Article

Supplementary Information

1. Supplementary Information

1.1. Surface morphology

Four samples (TiO_2, AC, TiO_2 /AC (ratio 1:1) and TiO_2 /AC (ratio 1:5) were characterized with SEM. Figure S1-A shows that the TiO_2 particles tend to agglomerate into micrometer-sized clusters. Figure S1-B is a typical AC particle. The generally observed AC particle size was in good agreement with the company's claim of 20 µm on average. Although other SEM images showed the AC powder to have quite diverse morphologies, as can be seen from Figure S1, one particular morphology was seen repeatedly, shown in Figure 1-B and D: a hexagonal form with sharp corners and a cylindrical hole in the middle, either seen as a honeycomb structure or long hexagonal fibers. Similar observations have been made by Rusheng et al.[1]. The same authors also found their nanosized TiO_2, agglomerated into micrometer-sized clusters. Pure TiO_2 particles (white particles shown in the figures) (Figure S1) were evenly distributed, compared to activated carbon, the size of TiO_2 was relatively small. Activated carbon (Figure 1 B) As can be seen in Figure S1 C/D, after synthesis, TiO_2 was coated on the surface of activated carbon. The porosity of the TiO_2 was 81.0 %, which resulted in a negligible pressure drop along the reactor. The specific surface area of TiO_2 was 1.52 m^2/g.

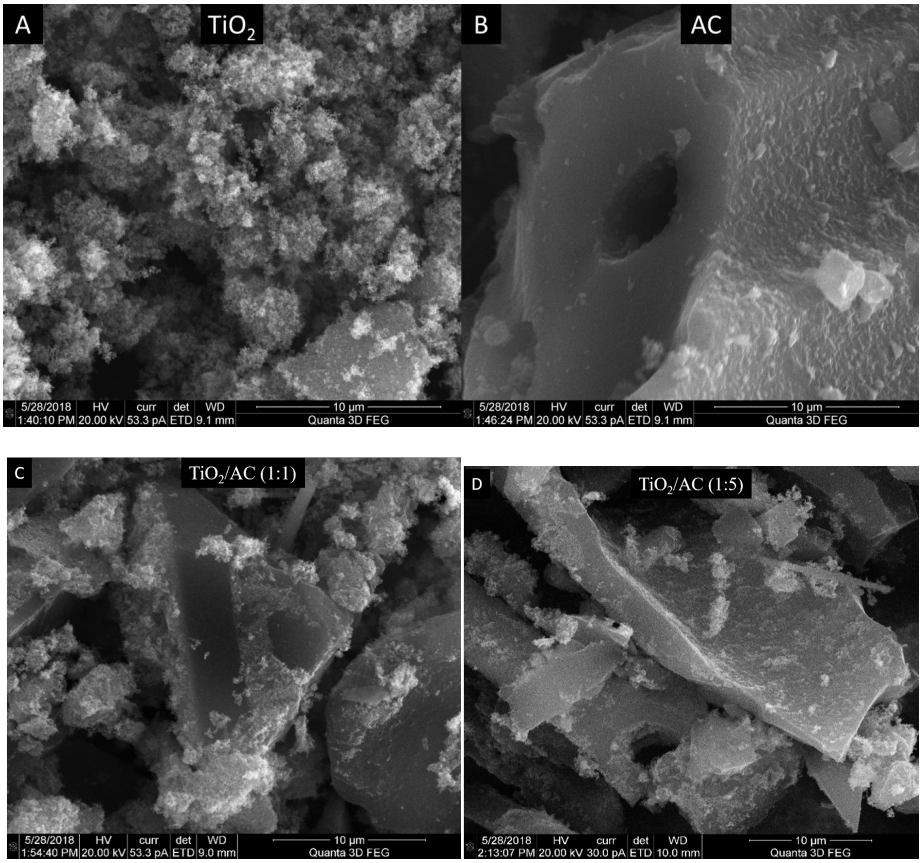

Figure 1. SEM images of samples. A: TiO_2, B: Activated Carbon, C: TiO_2/AC(1:1), d: TiO_2/AC(1:5)

