**Supplementary information for Strain and grain size of CeO2 and TiO2 nanoparticles: Comparing structural and morphological methods**

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**Supplementary Figures and Tables**



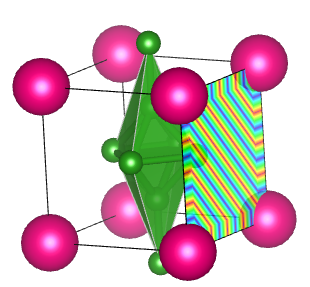
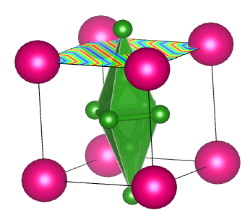
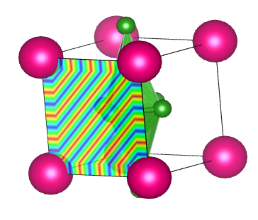
Figure S1. Pure p-XRD pattern of CeO2 (a) and TiO2 NPs (b).



Figure S2.The modified W-H analysis of CeO2 (a) and TiO2 NPs (b), assuming USDM. The modified W-H analysis of CeO2 (c) and TiO2 NPs (d), assuming UDEDM.

**Rietveld Refinement of LaB6 nano standard**

Figure S3a shows the Rietveld refinement of the LaB6 pattern which allowed us to obtain crystal structure information by X-ray diffraction (XRD). The Rietveld refinement with the TCH function of this pattern gave a unit-cell parameter (a) and boron atomic position (z) of 4.155728 Å and 0.20395, respectively (Rwp = 11.4 %, RB = 5.104%).  Therefore, refinement of the pattern subtracts the broadening caused by the instrument, so that the sample contributes 100% of the peak broadening, thus being able to calculate the mean apparent size of the LaB6 standard, which was 40.5 nm.



**a)**

b)

c)

d)

Figure S3**.** Rietveld refinement using the TCH function for LaB6 (a). The observed experimental diffractograms are given by the red lines (Iobs), the black lines (Ical) are calculated diffractograms, and the residual lines are shown in blue color. Electron density model with 0.4 Å resolution of LaB6 for the (hkl) lattice planes (1 0 0) (b), (0 0 1) (c), and (0 1 0) (d).

Table S1. Rietveld refinement parameters of nano LaB6 standard using the Fullprof program.

|  |  |
| --- | --- |
| **Refinement Parameters** | **LaB6** |
| a (Å) | 4.155728 |
| b (Å) | 4.155728 |
| c (Å) | 4.155728 |
| α (Å) | 90 |
| β (Å) | 90 |
| γ (Å) | 90 |
| V (Å3) | 71.7697 |
| FWHM parameters |  |
| U | 0.075526 |
| V | -0.068130 |
| W | 0.059013 |
| Global average size (nm) | 40.5 |
| Rp (%) | 11.6 |
| Rwp (%) | 11.44 |
|  |  |

