

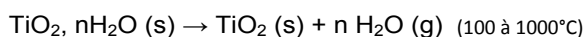
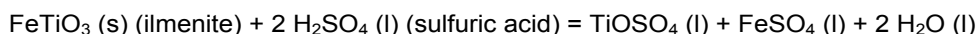
## Electronic Supplementary Information

### Part 1 : Powder manufacturing processes and applications for TiO<sub>2</sub> and SiO<sub>2</sub>

#### Titanium Dioxide powders (TiO<sub>2</sub>)<sup>1, 2</sup>

- Sulfate process (TiO<sub>2</sub> A, C, D and E)

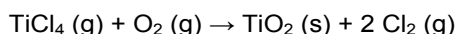
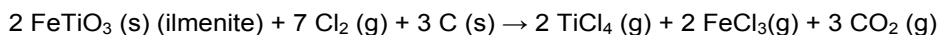
The sulfate process harnessed for TiO<sub>2</sub> synthesis combines several dissolution-precipitation reactions. Sulfuric acid is used to dissolve the gangue from the natural TiO<sub>2</sub> ore ilmenite. Calcination of the precipitated amorphous TiO<sub>2</sub> particles leads to the anatase structure for temperatures under 500°C. Above this limit, rutile structure appears but it is also possible to work under 500°C and add rutile crystals to generate rutile particles growth in the final product. The three main steps of the sulfate process are summarized here after:



The first step is reversible whereas the second and third steps are direct. The powder obtained by this process is more or less hydrated, depending on the temperatures used in the third step. The more the temperature is, the dryer the powder will be.

- Chloride process (TiO<sub>2</sub> B)

The chloride process only leads to the rutile structure. It can be compared to a carbo-thermic reduction. The TiO<sub>2</sub> ore ilmenite is reduced in Titanium by chlorine and carbon in gas phase. Then, the Titanium tetrachloride is oxidized at high temperature (>1000°C) to lead to rutile. The final product is totally dried. The two main steps of the chloride process are summarized here after:



- Applications of TiO<sub>2</sub>

TiO<sub>2</sub> has been widely used for ages in food (sweets, transformed products of fish, biscuits...) and paints as a **white colorant**.

The **photocatalytic properties** of TiO<sub>2</sub> nanoparticles (anatase and rutile) have been implying more and more using in buildings for auto-cleaning windows for instance or in depollution applications. Also, **UV-absorbent** properties of TiO<sub>2</sub> nanoparticles have been leading to add TiO<sub>2</sub> in solar creams and other cosmetic products.

#### Silicon dioxide powders (SiO<sub>2</sub>)<sup>3-6</sup>

- Electrometallurgy

SiO<sub>2</sub> A1 and A2 are unintentional amorphous silica produced during the carbo-thermic reduction of SiO<sub>2</sub> from sand in silicon Si (electrometallurgy process). The SiO<sub>2</sub> fumed produced by this process are extracted in powder form.

- Pyrogenic (SiO<sub>2</sub> B, C, D and E)

The pyrogenic process can be compared with the chloride process for TiO<sub>2</sub>. In this case, the SiCl<sub>4</sub> gas is hydrolyzed at 1000°C to obtain an amorphous SiO<sub>2</sub> powder.

- Precipitated (SiO<sub>2</sub> 244FP and SiO<sub>2</sub> 4850MR)

Precipitated SiO<sub>2</sub> are synthesized by a sol-gel type process in basic media.

- Applications of SiO<sub>2</sub>

Applications of SiO<sub>2</sub> nanomaterial powders are mainly related to the **mechanical particle properties** highlighted at the nanoscale and their relative **chemical inertia**.

Initially, the silica produced by electrometallurgy process were considered as waste. They are totally recycled and used in buildings to improve mechanical properties of cements and concretes.

Pyrogenic and precipitated silica are used in many applications in buildings, pharmaceuticals, inks, food, health and so forth as anti-agglomerating agent, moisture absorbent, reinforcing agent. Several studies have been working on the possibility to use SiO<sub>2</sub> as a vector to carry active principles of medicine to a tumor for treatment.

## Part 2 : Transmission Electron Microscopy sample preparation and data analysis

### Zeta potential

Zeta potential can be used as an indicator of colloidal suspension stability <sup>7, 8</sup>. TEM require a colloidal suspension for analysis. Therefore, it is important to use well dispersed particles in a medium. Zeta potential characterizes the surface charge of particles. This phenomenon is usually described by the Stern Layer model in which the charge distribution is established as a function of the distance from the solid. Particles in a solvent with the same electrical charge will tend to repulse. When the media cumulate opposite charges, the repulsion is less important and the particles will agglomerate.

