Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

On the electrochemical encounter between sodium and mesoporous anatase TiO_2 as Na-ion electrode.

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Table S1. XPS analysis results for both powder and electrode sample of sol-gel TiO_2.

Element	Powder at.%	Electrode at.%
C 1s	33.39	51.02
O 1s	47.86	35.49
Ti 2p	18.74	0.34
Na 1s	0.00	13.16
Total:	100.00	100.00

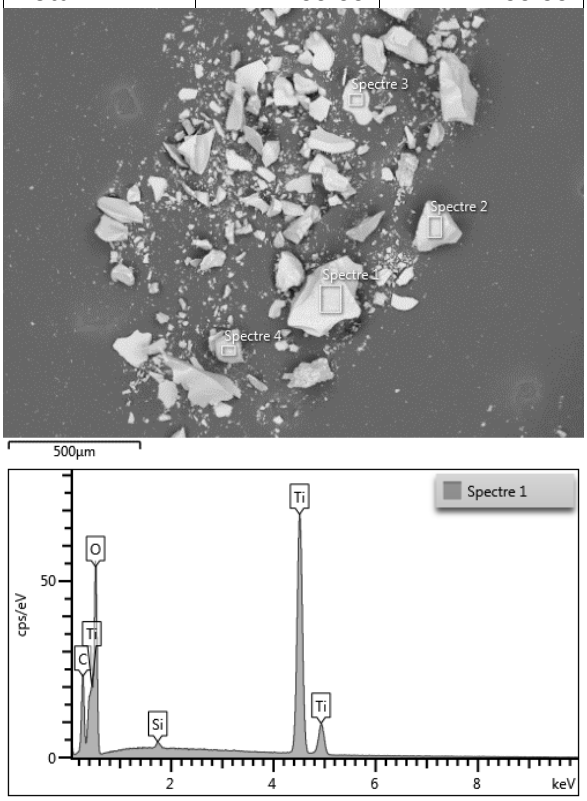

Figure S1. SEM image and EDX spectrum of powder sample of sol-gel TiO_2. The squares represent the areas studied by EDX.

Table S2. EDX results for powder sample of TiO_2.

Element	Wt.%	At.%
O	36.93	63.59
Si	0.32	0.31
Ti	62.76	36.10
Total:	100.00	100.00

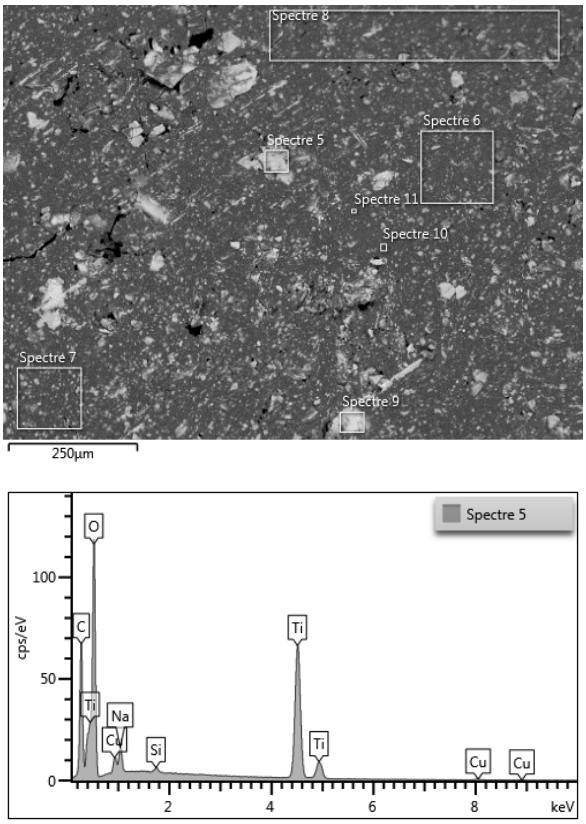

Figure S2. SEM image and EDX spectrum of an electrode sample of sol-gel TiO_2. The squares represent the areas studied by EDX.

Table S3. EDX results for electrode sample of TiO_2.

