Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Controlling the window size in mesoporous SBA-16.

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KEYWORDS SBA-16, mesoporous, minimal surface, curvature.

SUPPLEMENTARY MATERIAL

Experimental set-up for ozone treatment

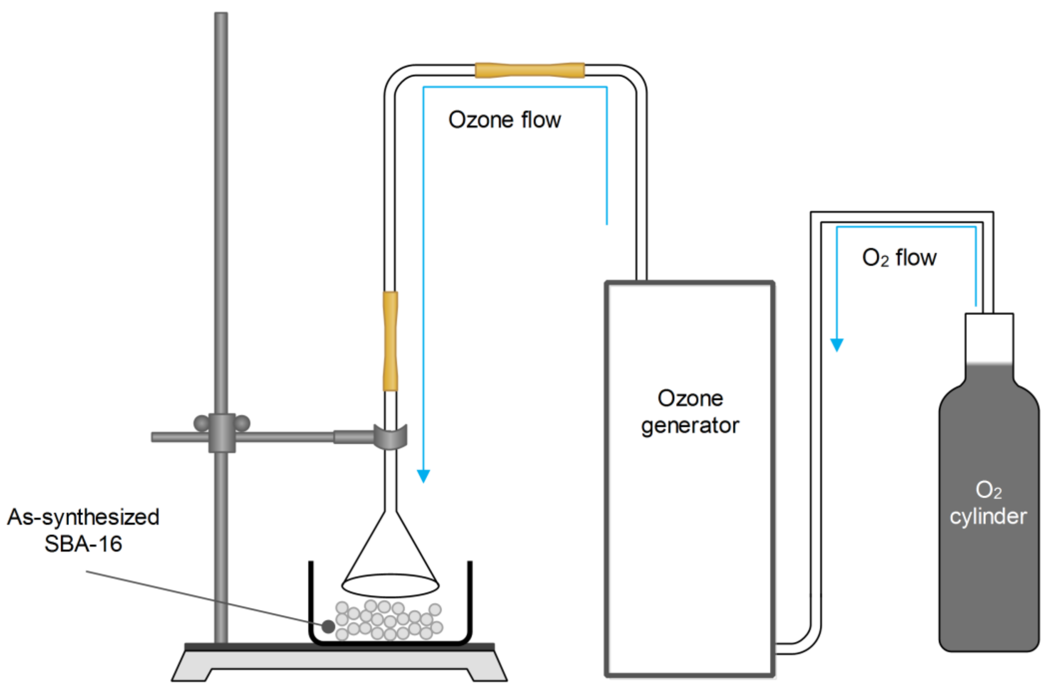


Figure S1. The apparatus setup of the ozone treatment of as-synthesized SBA-16.

Ozone interaction

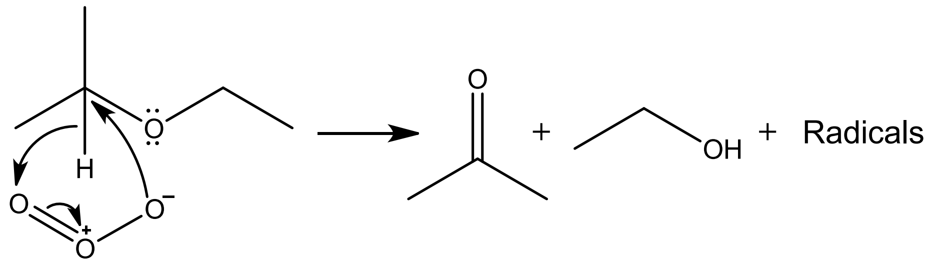


Figure S2. The reaction mechanism of the oxidation of F127 by ozone.

