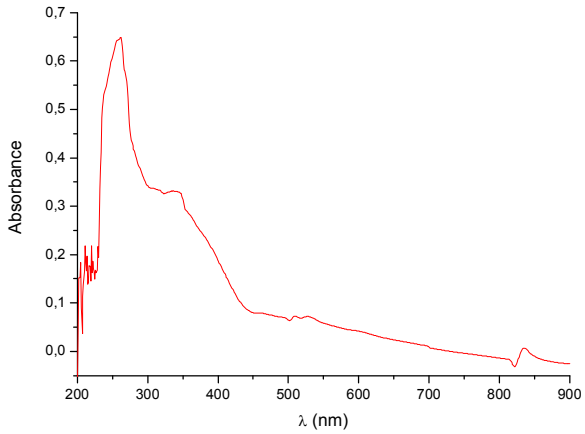

Figure 6. UV-vis spectrum of **S1**

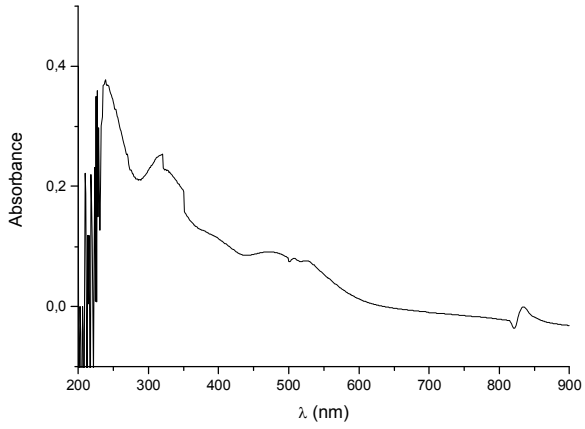

Figure 7. UV-vis spectrum of **S2**

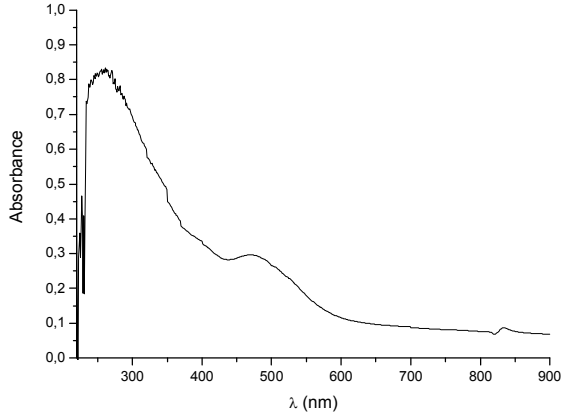

Figure 8. UV-vis spectrum of **S3**

5. FT-IR of S1–S3

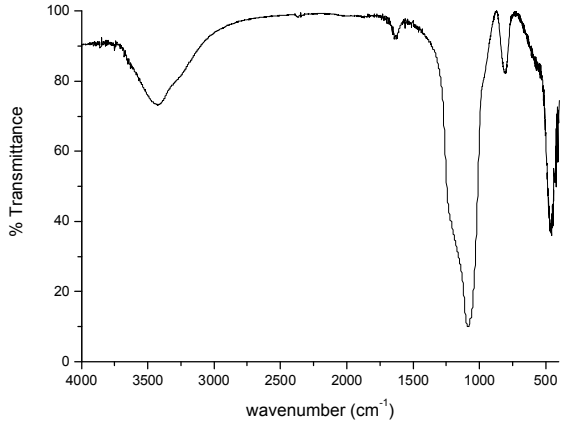

Figure 9. FT-IR spectrum of **S1**