1.2. X-ray diffraction (XRD)

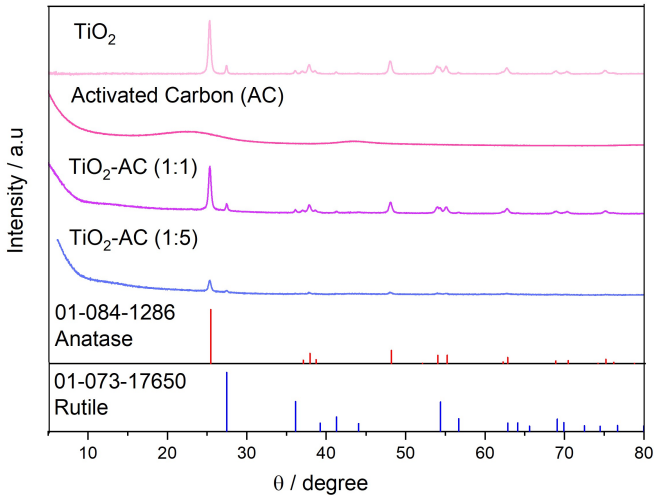

Figure 2. XRD

Figure S2 shows the XRD patterns of samples. The JCPSD database was used as a reference in determining the structure of samples. All peaks can be assigned to the two phases; no additional phases or contaminations are indicated. The diffractogram for the crystal structure Brookite was specifically tested for, since it is a common TiO_2 structure, but no peaks matched. Another observation is the signal of activated carbon. Since activated carbon is an amorphous compound its diffractogram has no defined peaks. It is not perfectly amorphous, so some broad signals are seen. In the mixed samples the broad signals are present below the well defined TiO_2 peaks. The ratio of anatase to rutile was calculated to be around 80:20. Activated carbon showed two characteristic peaks at around 20°to 30°and 40°to 50°, corresponding to the known peaks of activated carbon([2]). After synthesis the crystal structure didn't change. The spectrum also showed the characteristic peak of activated carbon at 10°, which indicates that after synthesis, the TiO_2/AC (1:1 and 1:5) samples contained anatase-and-rutile-phase TiO_2 and AC, which match the SEM image. The peak intensity of anatase and rutile weakened when a higher concentration activated carbon was introduced into TiO_2. No unexpected phases were observed in this experiment. Next, the ratio between the two phases were calculated. For that a Rietveld Refinement was done. TiO_2 was identified as consisting of two phases (shown in Figure S3): anatase and rutile. No brookite peak was found.

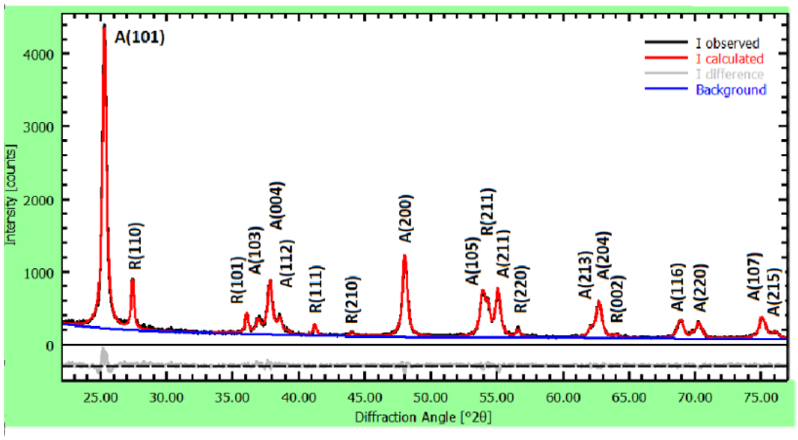

Figure 3. Facet measurement by using refinement Profex(Each peak has been assigned to a miller plane using JCPDS cards 01-084-1286 and 01-073-17650. A is Anatase and R is Rutile peaks.).

1.3. Brunauer-Emmett-Teller (BET) surface area

Table 1: Specific surface area, average particle size and total pore volume of samples.

Sample	TiO_2	AC	TiO_2-AC (1:1)	TiO_2-AC (1:5)
Surface area (m^2/g)	49.53	3907.80 (lm)	1315.77 (1966.94 lm)	2166.31 (3268.95)
Total Pore volume(cm^3/g)	1.74	0.33	1.58	1.72
Average pore size	7.04	1.21	2.41	1.57

The surface area, total pore volume and average pore size were measured. The surface area of activated carbon is determined using the Langmuir equation([3]), while the other parameters were determined by using the BET method. As shown in Table 1, activated carbon has the largest surface area and the smallest pore size. TiO_2 has the smallest surface area and the largest average pore size. The surface area decrease with doping the TiO_2. The same trend are observed both with total pore volume and average pore size.