Infra-red spectroscopy

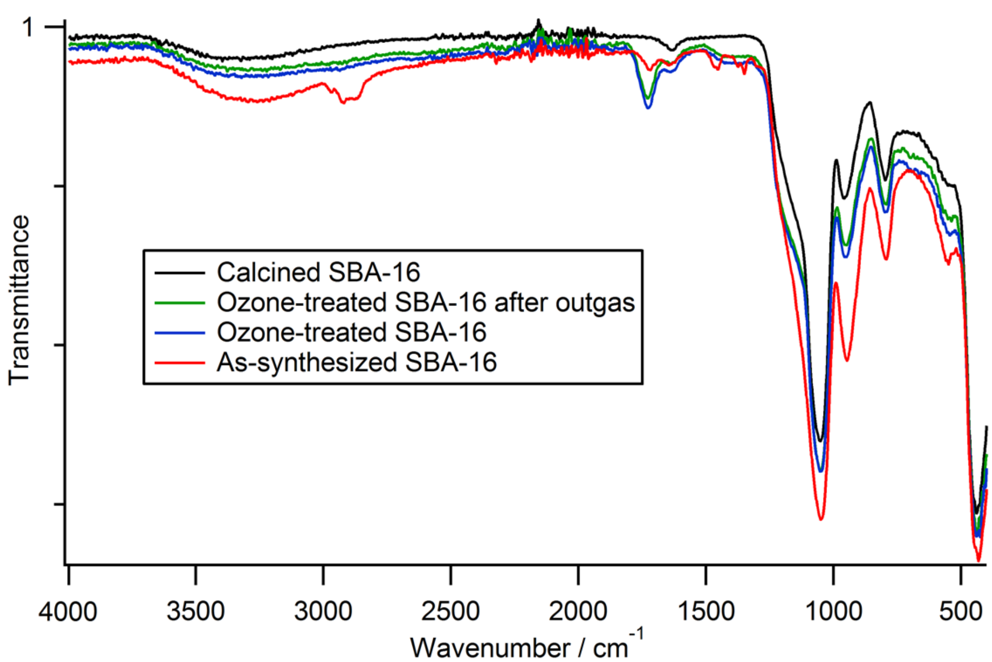
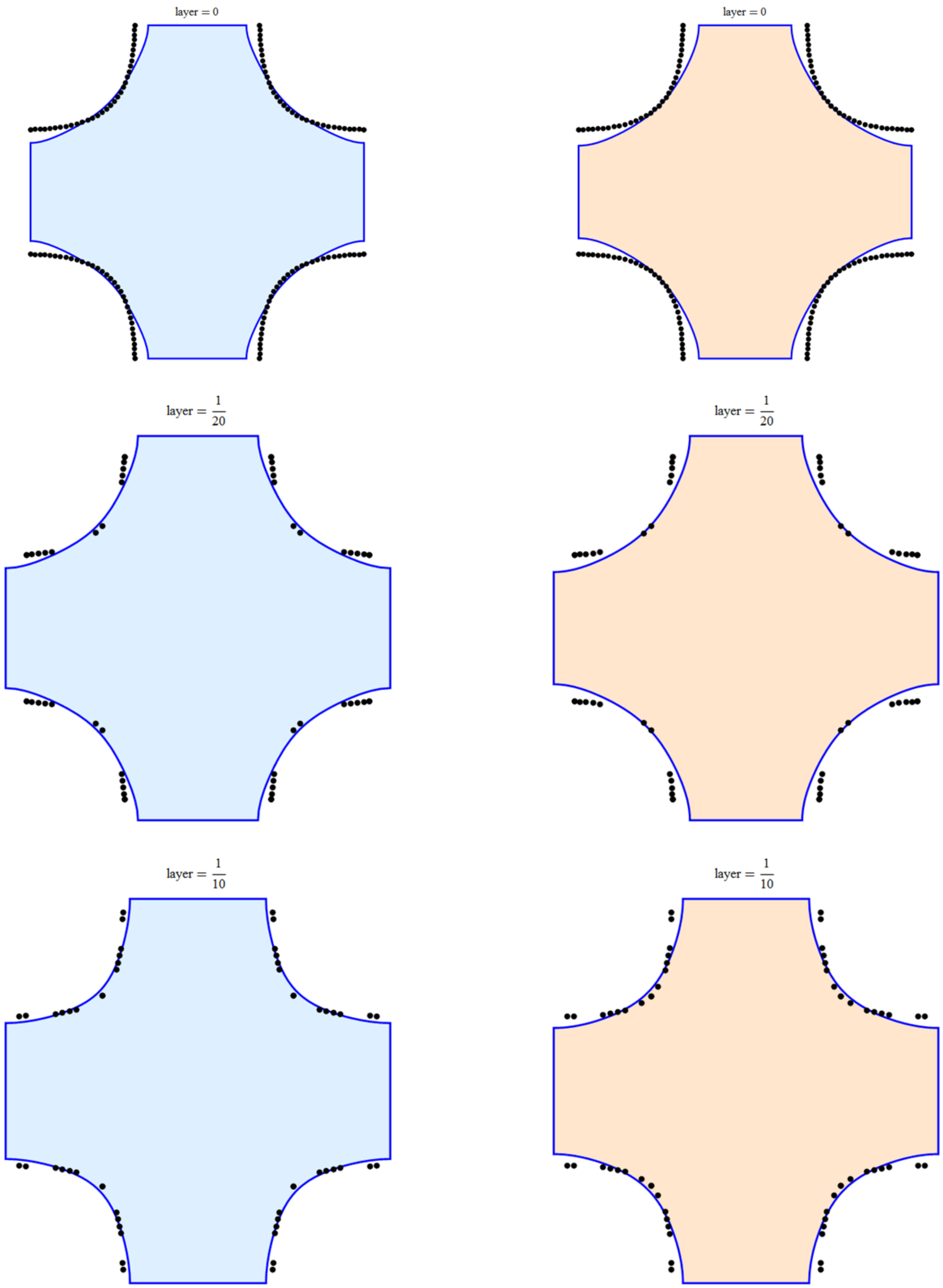


Figure S3. Infra-red spectra of SBA-16 samples as-synthesised and following various treatments.

(i) 2D slices comparison between iso-electron density contour of the silica interface (solid line) and simulated constant mean curvature surface (dotted). Left: calcined SBA-16 and surface with mean curvature of 0.00978 Å^{-1}; Right: ozone-treated SBA-16 and surface with mean curvature of 0.00830 Å^{-1}.