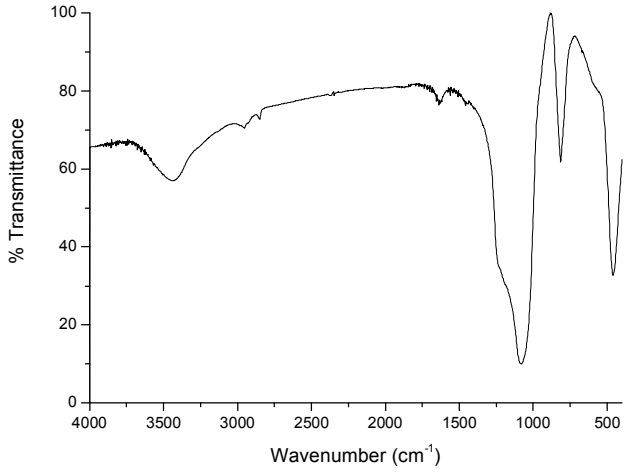

Figure 10. FT-IR spectrum of **S2**

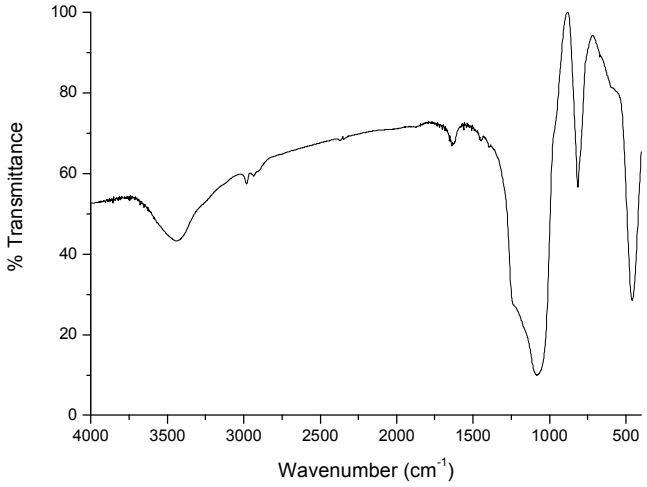

Figure 11. FT-IR spectrum of **S3**

6. Pore distribution of S1–S3

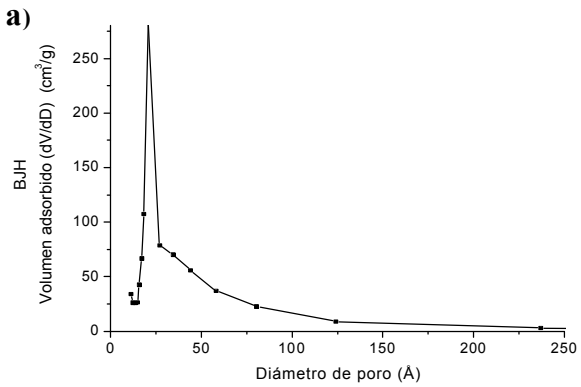

Figure 12. Pore size distribution for **S1**.

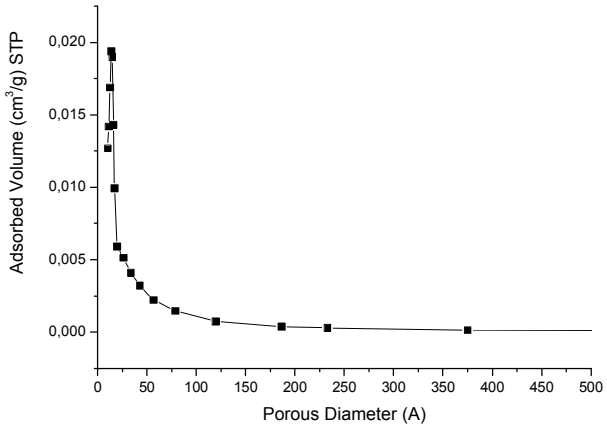

Figure 13. Pore size distribution for **S2**.