1.4. X-ray photoelectron spectroscopy (XPS)

Figure S4 and S5 present high resolution XPS spectra of carbon C 1s and titanium Ti 2p region for samplesTiO_2, AC, and 2 samples TiO_2 / AC with ratio 1:1 and 1:5. The Ti 2p signal remains the same for all samples meaning that the chemical state of Ti in the particles do not change. In the C 1s, carbon from C-C (285 eV), C-O (286 eV) and O-C=O (289 eV) is detected on the pure TiO_2 particles, probably small contamination from the synthesis method. The C 1s line for the TiO_2 /AC 1:1 with the highest content of particles is a combination of pure TiO_2 signal and AC signal.

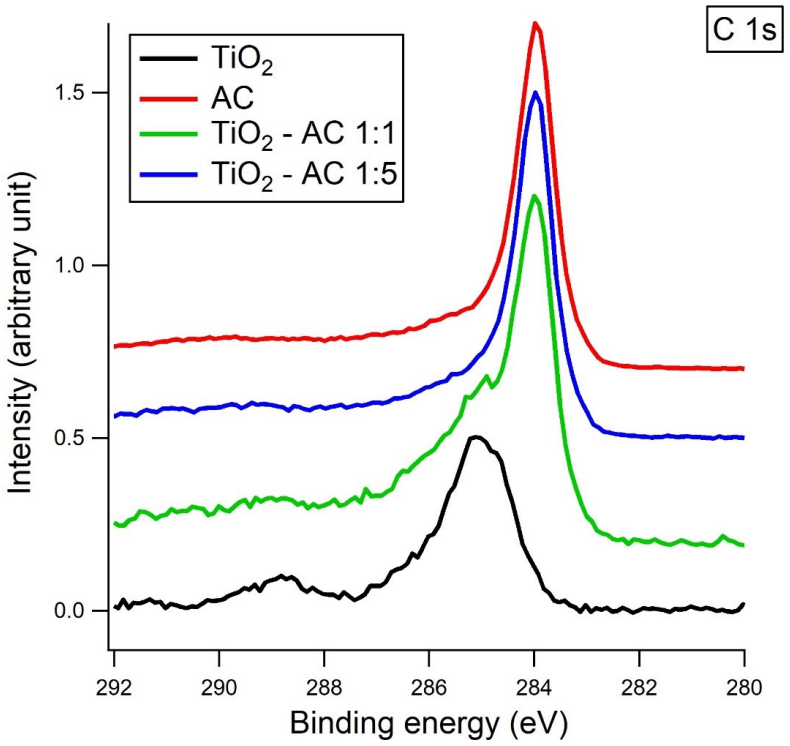

Figure 4. High resolution XPS spectra of C 1s region for TiO_2, AC, and 2 samples TiO_2 – AC with ratio 1:1 and 1:5. The mixed sample with the highest content of TiO_2 (green line) is a combination of TiO_2 carbon signal (black line) and pure AC carbon signal (red line)