Calcined SBA-16 + mean curvature of 0.00978 Å^{-1}

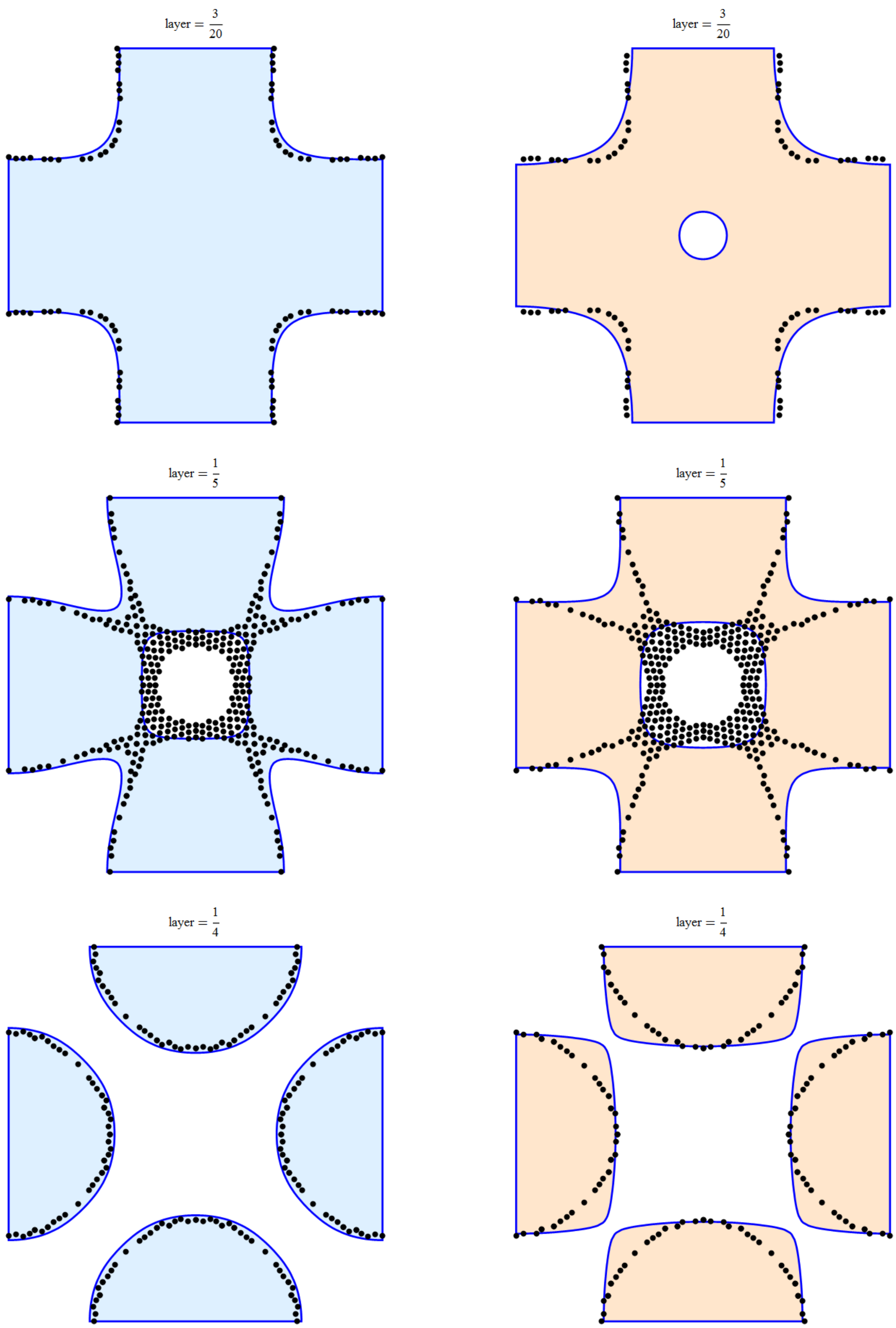
Ozone-treated SBA-16 + mean curvature of 0.00830 Å^{-1}



(*continuous*)

Calcined SBA-16 + mean curvature of 0.00978 Å^{-1}

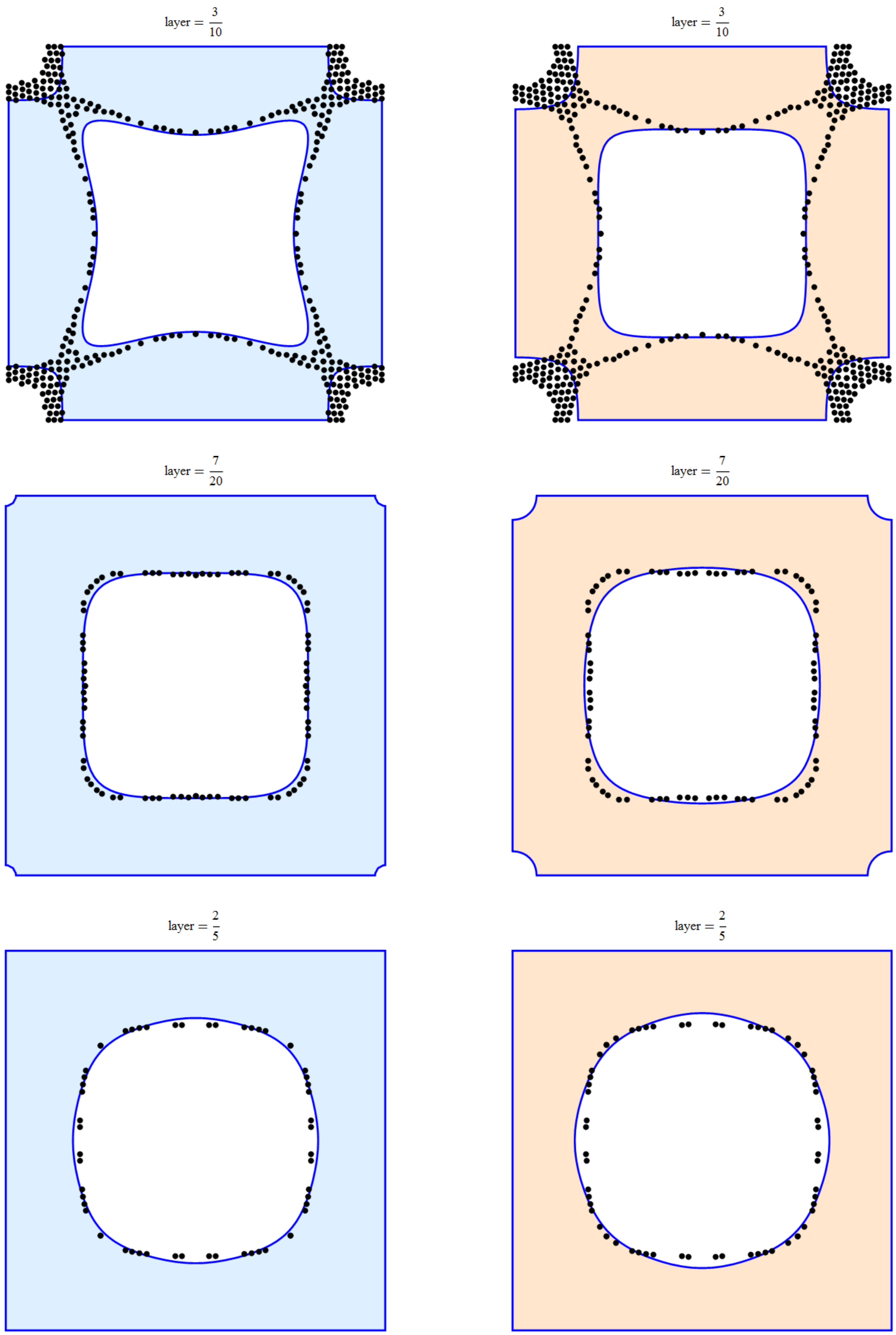
Ozone-treated SBA-16 + mean curvature of 0.00830 Å^{-1}