7. Thermogravimetric curve of S1

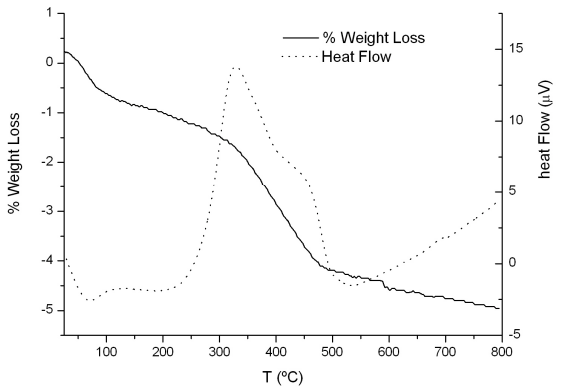

Figure 14. Thermogravimetric curve of **S1**

8. Full details and figures of the DFT calculations of titanocene derivatives 2 and 3

Energies and Cartesian Coordinates of Atom Positions of Calculated Molecules

8.1 Complex 2

Sum of electronic and zero-point Energies	-3538.307668
Sum of electronic and thermal Energies	-3538.262528
Sum of electronic and thermal Enthalpies	-3538.261584
Sum of electronic and thermal Free Energies	-3538.397706

	x	y	z
Ti	-0.06844000	3.46930900	0.01207400
C	-0.87716500	4.50367100	2.03102600
C	0.54216300	4.64430200	2.03102400
H	-1.60148500	5.30422200	1.98417800
C	0.04261100	2.41462100	2.18835200
C	1.10617600	3.35800700	2.13356500
H	1.08956300	5.57432700	1.96822000

H	0.14805500	1.34309300	2.26471900
H	2.16192300	3.13133800	2.14295500
C	-0.45249500	4.13145400	-2.31028500
C	-1.31236000	4.91454300	-1.49156800
C	0.88129400	4.47503400	-1.99517400
H	-0.76287200	3.38397600	-3.02482900
C	-0.50299100	5.74116000	-0.67779600
H	-2.39237500	4.87593800	-1.48864300
C	0.85593700	5.45480900	-0.97067300
H	-0.85837000	6.46620200	0.03983500
H	1.72236200	5.91567300	-0.51676500
H	1.76755200	4.04936400	-2.44170700
H	-2.17081600	2.70761900	2.17950400
C	-1.17813700	3.13029600	2.15305800
S	1.77124000	2.06195300	-0.68097600
S	-1.90573800	2.06504900	-0.69413800
C	2.15125500	0.65260400	0.45152400
H	2.50278300	1.03075500	1.41825800
H	1.24177600	0.07052400	0.63031300
C	3.22437300	-0.25192600	-0.16676200
H	2.87864300	-0.60451300	-1.14435800
H	4.13207100	0.33377000	-0.34884000
C	3.55218700	-1.45949300	0.73617500
H	3.90732800	-1.10955800	1.71560700
H	2.64118200	-2.04163800	0.93138200
C	-1.99859200	0.48616700	0.25334400
H	-1.07064100	-0.07057200	0.08540400

H	-2.07851100	0.68451000	1.32799800
C	-3.19765200	-0.35224400	-0.20670100
H	-3.12380500	-0.52588600	-1.28565100
H	-4.12085000	0.21478800	-0.04402600
C	-3.27713700	-1.70409300	0.53244200
H	-2.35236400	-2.27503700	0.37297500
H	-3.34901900	-1.53408900	1.61610300
Si	4.82291900	-2.62997500	0.02855400
Si	-4.70654400	-2.78638300	0.01091200
O	-4.62718100	-3.06904300	-1.61122800
O	-6.08567900	-1.97018700	0.43852300
O	-4.67988200	-4.29064600	0.72118300
O	5.01611800	-4.01200700	0.93435800
O	6.24964400	-1.78700400	-0.04449900
O	4.32564300	-3.14852400	-1.45530000
C	-4.97601800	-4.26030200	-2.30236700
H	-4.37077600	-4.31916400	-3.21224900
H	-4.79111500	-5.15044700	-1.69240700
H	-6.03427800	-4.24539800	-2.59339000
C	-4.82225600	-4.50660900	2.11711100
H	-5.68648700	-3.96903500	2.52739300
H	-4.96603300	-5.57786800	2.28736700
H	-3.92416400	-4.18986800	2.66397100
C	-7.38555800	-2.29400500	-0.03436600
H	-7.45540600	-2.16899600	-1.12203200
H	-7.66638400	-3.32520400	0.21806600
H	-8.10120100	-1.61589900	0.43979200