Element	Wt.%	At.%
O	46.91	71.91
Na	2.25	2.40
Si	0.33	0.29
Ti	46.82	23.97
Cu	3.68	1.42
Total:	100.00	100.00

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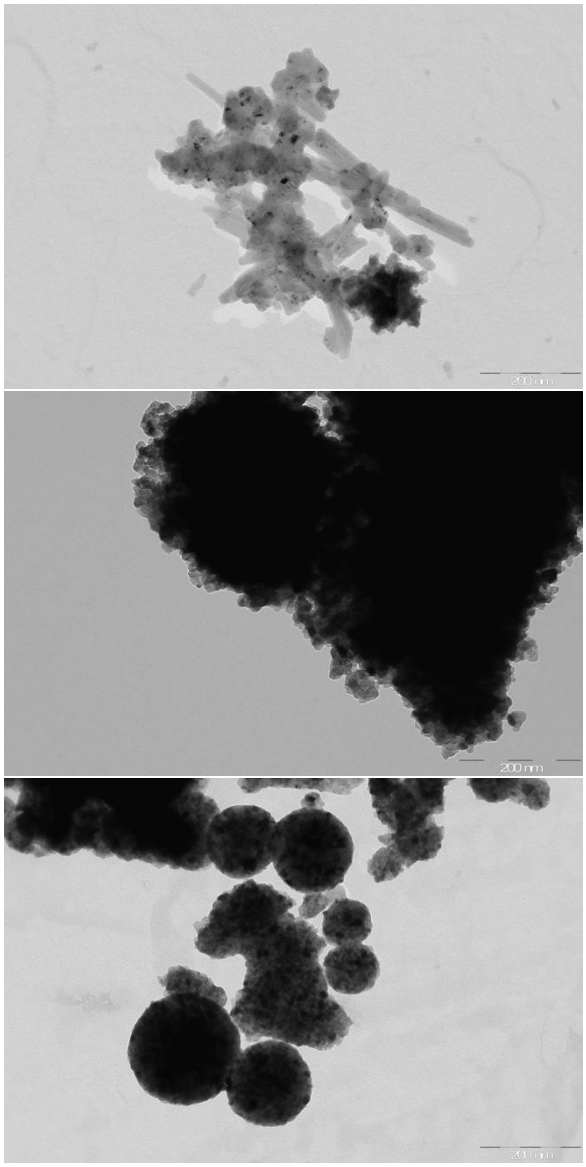

Figure S3. TEM images of sol-gel TiO_2 powder sample before (top image) and after calcination at 400 °C (middle and bottom images).

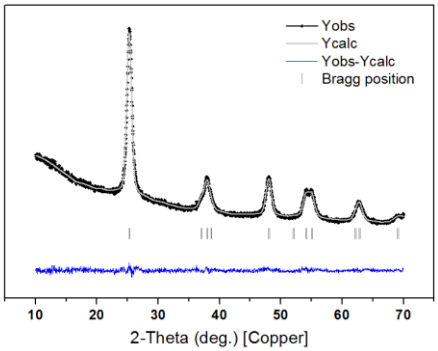

Figure S4. Profile matching result for the XRD pattern of TiO_2-C400 (experimental points = black squares; simulated pattern = grey line; difference between experimental and simulated points = blue line; Bragg's peaks position = grey marks).