The most available technique to measure the zeta potential is the light scattering electrophoresis by laser Doppler. It consists to apply an electrical field to the colloidal suspension in a cell equipped with electrodes. The charged particles will move in the solvent to the opposite of the electrical field applied. The displacement velocity  $V$  is measured by laser Doppler principle and lead to calculate the mobility.  $\mu_e$  knowing the electrical field (equation 1).

$$\mu_e = \frac{V(cm.s^{-1})}{E(V.cm^{-1})} \quad (1)$$

Zeta potential is measured in practical unit in mV and determined from on  $\mu_e$  based on the Smoluchowski principle (Brownian motion of the particles in a solvent in this case).

A colloidal suspension is considered as stable when zeta potential is closed to 30 mV  $\pm 5$  <sup>7</sup> in absolute value. Zeta potential closed to 0 mV clearly indicates a very bad stability of the suspension.

The most influencing parameters on colloidal suspension stability are **pH**, **solvent nature** and **concentration**. In this work a ZetaSizer Nano (Malvern) was used and this apparatus is limited in concentration, so it was chosen to prepare all the colloidal suspensions at 0.5 mg/mL which is a well-accepted concentration for the device.

The sample preparations for zeta potential measurements were done using the following step:

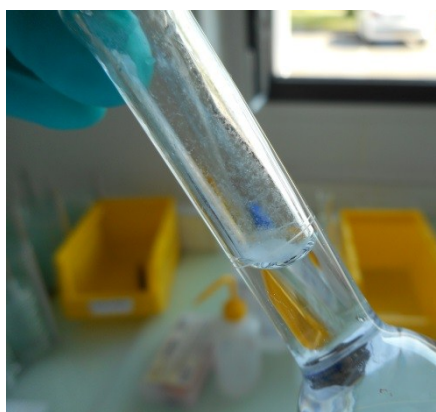
1. Selection of a unique concentration and a solvent for the colloidal suspension.
  2. Preparation of the suspension aliquots with different pH.
  3. Zeta potential measurements.
  4. Analysis of the sigmoidal functions zeta potential according to pH.
  5. Formulation of the most stable suspension based on the results.
- Choice of the appropriate solvent for dispersion.

For this, two solvents were tested in this work: **water** and **isopropanol**. Both are accepted by the ZetaSizerNano for the measurements.

Two flasks of 10 mL (one with MilliQ water (180Ω), one with pure isopropanol) were prepared at the powder concentration of 0,5 mg/mL.

Figure S1 show one example of bad dispersion of SiO<sub>2</sub> D powder in pure water. SiO<sub>2</sub> D is clearly a hydrophobic powder. Water is not convenient for a well dispersion and mixture of water and isopropanol or pure isopropanol must be considered and tested.

Figure S2 shows two examples of well dispersions of powders in pure water. The SiO<sub>2</sub> B and SiO<sub>2</sub> C suspensions are homogeneous with the water solvent, so this liquid can be used for the next steps.



**Figure S1** : Photographs of dispersions in pure water for SiO<sub>2</sub> D powder at 0.5mg/mL.



**Figure S2** : Photographs of dispersions in pure water for SiO<sub>2</sub> B (left) and SiO<sub>2</sub> C (right) powders at 0.5 mg/mL.

- Preparation of aliquots with different pH.

When the appropriate solvent is chosen, a minimum of 10 aliquots of 1.5 mL containing the suspensions (chosen solvent + powder at 0.5 mg/mL) with different pH values comprised between 2 and 12 were prepared. For this, a pH –meter (Mettler Toledo) and two solutions: acidic solution (HCl) and basic solution (NaOH) at the concentration of 1M were used to adjust the pH of the initial suspension.

The suspensions at 0.5 mg/mL were continuously agitated with a magnetic stirrer and the pH was adjusted by addition of 2  $\mu$ L of acid (lower the pH) or base (increase the pH) depending on the pH value desired. When the pH value was stable, 1.5 mL was sampled and transferred in the 1.5 mL aliquot (Ependorff® tube).