C	4.55058000	-4.42168500	-2.04438500
H	4.51767400	-5.22322700	-1.29913700
H	3.76944400	-4.59592000	-2.79058000
H	5.52375800	-4.45246800	-2.55133200
C	5.55197000	-4.02614500	2.24916700
H	6.47815800	-3.44181400	2.31855200
H	4.83345600	-3.62673200	2.97736100
H	5.77289100	-5.06291300	2.52050000
C	7.38044300	-2.19510400	-0.80165100
H	8.18609600	-1.47555400	-0.62866600
H	7.73538000	-3.19020000	-0.50186800
H	7.15415800	-2.21298000	-1.87492400

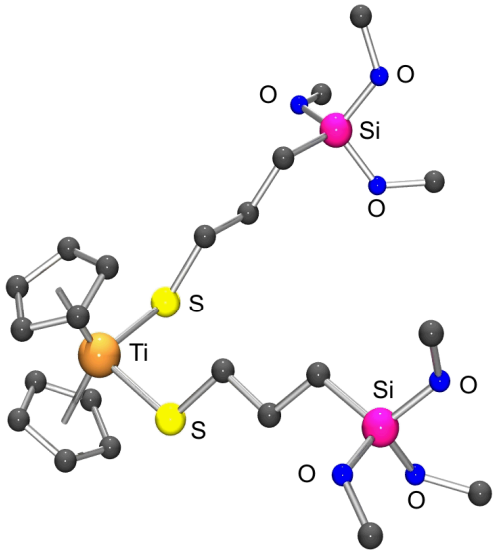

Figure 15. DFT-calculated structure of **2**

8.2 Complex 3

Sum of electronic and zero-point Energies	-3774.067518
Sum of electronic and thermal Energies	-3774.014961
Sum of electronic and thermal Enthalpies	-3774.014017
Sum of electronic and thermal Free Energies	-3774.171982

	x	y	z
Ti	0.05625100	4.00240300	-0.05257400
C	0.86053600	5.05057400	-2.06625400
C	-0.56034800	5.17531200	-2.07046500
H	1.57567700	5.85905100	-2.01454500
C	-0.03538000	2.95175100	-2.23179900
C	-1.10946800	3.88300100	-2.17882200
H	-1.11838700	6.09896100	-2.00681900
H	-0.12855300	1.87923000	-2.31047000
H	-2.16257600	3.64459400	-2.19270200
C	0.43459400	4.66219100	2.27146500
C	1.28497600	5.45697300	1.45424300
C	-0.90321600	4.99183400	1.95840800
H	0.75375600	3.91625100	2.98373600
C	0.46571900	6.27689400	0.64347200
H	2.36535100	5.43041400	1.45045500
C	-0.88963500	5.97482500	0.93679000
H	0.81237800	7.00792100	-0.07232700
H	-1.76147500	6.42713000	0.48460100
H	-1.78432500	4.55503100	2.40439200
H	2.17475300	3.26973100	-2.21442100