(*continuous*)

Calcined SBA-16 + mean curvature of 0.00978 Å^{-1}

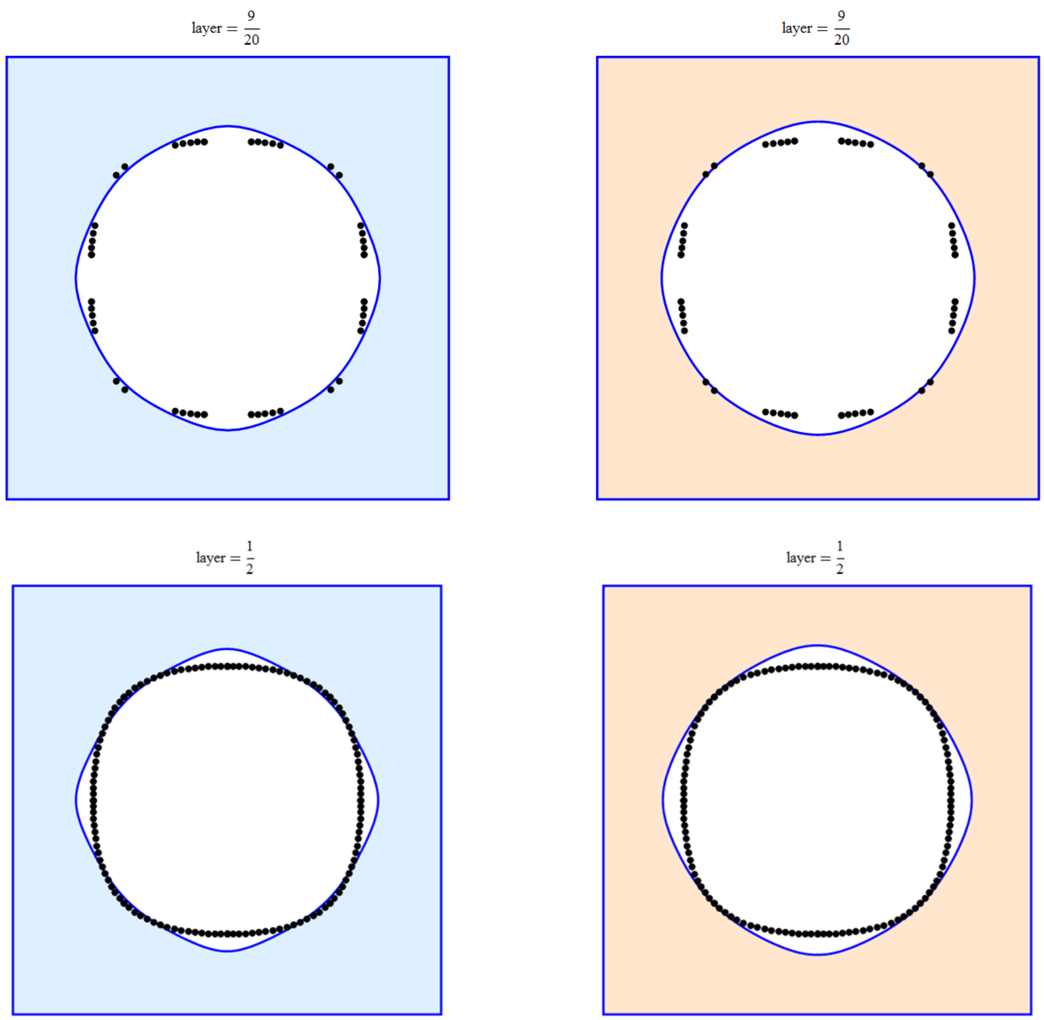
Ozone-treated SBA-16 + mean curvature of 0.00830 Å^{-1}