|  |  |  |
| --- | --- | --- |
|  |  |  |
| **Supplementary Matlab code R2017b**  clear,clc  betha=input('Enter betha in brackets (rad): ');  theta\_1=input('Enter 2\*tetha in brackets (rad): ');  theta=theta\_1\*pi/180;  betha\_S=betha.\*(pi/180);  h=input('Enter the plane h: ');  k=input('Enter the plane k: ');  l=input('Enter the plane l: ');  a=input('Enter the cell parameter a: ');  b=input('Enter the cell parameter b: ');  c=input('Enter the cell parameter c: ');  n=length(betha);  crystal=input('Enter the crystal system: ','s');  for i=1:n      %betha correction      betha\_Cor(i)=sqrt(betha(i)^2-0.01^2);      betha\_C(i)=betha\_Cor(i)\*pi/180; %radians      %scherrer      D0(i)=0.154056\*0.94/(betha\_C(i)\*cos(theta(i)/2));      %Modified Scherrer Equation (Monshi–Scherrer Method)      x0(i)=log(1/cos(theta(i)/2));%(degree)      y0(i)=log(betha\_C(i));%(radians)      %Williamson–Hall’s (W-H) (UDM)      x1(i)=4\*sin(theta(i)/2);y1(i)=betha\_C(i)\*cos(theta(i)/2);      %Williamson–Hall’s (W-H) (USDM)      %young's modulus and interplanar distance      switch crystal          case 'cubic'              C11=455.06\*10^9;C12=188.74\*10^9;C44=81.48\*10^9;%N/m^2              s11=(C11+C12)/((C11-C12)\*(C11+2\*C12));s12=-C12/((C11-C12)\*(C11+2\*C12));s44=1/C44;              l\_yhkl(i)=s11-2\*((s11-s12)-1/2\*s44)\*((h(i)^2\*k(i)^2+k(i)^2\*l(i)^2+...              l(i)^2\*h(i)^2)/(h(i)^2+k(i)^2+l(i)^2)^2);              Yhkl(i)=(1/l\_yhkl(i))\*10^-12; %Tpas              Yhkl2(i)=(1/l\_yhkl(i))\*10^-9; %Gpas              l\_d(i)=(h(i)^2+k(i)^2+l(i)^2)/a^2;              dhkl(i)=sqrt(1/l\_d(i));          case 'tetragonal'              s11=5.1\*10^-12;s12=-8\*10^-13;s13=-3.3\*10^-12;s33=1.07\*10^-11;              s44=1.85\*10^-11;s66=1.67\*10^-11;              Yhkl(i)=((h(i)^2+k(i)^2+l(i)^2)^2/(s11\*(h(i)^4+k(i)^4)+(2\*s12+s66)\*...                  h(i)^2\*k(i)^2+(2\*s13+s44)\*(h(i)^2+k(i)^2)\*l(i)^2+s33\*l(i)^4))\*10^-12;              l\_d(i)=(h(i)^2+k(i)^2)/a^2+l(i)^2/c^2;              dhkl(i)=sqrt(1/l\_d(i));              Yhkl2(i)=(Yhkl(i))\*10^3; %Gpas           otherwise              disp('error')      end      x2(i)=4\*sin(theta(i)/2)/Yhkl(i);y2(i)=betha\_C(i)\*cos(theta(i)/2);      %UDEDM      x3(i)=4\*sin(theta(i)/2)\*(2/Yhkl(i))^0.5;y3(i)=betha\_C(i)\*cos(theta(i)/2);      %size-strain (SSP)      x4(i)=(dhkl(i)\*0.1)^2\*betha\_C(i)\*cos(theta(i)/2)/0.154056;      y4(i)=(dhkl(i)\*0.1\*betha\_C(i)\*cos(theta(i)/2)/0.154056)^2;      %Halder–Wagner (H-W)      x5(i)=betha\_C(i)\*(cos(theta(i)/2)/0.154056)/(2\*dhkl(i)\*sin(theta(i)/2)/0.154056)^2;      y5(i)=(betha\_C(i)\*(cos(theta(i)/2)/0.154056)/(2\*dhkl(i)\*sin(theta(i)/2)/0.154056))^2;    end  disp('--------------------------------------------------------------------------')  disp('hkl   2\*theta theta(Degree)  betha    b\_corrected  betha    yhkl    dhkl')  disp('     (Degree)   (Degree)    (Degree)   (Degree)   (radian)  (Tpa)   (A°)')  disp('--------------------------------------------------------------------------')  for i=1:n  fprintf('%1.0f%1.0f%1.0f  %4.4f    %4.4f      %2.4f    %2.4f     %2.4f    %2.4f    %2.4f\n',...      