C	1.17727800	3.68105600	-2.19033200
S	-1.77810600	2.58233700	0.62938400
S	1.90006500	2.60796900	0.65498700
C	-2.13480300	1.16530700	-0.50130500
H	-2.47330200	1.53596000	-1.47553000
H	-1.21987000	0.58663600	-0.66283900
C	-3.21279100	0.25940400	0.10636700
H	-2.88265000	-0.08148100	1.09339300
H	-4.12704300	0.84146100	0.26671800
C	-3.51741700	-0.95960200	-0.78911800
H	-3.85478400	-0.62288400	-1.77938300
H	-2.60012900	-1.53971600	-0.95943900
C	2.01234700	1.03635200	-0.30281800
H	1.08336800	0.47587200	-0.15449400
H	2.10936500	1.24318000	-1.37445200
C	3.20555000	0.19671400	0.16996500
H	3.11790500	0.01915000	1.24719700
H	4.13065800	0.76464300	0.02130200
C	3.29459100	-1.15269100	-0.57220300
H	2.36841900	-1.72453100	-0.42393400
H	3.37782400	-0.98014200	-1.65461100
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Si	4.71932400	-2.23598300	-0.03711600
O	4.63060900	-2.49579400	1.58926500
O	6.10361100	-1.43061200	-0.47087800
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O	-6.23559400	-1.29642900	-0.08194900
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H	7.65214200	-2.80042700	-0.23707200
C	-4.60084000	-3.84083300	2.06868700
H	-4.57333100	-4.65667700	1.33687700
H	-5.61124800	-3.81706900	2.50132500
C	-5.44456600	-3.60260400	-2.30100400
H	-6.37904000	-3.03111800	-2.38648800
H	-4.71873700	-3.15008400	-2.99236800
C	-7.39177800	-1.67881100	0.66388800
H	-7.69531400	-2.70132800	0.39584400
H	-7.15589700	-1.67517600	1.73680400
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H	8.19156000	0.21890700	-0.41755300
H	9.43440900	-1.04649800	-0.30831900
H	8.39627200	-0.93630700	-1.74619700
C	4.18909800	-3.72845000	3.60535200
H	4.46996200	-4.60989000	4.19210400
H	4.37253200	-2.83567900	4.21048000

H	3.11754200	-3.78098600	3.39078200
C	4.99324700	-5.48484600	-2.36267300
H	4.13414900	-6.03634400	-1.96930500
H	5.08402000	-5.69965900	-3.43275500
H	5.89315900	-5.84915800	-1.85796400
C	-3.56946600	-4.06308000	3.16387600
H	-3.76867400	-5.00215000	3.69157700
H	-2.56221100	-4.11009400	2.73935400
H	-3.59619200	-3.24463900	3.88934300
C	-8.51983500	-0.70273500	0.36887600
H	-9.41737400	-0.96986800	0.93685900
H	-8.22525300	0.31467400	0.64228500
H	-8.76779900	-0.71198900	-0.69684100
C	-5.67787000	-5.05891000	-2.67201100
H	-6.04463500	-5.13944700	-3.70082800
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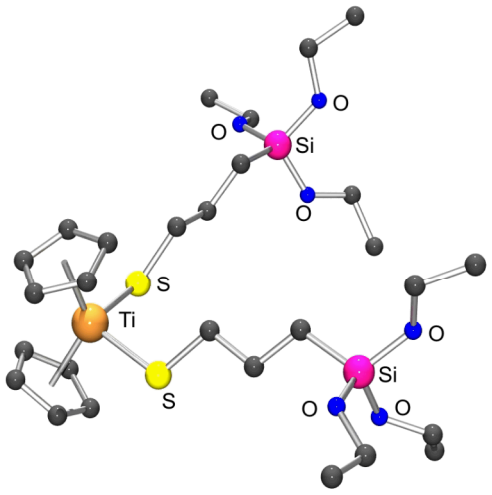

Figure 16. DFT-calculated structure of **3**

9. TEM images of S1, S2 and S3

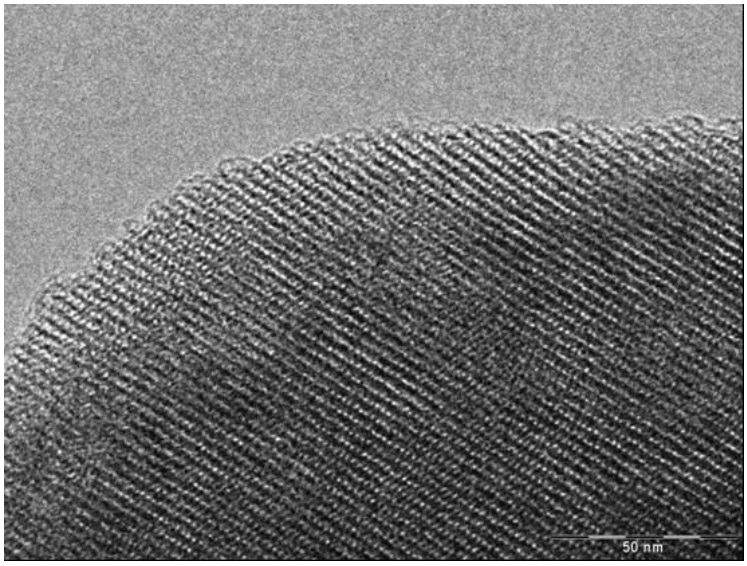

Figure 17. TEM image of **S1** (channels are clearly observed)