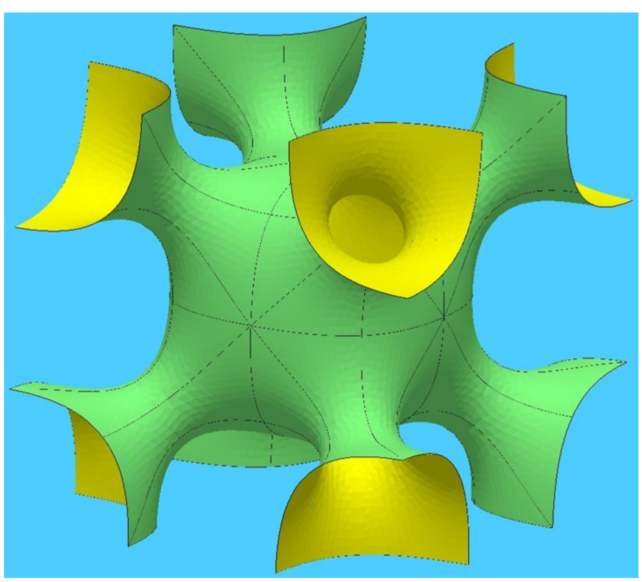
(*continuous*)

Calcined SBA-16 + mean curvature of 0.00978 Å^{-1}

Ozone-treated SBA-16 + mean curvature of 0.00830 Å^{-1}



(ii) Calculated surface of constant mean surface for calcined SBA-16.



(iii) Surface evolver data file for the constant mean curvature surfaces with $Im\bar{3}m$ symmetry

Note:

- Contexts initialed with // are comments and ignored by Surface Evolver.
- The refinements for calcined and ozone-treated SBA-16 are identical.
- Typing commands are italic in Operation session.

Operation:

Step 1: set target mean curvature, for example 0.50:
h_zero := 0.50

Step 2: run *yao*, *cube* and *sho* successively;

Step 3: execute the refinement:
gogo

Step 4: Run *qin* for further evolution to minimization. This process needs to be followed by *qin2* if more refinements are required:
qin; qin2

Programme:

```
// Surface Evolver file for SBA-16 structure
// File evolved using Hessian mathematics
// 1/48th of the SBA-16 surface is plotted

quantity sqmean energy method star_perp_sq_mean_curvature global

// Edges along the boundaries of the 1/48th section are constrained as follows
CONSTRAINT 1   // top
FUNCTION:  z  = 1
CONTENT
C1: 0.5*(y-1)
C2: -0.5*(x-1)
C3: 0

CONSTRAINT 2  // right side
FUNCTION:  y - x  = 0

CONSTRAINT 3  // left  side
FUNCTION:  -y  = 0

CONSTRAINT 4  // front bottom
FUNCTION:  x - z  = 0
CONTENT
C1: (2*x+1)*y/6
C2: -(2*x+1)*(x-1)/6
C3: 0

// Transform generators that enable entire unit cell to be visualized

view_transform_generators 4
1,0,0,0 , 0,1,0,0 , 0,0,-1,2 , 0,0,0,1  ,
0,1,0,0 , 1,0,0,0 , 0,0,1,0 , 0,0,0,1  ,
1,0,0,0 , 0,-1,0,0 , 0,0,1,0 , 0,0,0,1  ,
0,0,1,0 , 0,1,0,0 , 1,0,0,0 , 0,0,0,1  ,

// 1/48th section of SBA-16, and boundaries of cell defined points 1 to 4 are the points making up the
// SBA-16 surface points 5 to 8 define the 1/48th sections boundaries

vertices
  1  1   0.5   1          constraints 1 4
  2  0.5 0.5   1          constraints 1 2
  3  0.0 0.0   0.5        constraints 2 3
  4  0.5 0     0.5        constraints 3 4
  5  0   0     0          fixed  bare
  6  0   0     1          fixed  bare
  7  1   0     1          fixed  bare
  8  1   1     1          fixed  bare
```

```
edges
1   1 2 constraint 1
2   2 3 constraint 2
3   3 4 constraint 3
4   4 1 constraint 4
5   5 6 fixed bare no_refine // for tetrahedron display
6   5 7 fixed bare no_refine
7   5 8 fixed bare no_refine
8   6 7 fixed bare no_refine
9   6 8 fixed bare no_refine
10  7 8 fixed bare no_refine

facets
1  1 2 3 4

bodies
1  1 volconst -1/3

read

hessian_normal

set facet tension 0

// Pre-programmed short cuts for use in evolver

// to display cubical cell
cube := {
  set edge color clear where bare;
  transform_expr "3(bcd)"}

// typical evolution
gogo := { r; u; g 5; refine edge where valence==1;
        u; V; g 5; r; g 12; u; V;
        convert_to_quantities;
        r;{u; V;} 30;}
qin := {l 0.125; t 0.03125; {{u; V;} 5; g 500;  { hessian_seek; } 5;} 10; {g 500;  { hessian_seek; } 5;} 100;}

qin2 := {{g 500;  { hessian_seek; } 5;} 100;}

// For turning off surface tension, leaving mean curvature along in energy.(execute before actual iterations)

yao := {set facet tension 0;
  sqmean.modulus := 1;}

us := {unset body target where id==1}
fr := {set facet frontcolor lightgreen;
set facet backcolor lightblue}
re := {refine edges where valence==1}
con := {convert_to_quantities}
sho := {show_all_quantities}
uv := {u;V;u;V;u;V;u;V;u;V}
hs := {hessian_seek;hessian_seek;hessian_seek;hessian_seek;hessian_seek}
hess := {hessian;hessian;hessian;hessian;hessian}
sf := {set facet tension 0}
```

(iv) Mathematica data files for the calculation of iso-electron density contour of calcined SBA-16

Note:

- All the text bracketed by (* and *) is comment in the programme and will not be read by Mathematica.
- Commands and variables in Mathematica are case-sensitive.
- The numbers in light blue are the output results from the above command.
- Graphic outputs are excluded.
- 16SBA09 is an SBA-16 sample prepared with the same recipe to 16SBA05.