h(i),k(i),l(i),theta\_1(i),theta\_1(i)/2,betha(i),betha\_Cor(i),betha\_C(i),Yhkl(i),dhkl(i))  end  disp('=============Scherrer´s method================')  D\_prom=sum(D0)/n;  fprintf(' Crystal size =%6.6f nm \n',D\_prom)  disp('==Modified Scherrer (Monshi–Scherrer Method)===')  Ec0=polyfit(x0,y0,1);D00=0.154056\*0.94/(exp(Ec0(2)));R0=corrcoef(x0,y0);  R0\_1=1-(n-1)/(n-length(Ec0))\*(1-R0(1,2)^2);  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n',Ec0(2),Ec0(1),R0\_1)  fprintf('Crystal size=%6.6f nm\n',D00)  disp('============== UDM method  ===================')  Ec1=polyfit(x1,y1,1);D1=0.154056\*0.94/Ec1(2);R1=corrcoef(x1,y1);  R2\_1=1-(n-1)/(n-length(Ec1))\*(1-R1(1,2)^2);  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n',Ec1(2),Ec1(1),R2\_1)  fprintf('Crystal size=%6.6f nm\n strain=%6.6f\n',D1,Ec1(1))  disp('============== USDM method ==================')  Ec2=polyfit(x2,y2,1);D2=0.154056\*0.94/Ec2(2);  R2=corrcoef(x2,y2);R2\_3=1-(n-1)/(n-length(Ec2))\*(1-R2(1,2)^2);  ep=Ec2(1)/(sum(Yhkl(i))/n); Young=sum(Yhkl2)/n;  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n  Young=%6.5f Gpas\n',Ec2(2),Ec2(1),R2\_3,Young)  fprintf('Crystal size=%6.6fnm\n stress=%6.6f TPa\n eps=%6.6f\n',D2,Ec2(1),ep)  disp('============== UDEDM method ================')  Ec3=polyfit(x3,y3,1);D3=0.154056\*0.94/Ec3(2);R3=corrcoef(x3,y3);  R2\_5=1-(n-1)/(n-length(Ec3))\*(1-R3(1,2)^2);  U=sqrt(Ec3(1));sigmaprom=sqrt(U\*2\*(sum(Yhkl(i))/n));  epsprom1=sigmaprom/(sum(Yhkl(i))/n);  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n',Ec3(2),Ec3(1),R2\_5)  fprintf('Crystal size=%6.6fnm\n U=%6.6f TJ/m^3\n',D3,U)  fprintf('stress=%6.6f TPa\n eps=%6.6f\n\n',sigmaprom,epsprom1)  disp('==============size-strain (SSP)==============')  Ec4=polyfit(x4,y4,1);D4=0.75/Ec4(1);R4=corrcoef(x4,y4);  R2\_7=1-(n-1)/(n-length(Ec4))\*(1-R4(1,2)^2);  epsprom2=sqrt(abs(Ec4(2))\*4);  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n ',Ec4(2),Ec4(1),R2\_7)  fprintf('Crystal size=%6.6fnm\n eps=%6.6f\n',D4,epsprom2)  disp('==============Halder–Wagner (H-W)==============')  Ec5=polyfit(x5,y5,1);D5=1/Ec5(1);R5=corrcoef(x5,y5);  R2\_9=1-(n-1)/(n-length(Ec5))\*(1-R5(1,2)^2);  eps5=sqrt(abs(Ec5(2))\*4);  fprintf('intercept=%6.6f\n slope=%6.6f\n R^2=%2.4f\n ',Ec5(2),Ec5(1),R2\_9)  fprintf('Crystal size=%6.6fnm\n eps=%6.6f\n',D5,eps5)  **1.- TiO2**  Crystal system: tetragonal  Enter betha in brackets (rad):  [0.58184;1.22664;0.53095;0.99278;0.68039;0.95882;0.85614;0.91353;1.11756;1.04971;1.48319;1.32014]  Enter 2\*tetha in brackets (rad):  [25.41164;37.29742;37.94847;38.51314;48.16671;54.12399;55.16213;62.78055;69.00174;70.38002;75.31759;82.91796]  Enter the plane h: [1;1;0;1;2;1;2;2;2;1;2;2]  Enter the plane k: [0;0;0;1;0;0;1;1;0;1;2;1]  Enter the plane l: [1;3;4;2;0;5;1;3;4;6;0;5]  Enter the cell parameter a: 3.7892  Enter the cell parameter b: 3.7892  Enter the cell parameter c: 9.5370  Enter the crystal system: tetragonal  --------------------------------------------------------------------------  hkl   2\*theta theta(Degree)  betha    b\_corrected  betha    yhkl    dhkl       (Degree)   (Degree)    (Degree)   (Degree)   (radian)  (Tpa)   (A°)  --------------------------------------------------------------------------  101  25.4116    12.7058      0.5818    0.5818     0.0102    0.1444    3.5214  103  37.2974    18.6487      1.2266    1.2266     0.0214    0.1022    2.4354  004  37.9485    18.9742      0.5310    0.5309     0.0093    0.0935    2.3843  112  38.5131    19.2566      0.9928    0.9927     0.0173    0.1234    2.3359  200  48.1667    24.0834      0.6804    0.6803     0.0119    0.1961    1.8946  105  54.1240    27.0620      0.9588    0.9588     0.0167    0.0967    1.7037  211  55.1621    27.5811      0.8561    0.8561     0.0149    0.1657    1.6684  213  62.7805    31.3903      0.9135    0.9135     0.0159    0.1265    1.4954  204  69.0017    34.5009      1.1176    1.1175     0.0195    0.1117    1.4833  116  70.3800    35.1900      1.0497    1.0497     0.0183    0.0979    1.3670  220  75.3176    37.6588      1.4832    1.4832     0.0259    0.1581    1.3397  215  82.9180    41.4590      1.3201    1.3201     0.0230    