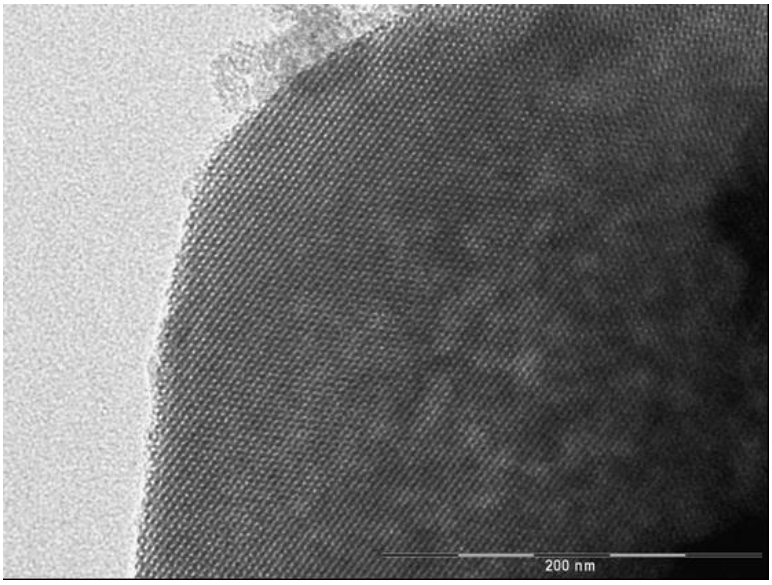

Figure 18. TEM image of **S2** (hexagonal distribution of pores is clearly observed)

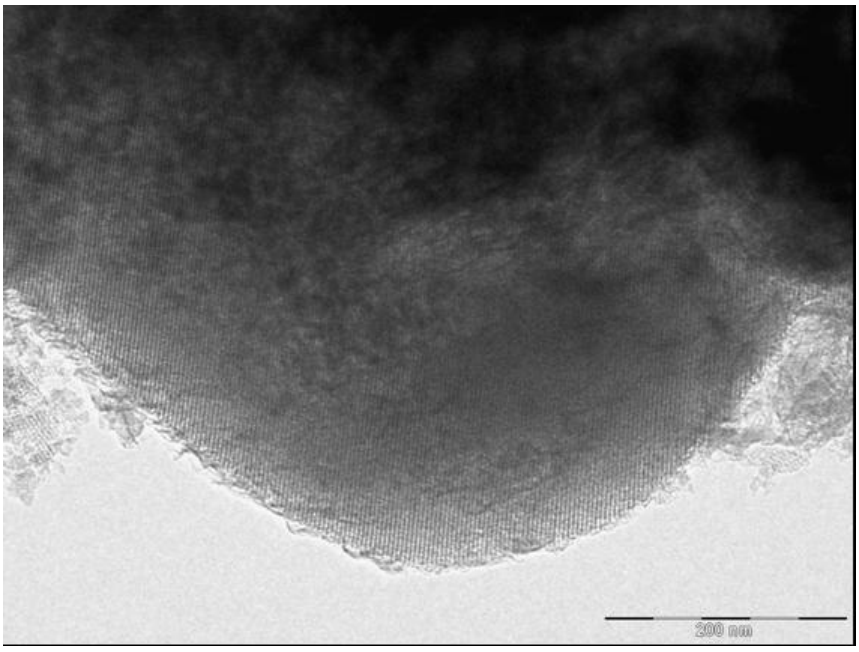

Figure 19. TEM image of **S3** (channels are clearly observed)