Programme:

(* 16SBA09 Calcined ($Im\bar{3}m$) at 550 °C Structure Factors , silica density = 2.2 g cm^{-3}, micropore volume determined by t-plot is 0.1084 cm^3 g^{-1}, therefore non-mesopore ratio is 0.6232, only employ first four diffraction peaks *)

```
g[h_,k_,l_]:=Cos[2π (h x)] Cos[2π (k y)] Cos[2π (l z)];
(* Intensity recorded and calculated from 16SBA09-calcined on 29 Nov 2010 02:28:19 *)
(* set pre-factor as 1 or -1, indicating the signs *)
a=1;
b=1;
c=1;
d=1;
f[x_,y_,z_]:=a*(100)/2(g[1,1,0]+g[1,0,1]+g[0,1,1])+
        b*(19.23)/4(g[2,0,0]+g[0,2,0]+g[0,0,2])+
        c*(1.84)(g[2,1,1]+g[1,2,1]+g[1,1,2])+
        d*(14.09)/2(g[2,2,0]+g[0,2,2]+g[2,0,2])
(* build the asymmetric unit and fill points evenly within the asymmetric unit *)
data=Array[m,{50,50,50}];
Do[data[[i,j,k]]=Array[n,3],{i,1,50},{j,1,50},{k,1,50}];Do[data[[i,j,k,1]]=(i-1)/98,{i,1,50},{j,1,50},{k,1,50}];
Do[data[[i,j,k,2]]=(j-1)/98,{j,1,50},{i,1,50},{k,1,50}];
Do[data[[i,j,k,3]]=(k-1)/196,{k,1,50},{j,1,50},{i,1,50}];
variable=Partition[Flatten[data],3];
assymmetryunit=Select[variable,#[[2]]≤#[[1]]&&#[[3]]≤Min[1/2-#[[1]],#[[2]]]&];
Leng=Length[assymmetryunit]
ListPointPlot3D[assymmetryunit]
21475
(* calculate the electron density on every point *)
value=Array[o,Leng];
Do[x=assymmetryunit[[i,1]];y=assymmetryunit[[i,2]];z=assymmetryunit[[i,3]];value[[i]]=f[x,y,z],{i,1,Leng}]
(* employ Monte Carlo method and refine the iso-electron density contour of silica interface *)
Table[N[Count[value,x_/;x ≤ i]/Leng],{i,0,-10,-1}]
{0.63553,0.626868,0.616997,0.608847,0.599022,0.590501,0.57979,0.570664,0.561118,0.551385,0.540303}
Table[N[Count[value,x_/; x ≤ i]/Leng],{i,-1,-2,-0.1}]
{0.626868,0.62617,0.625378,0.62468,0.623702,0.622491,0.621513,0.621048,0.619884,0.618347,0.616997}
Table[N[Count[value,x_/; x ≤ i]/Leng],{i,-1.4,-1.5,-0.01}]
{0.623702,0.623562,0.623423,0.623329,0.623143,0.623003,0.622817,0.622817,0.622631,0.622491,0.622491}
Table[N[Count[value,x_/; x ≤ i]/Leng],{i,-1.44,-1.45,-0.001}]
{0.623143,0.623143,0.623143,0.623143,0.623097,0.623097,0.623097,0.623097,0.623097,0.62305,0.623003}
N[Count[value,x_/;x ≤ -1.444]/Leng]
0.623097
 (* Wall region plot*)
wallregion1=RegionPlot3D[f[x,y,z] ≤-1.444,{x,0,1}, {y,0,1}, {z,0,1}, Mesh→None, PerformanceGoal→"Quality", PlotPoints→25 (*,PlotLabel→"calcined ++++ contour -1.444"*), Boxed→False, Axes→False]
 (* Pore region plot*)
poreregion=RegionPlot3D[f[x,y,z] ≥ -1.444,{x,0,1}, {y,0,1}, {z,0,1}, Mesh→None, PerformanceGoal→"Quality", PlotPoints→25, PlotLabel→"calcined ++++ contour -1.444"]
```

(v) Mathematica data file for the comparison between scatter plot from the simulated constant mean curvature surface by Surface Evolver and the iso-electron density contour of silica wall from experimental SAXS pattern of the calcined SBA-16

Note:

- All the text bracketed by (* and *) is comment in the programme and will not be read by Mathematica.
- Commands and variables in Mathematica are case-sensitive.
- Graphic outputs are excluded.
- The coordinates are treated in a unit cell with a length of 6 before plotting out the 2-D scatter slices.
- Scatter coordinates are imported from a text file generated by Surface Evolver.