0.1081    1.2668  =============Scherrer´s method================   Crystal size =10.493920 nm  ==Modified Scherrer (Monshi–Scherrer Method)===  intercept=-4.472674  slope=2.678714  R^2=0.4342  Crystal size=12.684231 nm  ============== UDM method  ===================  intercept=0.008894   slope=0.003206   R^2=0.1455  Crystal size=16.281429 nm   strain=0.003206  ============== USDM method ==================  intercept=0.010850   slope=0.000256   R^2=0.0757    Young=127.01714 Gpas  Crystal size=13.347166nm   stress=0.000256 TPa   eps=0.028390  ============== UDEDM method ================  intercept=0.009573   slope=0.000698   R^2=0.1288  Crystal size=15.127003nm   U=0.026424 TJ/m^3  stress=0.021824 TPa   eps=2.421569  ==============size-strain (SSP)==============  intercept=-0.000011   slope=0.099077   R^2=0.7394   Crystal size=7.569883nm   eps=0.006751  ==============Halder–Wagner (H-W)==============  intercept=-0.000087   slope=0.196469   R^2=0.9657   Crystal size=5.089850nm   eps=0.018624  **2.- CeO2**  Crystal system: cubic  matlab program:  Enter betha in brackets (rad): [0.37541;0.38647;0.40748;0.43751;0.41716;0.47768;0.54051;0.51532;0.66622;0.73322]  Enter 2\*tetha in brackets (rad):  [28.56556;33.11107;47.55147;56.42074;59.16356;69.80874;76.80871;79.17714;88.55375;95.5336]  Enter the plane h: [1;2;2;3;2;4;3;4;4;3]  Enter the plane k: [1;0;2;1;2;0;3;2;2;3]  Enter the plane l: [1;0;0;1;2;0;1;0;2;3]  Enter the cell parameter a: 5.4097  Enter the cell parameter b: 5.4097  Enter the cell parameter c: 5.4097  Enter the crystal system: cubic  --------------------------------------------------------------------------  hkl   2\*theta theta(Degree)  betha    b\_corrected  betha    yhkl    dhkl       (Degree)   (Degree)    (Degree)   (Degree)   (radian)  (Tpa)   (A°)  --------------------------------------------------------------------------  111  28.5656    14.2828      0.3754    0.3753     0.0065    0.2226    3.1233  200  33.1111    16.5555      0.3865    0.3863     0.0067    0.3444    2.7048  220  47.5515    23.7757      0.4075    0.4074     0.0071    0.2442    1.9126  311  56.4207    28.2104      0.4375    0.4374     0.0076    0.2739    1.6311  222  59.1636    29.5818      0.4172    0.4170     0.0073    0.2226    1.5616  400  69.8087    34.9044      0.4777    0.4776     0.0083    0.3444    1.3524  331  76.8087    38.4044      0.5405    0.5404     0.0094    0.2375    1.2411  420  79.1771    39.5886      0.5153    0.5152     0.0090    0.2728    1.2096  422  88.5537    44.2769      0.6662    0.6661     0.0116    0.2442    1.1043  333  95.5336    47.7668      0.7332    0.7332     0.0128    0.2226    1.0411  =============Scherrer´s method================   Crystal size =20.778772 nm  ==Modified Scherrer (Monshi–Scherrer Method)===  intercept=-5.115142  slope=1.827695  R^2=0.9608  Crystal size=24.114843 nm  ============== UDM method  ===================  intercept=0.004994   slope=0.000992   R^2=0.6279  Crystal size=28.995433 nm   strain=0.000992  ============== USDM method ==================  intercept=0.005262   slope=0.000219   R^2=0.6747    Young=262.93949 Gpas  Crystal size=27.519766nm   stress=0.000219 TPa   eps=0.009852  ============== UDEDM method ================  intercept=0.005077   slope=0.000340   R^2=0.6808  Crystal size=28.525735nm   U=0.018450 TJ/m^3  stress=0.028663 TPa   eps=1.287381  ==============size-strain (SSP)==============  intercept=0.000005   slope=0.039794   R^2=0.9964   Crystal size=18.846957nm   eps=0.004653  ==============Halder–Wagner (H-W)==============  intercept=-0.000023   slope=0.096611   R^2=0.9986   Crystal size=10.350833nm   eps=0.009584 | | | |