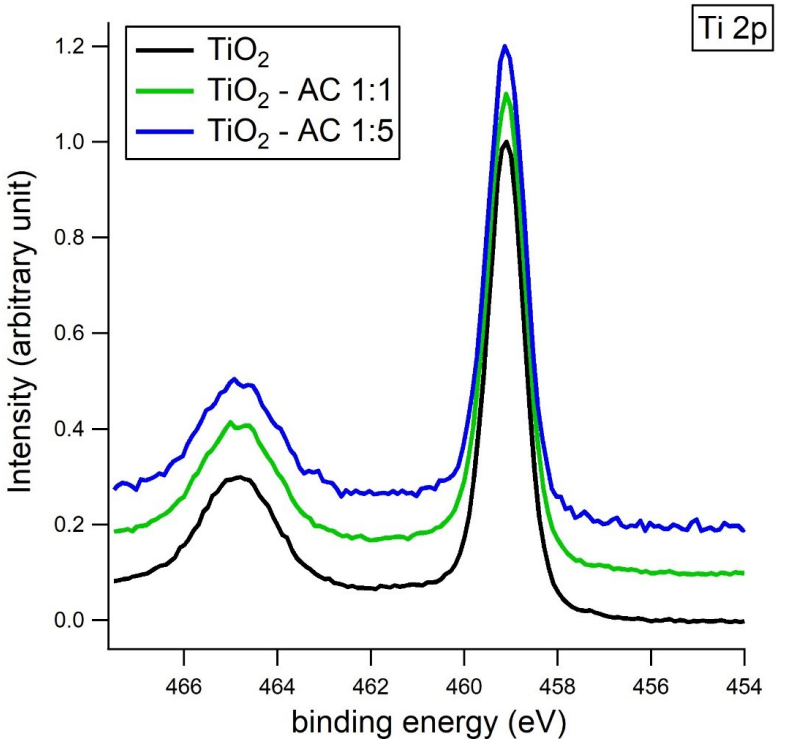

Figure 5. Chemical state of Ti 2p spectra of TiO_2, TiO_2/AC(1:1), TiO_2/AC(1:5)

In Figure S5 and S7, wide spectra for these four samples are displayed. No other element than C, O and Ti are detected meaning that no contamination is observed. It is clear than the signal from Ti (at 459 eV) is increasing with the amount in the

samples. The atomic percentages presented in Table 1 are derived from these graphs. No contamination is detected and only C, O and Ti signals are observed. The relative ratio between C and Ti varies with the amount of Ti in the sample with larger Ti signal for pure TiO_2 (black line) and smaller for TiO_2 / AC (1:5) (blue line). Data have been shifted in Y-axis for easier comparison.

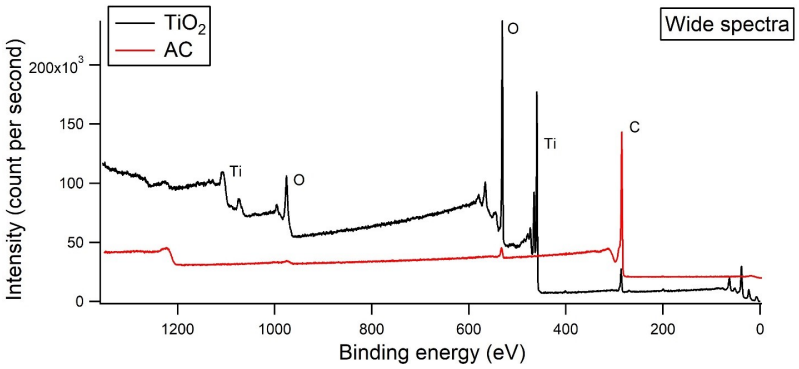

Figure 6. Wide XPS spectra of TiO_2, AC

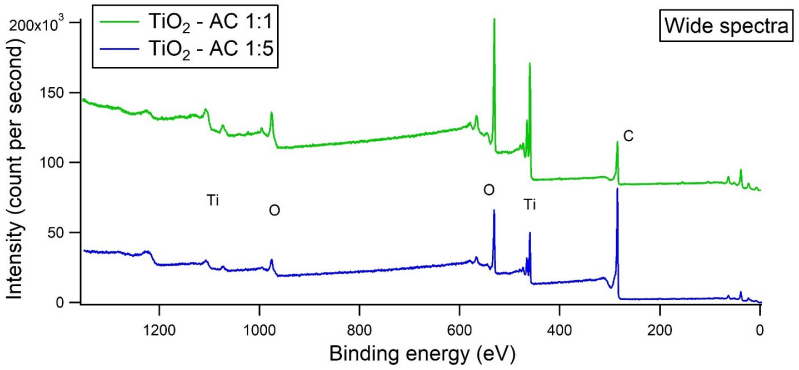

Figure 7. Wide XPS spectra of TiO_2, AC (top) and 2 samples TiO_2 / AC with ratio 1:1 and 1:5 (bottom)

References

1. Sun, X.; Xie, M.; Travis, J.J.; Wang, G.; Sun, H.; Lian, J.; George, S.M. Pseudocapacitance of amorphous TiO2 thin films anchored to graphene and carbon nanotubes using atomic layer deposition. *The Journal of Physical Chemistry C* **2013**, *117*, 22497–22508.
2. Danmaliki, G.I.; Saleh, T.A. Effects of bimetallic Ce/Fe nanoparticles on the desulfurization of thiophenes using activated carbon. *Chemical Engineering Journal* **2017**, *307*, 914–927.
3. Sposito, G. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena: II. The "two-surface" Langmuir equation. *Soil Science Society of America Journal* **1982**, *46*, 1147–1152.