Programme:

```
(* Scatter plot from surface evolver *)
A=Array[0,1];
T=OpenRead["C:/PhD/Modelling for mesoporous materials/SBA-16 modelling/surface evolver/calcined refined vertices 0.6787.txt"];
G=Flatten[ReadList[T, {Real,Real,Real}]];
A[[1]]=Partition[G,3];

(* Duplicate the coordinates in the asymmetric unit to the entire unit cell *)
MaxA=Length[A[[1]]];
B=Array[0,48];
Do[B[[n]]=Array[0,{MaxA,3}], {n,1,48}];
Do[B[[1,i,1]]=A[[1,i,1]]; B[[1,i,2]]=A[[1,i,2]]; B[[1,i,3]]=A[[1,i,3]], {i,1,MaxA}];

Do[
    B[[2,i,1]]=-B[[1,i,1]]+2;
    B[[2,i,2]]=-B[[1,i,2]]+2;
    B[[2,i,3]]=B[[1,i,3]];

    B[[3,i,1]]=-B[[1,i,1]]+2;
    B[[3,i,2]]=B[[1,i,2]];
    B[[3,i,3]]=-B[[1,i,3]]+2;

    B[[4,i,1]]=B[[1,i,1]];
    B[[4,i,2]]=-B[[1,i,2]]+2;
    B[[4,i,3]]=-B[[1,i,3]]+2;

    B[[5,i,1]]=B[[1,i,3]];
    B[[5,i,2]]=B[[1,i,1]];
    B[[5,i,3]]=B[[1,i,2]];

    B[[6,i,1]]=B[[1,i,3]];
    B[[6,i,2]]=-B[[1,i,1]]+2;
    B[[6,i,3]]=-B[[1,i,2]]+2;

    B[[7,i,1]]=-B[[1,i,3]]+2;
    B[[7,i,2]]=-B[[1,i,1]]+2;
    B[[7,i,3]]=B[[1,i,2]];

    B[[8,i,1]]=-B[[1,i,3]]+2;
    B[[8,i,2]]=B[[1,i,1]];
    B[[8,i,3]]=-B[[1,i,2]]+2;

    B[[9,i,1]]=B[[1,i,2]];
    B[[9,i,2]]=B[[1,i,3]];
    B[[9,i,3]]=B[[1,i,1]];

    B[[10,i,1]]=-B[[1,i,2]]+2;
    B[[10,i,2]]=B[[1,i,3]];
    B[[10,i,3]]=-B[[1,i,1]]+2;
```

```
B[[11,i,1]]=B[[1,i,2]];
B[[11,i,2]]=-B[[1,i,3]]+2;
B[[11,i,3]]=-B[[1,i,1]]+2;

B[[12,i,1]]=-B[[1,i,2]]+2;
B[[12,i,2]]=-B[[1,i,3]]+2;
B[[12,i,3]]=B[[1,i,1]];

B[[13,i,1]]=B[[1,i,2]];
B[[13,i,2]]=B[[1,i,1]];
B[[13,i,3]]=-B[[1,i,3]]+2;

B[[14,i,1]]=-B[[1,i,2]]+2;
B[[14,i,2]]=-B[[1,i,1]]+2;
B[[14,i,3]]=-B[[1,i,3]]+2;

B[[15,i,1]]=B[[1,i,2]];
B[[15,i,2]]=-B[[1,i,1]]+2;
B[[15,i,3]]=B[[1,i,3]];

B[[16,i,1]]=-B[[1,i,2]]+2;
B[[16,i,2]]=B[[1,i,1]];
B[[16,i,3]]=B[[1,i,3]];

B[[17,i,1]]=B[[1,i,1]];
B[[17,i,2]]=B[[1,i,3]];
B[[17,i,3]]=-B[[1,i,2]]+2;

B[[18,i,1]]=-B[[1,i,1]]+2;
B[[18,i,2]]=B[[1,i,3]];
B[[18,i,3]]=B[[1,i,2]];

B[[19,i,1]]=-B[[1,i,1]]+2;
B[[19,i,2]]=-B[[1,i,3]]+2;
B[[19,i,3]]=-B[[1,i,2]]+2;

B[[20,i,1]]=B[[1,i,1]];
B[[20,i,2]]=-B[[1,i,3]]+2;
B[[20,i,3]]=B[[1,i,2]];

B[[21,i,1]]=B[[1,i,3]];
B[[21,i,2]]=B[[1,i,2]];
B[[21,i,3]]=-B[[1,i,1]]+2;

B[[22,i,1]]=B[[1,i,3]];
B[[22,i,2]]=-B[[1,i,2]]+2;
B[[22,i,3]]=B[[1,i,1]];

B[[23,i,1]]=-B[[1,i,3]]+2;
B[[23,i,2]]=B[[1,i,2]];
B[[23,i,3]]=B[[1,i,1]];

B[[24,i,1]]=-B[[1,i,3]]+2;
B[[24,i,2]]=-B[[1,i,2]]+2;
B[[24,i,3]]=-B[[1,i,1]]+2;

B[[25,i,1]]=-B[[1,i,1]]+2;
B[[25,i,2]]=-B[[1,i,2]]+2;
B[[25,i,3]]=-B[[1,i,3]]+2;
```

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B[[26,i,1]]=B[[1,i,1]];
B[[26,i,2]]=B[[1,i,2]];
B[[26,i,3]]=-B[[1,i,3]]+2;

B[[27,i,1]]=B[[1,i,1]];
B[[27,i,2]]=-B[[1,i,2]]+2;
B[[27,i,3]]=B[[1,i,3]];

B[[28,i,1]]=-B[[1,i,1]]+2;
B[[28,i,2]]=B[[1,i,2]];
B[[28,i,3]]=B[[1,i,3]];

B[[29,i,1]]=-B[[1,i,3]]+2;
B[[29,i,2]]=-B[[1,i,1]]+2;
B[[29,i,3]]=-B[[1,i,2]]+2;