Table S4. Profile matching details for TiO_2-C400.

```
=> Wavelengths:  1.54056 1.54439
==> RESULTS OF REFINEMENT:
-------------------------------------------------------------
------------------&
 => Phase No.  1 TiO2                                    I
41/a m d
-------------------------------------------------------------
------------------
=>  No. of reflections for pattern#:   1:    22/2
==> PROFILE PARAMETERS FOR PATTERN#  1
=> Cell parameters      :
                             3.78721   0.00051
                             3.78721   0.00051
                             9.47664   0.00146
                            90.00000   0.00000
                            90.00000   0.00000
                            90.00000   0.00000

 => overall scale factor :      0.001000000     0.000000000
 => Eta(p-v) or m(p-vii) :     0.45731   0.00879
 => Overall tem. factor  :     0.00000   0.00000
 => Halfwidth parameters :     1.61766   0.10051
                              -0.00762   0.00000
                               0.82914   0.01193
==> GLOBAL PARAMETERS FOR PATTERN#  1
=> Zero-point:     0.0000    0.0000
 => Cos( theta)-shift parameter :  -0.0188  0.0045
 => Sin(2theta)-shift parameter :   0.0000  0.0000

 ==> RELIABILITY FACTORS WITH ALL NON-EXCLUDED POINTS FOR
PATTERN:  1

  => Cycle:  4 => MaxCycle: 15
 => N-P+C:  2301
 =>  R-factors (not corrected for background) for Pattern:
1
 => Rp:  2.88     Rwp:  3.77     Rexp:    3.37 Chi2:  1.25
L.S. refinement
 => Conventional Rietveld R-factors for Pattern:  1
 => Rp:  16.4     Rwp:  12.1     Rexp:   10.82 Chi2:  1.25
 => Deviance:  0.287E+04     Dev*  :   1.247
 => DW-Stat.:    1.0121     DW-exp:     1.8757
 => N-sigma of the GoF:    8.613

 ==> RELIABILITY FACTORS FOR POINTS WITH BRAGG CONTRIBUTIONS
FOR PATTERN:  1

 => N-P+C:  2007
 =>  R-factors (not corrected for background) for Pattern:
1
```

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```
 => Rp:  3.14     Rwp:  4.06     Rexp:    3.58 Chi2:  1.29
L.S. refinement
 => Conventional Rietveld R-factors for Pattern:  1
 => Rp:  13.9     Rwp:  11.5     Rexp:   10.12 Chi2:  1.29
 => Deviance:  0.257E+04     Dev*  :   1.278
 => DW-Stat.:    1.1302     DW-exp:     1.8673
 => N-sigma of the GoF:        9.105

 => Global user-weigthed Chi2 (Bragg contrib.):   1.44

     ---------------------------------------------------
     BRAGG R-Factors and weight fractions for Pattern #  1
     ---------------------------------------------------

 => Phase:  1     TiO2
 => Bragg R-factor:  0.217       Vol:  135.923( 0.033)
Fract(%):    0.00( 0.00)
 => Rf-factor= 0.234             ATZ:          0.000
Brindley:  1.0000


       ---------------------------------------------------
       -    ANALYSIS OF THE REFINEMENT FOR PATTERN #  1    -
       ---------------------------------------------------


 => GLOBAL INDICATORS:

    The first and last reflections appears at:
    2theta(degrees)/T.O.F(microsecs)/Energy(KeV) =>
25.305         68.973
    s (angstroms-1) =>      0.2844    0.7351
    D (angstroms  ) =>      3.5167    1.3604
    sin(theta/lamb) =>      0.1422    0.3675
    Q (angstroms-1) =>      3.5734    9.2372

    The average FWHM is:   1.0928   Fwhm(av)/step =   42.0300

 => Sum(Yiobs-Yical):     -821.29    1679.91   -1109.78
196.34 <- Four regions
            Total ->       -54.82

  Expected Rp (background uncorrected):     2.10 Observed->
2.88
  Expected cRp(background   corrected):    11.98 Observed->
16.41
  -> Ratio Rp/Exp=cRp/cExp:     1.37
  Weighted Average Bragg R-factor:     0.22
  Weighted Average      RF-factor:     0.23
  Reduced Chi-square :     1.29

 => Total number of "independent" reflections:     11
    Effective number (account for resolution) of
reflections:
                      at level p=1.00  :   7.3
                      at level p=0.50  :  11.0
                      at level p=0.25  :  11.0

    A reflection contributes as x/(x+nearest), where "x"
    is the fraction of the total area of the current phase
and
   "nearest" is the number of adjacent reflections verifying
the formula:

    Postn-p*FWHM <= Postn(adjacent) <= Postn+p*FWHM

   "nearest" is weighted by the corresponding "x(s)"

 =>             Number of global  refined parameters:      1
                Number of profile refined parameters:      5
    Number of intensity-affecting refined parameters:      0
      (Preferred orientation belongs to this class)

 => (Effective Number of reflections)/(Number of intensity
parameters)= refni
      Ratio ( Optimistic view,p=0.25):   11.0
      Ratio (Pessimistic view,p=1.00):    7.3
      Ratio (   Eclectic view,p=0.50):   11.0

 => PHASE DEPENDENT INDICATORS:

 => Positions and FWHM of the sharpest reflection

     Phase  2Theta/TOF  FWHM     Q       DQ      Delta
Dd/d(%)
       1      25.30    0.9530   1.7867  0.06619  0.36394
3.705
   Q ,DQ(FWHM in Q-space) and Delta are given in 1/angstroms
 Delta is the expected step between consecutive reflections
at Q
Phase    %Cont  Nintdp  Nprofp   Nref      Enref(Effective)
                                          R:p=1  R:p=1/2
R:p=1/4
     1  100.00       0       5      11    7.33   11.00
11.00
                                                 7.33   11.00
11.00
  Where:
  %Cont: percentage of the total integrated intensity (100x)
 Nintdp: Number of intensity-affecting refined parameters
 Nprofp: Number of profile refined parameters
   Nref: Number "independent" contributing reflections
  Enref: Effective Number of reflections for each p-value
R:p=1/n: Ratio Enref(Effective)/Nintdp
=> ANALYSIS OF STANDARD DEVIATIONS
    Phase:  1 Degrees of freedom for p=1, 1/2, 1/4:     7.33
11.00   11.00
              Chi2 based on integrated intensities:     0.53
0.36    0.36
              Calculated with Scott'S FORMULA     :    79.55
53.36   53.36
=> Standard deviations concern the PRECISION of parameters
and
    represent ACCURACY only if there is no systematic errors
    A better estimate of the accuracy of structural
parameters
    is obtained multiplying sigmas by the parameter SCOR
 -> SCOR =    1.8979 { Berar'S FORMULA}
 -> SCOR =    6.4831 {Pawley'S FORMULA}
 -> Application of modified Scott'S FORMULA
    SCOR(p=1,1/2,1/4) =    0.6434  0.5253  0.5253
    SCOR(expected Si) =    7.8604  6.4382  6.4382
   Warning! Do not take into account Scott'S SCOR
            These indicators are under test....
=> ANALYSIS OF CORRELATED PARAMETERS
  -> The parameter:    2 appears   2 times
  -> The number of correlated parameters is :   1
=> Your refinement seems to be very good!
```

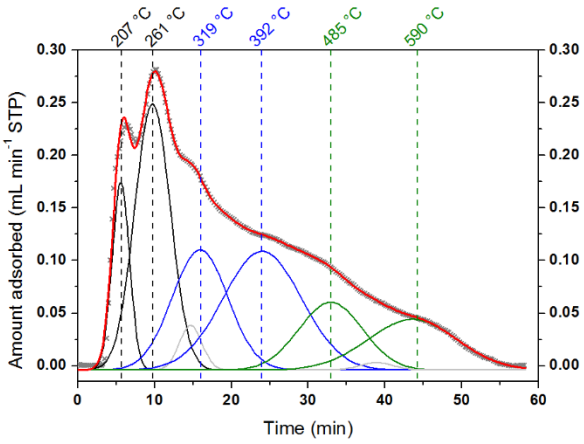

Figure S5. Temperature-programmed desorption of NH_3 for TiO_2-C400.

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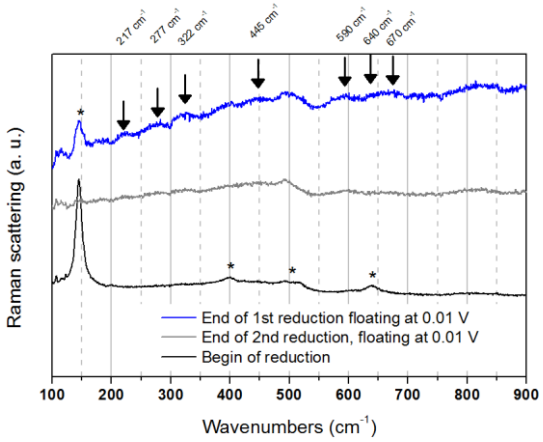

Figure S6. *In situ* Raman spectra of TiO_2-C400 at the beginning (black line), at the end of the 1st galvanostatic discharge (blue line), and at the end of the 2nd galvanostatic discharge (grey line). Each reduction is followed by a 2 hr floating at 0.01 V vs Na^+/Na (potentiostatic mode).