B[[30,i,1]]=-B[[1,i,3]]+2;
B[[30,i,2]]=B[[1,i,1]];
B[[30,i,3]]=B[[1,i,2]];

B[[31,i,1]]=B[[1,i,3]];
B[[31,i,2]]=B[[1,i,1]];
B[[31,i,3]]=-B[[1,i,2]]+2;

B[[32,i,1]]=B[[1,i,3]];
B[[32,i,2]]=-B[[1,i,1]]+2;
B[[32,i,3]]=B[[1,i,2]];

B[[33,i,1]]=-B[[1,i,2]]+2;
B[[33,i,2]]=-B[[1,i,3]]+2;
B[[33,i,3]]=-B[[1,i,1]]+2;

B[[34,i,1]]=B[[1,i,2]];
B[[34,i,2]]=-B[[1,i,3]]+2;
B[[34,i,3]]=B[[1,i,1]];

B[[35,i,1]]=-B[[1,i,2]]+2;
B[[35,i,2]]=B[[1,i,3]];
B[[35,i,3]]=B[[1,i,1]];

B[[36,i,1]]=B[[1,i,2]];
B[[36,i,2]]=B[[1,i,3]];
B[[36,i,3]]=-B[[1,i,1]]+2;

B[[37,i,1]]=-B[[1,i,2]]+2;
B[[37,i,2]]=-B[[1,i,1]]+2;
B[[37,i,3]]=B[[1,i,3]];

B[[38,i,1]]=B[[1,i,2]];
B[[38,i,2]]=B[[1,i,1]];
B[[38,i,3]]=B[[1,i,3]];

B[[39,i,1]]=-B[[1,i,2]]+2;
B[[39,i,2]]=B[[1,i,1]];
B[[39,i,3]]=-B[[1,i,3]]+2;

B[[40,i,1]]=B[[1,i,2]];
B[[40,i,2]]=-B[[1,i,1]]+2;
```

```
        B[[40,i,3]]=-B[[1,i,3]]+2;

        B[[41,i,1]]=-B[[1,i,1]]+2;
        B[[41,i,2]]=-B[[1,i,3]]+2;
        B[[41,i,3]]=B[[1,i,2]];

        B[[42,i,1]]=B[[1,i,1]];
        B[[42,i,2]]=-B[[1,i,3]]+2;
        B[[42,i,3]]=-B[[1,i,2]]+2;

        B[[43,i,1]]=B[[1,i,1]];
        B[[43,i,2]]=B[[1,i,3]];
        B[[43,i,3]]=B[[1,i,2]];

        B[[44,i,1]]=-B[[1,i,1]]+2;
        B[[44,i,2]]=B[[1,i,3]];
        B[[44,i,3]]=-B[[1,i,2]]+2;

        B[[45,i,1]]=-B[[1,i,3]]+2;
        B[[45,i,2]]=-B[[1,i,2]]+2;
        B[[45,i,3]]=B[[1,i,1]];

        B[[46,i,1]]=-B[[1,i,3]]+2;
        B[[46,i,2]]=B[[1,i,2]];
        B[[46,i,3]]=-B[[1,i,1]]+2;
        B[[47,i,1]]=B[[1,i,3]];
        B[[47,i,2]]=-B[[1,i,2]]+2;
        B[[47,i,3]]=-B[[1,i,1]]+2;

        B[[48,i,1]]=B[[1,i,3]];
        B[[48,i,2]]=B[[1,i,2]];
        B[[48,i,3]]=B[[1,i,1]],

        {i,1,MaxA}];

(* Save the results as an array of coordinates *)
axisshrink=Partition[Flatten[B]/2,3];
lengaxis=Length[axisshrink];
(* Convert 3-D plot into multiple 2-D slices *)
scatter3d=Array[0,21];
Do[scatter3d[[m]]=Select[axisshrink,Abs[#[[3]]-(m-1)/20] ≤ 0.006&], {m,1,21}];
scatter2d=Array[0,21];
Do[scatter2d[[m]] = #[[All,1;;2]] & [scatter3d[[m]]],{m,1,21}];
scatterplot2d=Table[ListPlot[scatter2d[[i]], PlotRange → {{0,1}, {0,1}}, PlotStyle → {PointSize[0.015], Black}, AspectRatio → 1],{i,1,21}]
 (* electron density contour from saxs *)
g[h_,k_,l_]:=Cos[2π (h x)] Cos[2π (k y)]Cos[2π (l z)];
 (* Intensity recorded and calculated from 16SBA09-calcined on 29 Nov 2010 02:28:19 *)
a=1;
b=1;
c=1;
d=1;
f[x_,y_,z_]:=a*(100)/2(g[1,1,0]+g[1,0,1]+g[0,1,1])+
                    b*(19.23)/4(g[2,0,0]+g[0,2,0]+g[0,0,2])+
                    c*(1.84)(g[2,1,1]+g[1,2,1]+g[1,1,2])+
                    d*(14.09)/2(g[2,2,0]+g[0,2,2]+g[2,0,2])
xrdplot=Table[z=i;RegionPlot[f[x,y,z] ≤ -1.444,{x,0,1}, 75, PerformanceGoal → "Quality", PlotStyle → LightBlue, BoundaryStyle →
                     {Thickness[0.005],Blue}], {i,0,1,0.05}];
 (* make a comparison *)
Table[Show[xrdplot[[i]], scatterplot2d[[i]], PlotLabel → layer = (i-1)/20, AspectRatio → 1, Frame → False],{i,1,11}]
```