- Zeta potential measurements

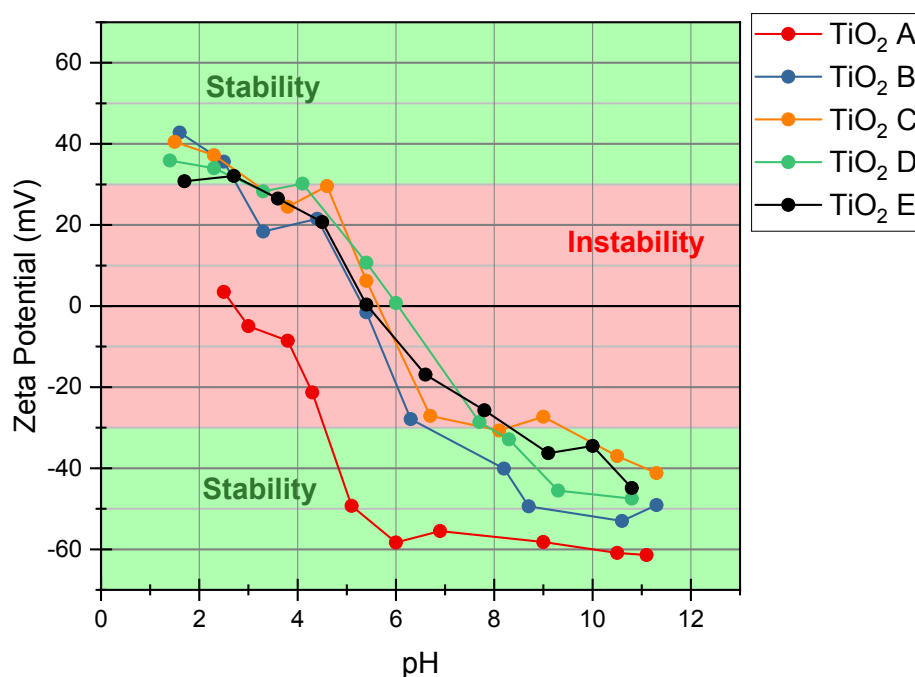
The zeta potential was measured for each aliquot with the ZetaSizer Nano (Malvern) device. The measurement parameters required to apply the Smoluchowski equation are the dielectric constant and viscosity of the solvent and refractive indexes of the solvent and the particles. These values are available in chemistry tables. Before each zeta potential measurement, the samples were sonicated at 50 W during 10 min.

The ZetaSizer Nano was previously checked with the Pre-size® material before the measurements. Pre-size® consists of powder silica contained in a 2 mL tube furnished by the supplier in which MilliQ water has to be added. The 2 mL were used for one zeta potential measurement with the parameters of water and silica (refractive index, dielectric constant and viscosity). The zeta potential to be measured is  $-35,4 \text{ mV} \pm 3.7$  in these conditions. It was obtained  $-36.8 \text{ mV} \pm 3.9$  which is in accordance with the expected value.

Table S1 summarizes all the colloidal suspension formulations we considered as sufficiently stable. Figure S3 shows an example of zeta potential as a function of pH obtained on TiO<sub>2</sub> powders.

**Table S1** Summary of the colloidal suspension formulations for subsequent TEM.

Powder	Solvent	Concentration (mg/mL)	pH	Corresponding zeta potential (mV)
TiO <sub>2</sub> A	H <sub>2</sub> O MilliQ	0.5	11.1	-61.4
TiO <sub>2</sub> B			10.6	-53
TiO <sub>2</sub> C			11.3	-41.2
TiO <sub>2</sub> D			10.8	-47.5
TiO <sub>2</sub> E			10.8	-44.9
SiO <sub>2</sub> A1			10.9	-56.7
SiO <sub>2</sub> A2			11.6	-72.2
SiO <sub>2</sub> B			11.9	-58
SiO <sub>2</sub> C			10.9	-46.2
SiO <sub>2</sub> D	H <sub>2</sub> O MilliQ/isopropanol (50/50)		12.2	-14.7
SiO <sub>2</sub> E	H <sub>2</sub> O		11.9	-42.3
SiO <sub>2</sub> 244FP			12.1	-41.7
SiO <sub>2</sub> 4850MR			7.9	-43.6
ZnO			10.9	-36.5
CuO	H <sub>2</sub> O MilliQ/isopropanol (50/50)		12	-21.3



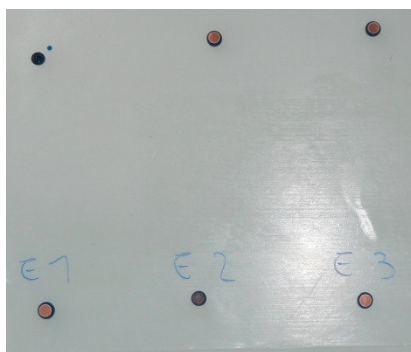
**Figure S3** : Zeta potential curves as a function of pH obtained for the five TiO<sub>2</sub> powders of this study.

It can be seen from table S1, 13 powders are stable in pure water and at neutral or basic pH as the zeta potential revealed to be above 30 mV in absolute value. The formulations indicated for SiO<sub>2</sub> D and CuO correspond to the best we could have obtained for these three materials. SiO<sub>2</sub> D and CuO are not sufficiently stable because their zeta potential are under the 30 mV absolute value threshold, but it was not possible to investigate more conditions for these three powders in our study.

The TiO<sub>2</sub> powders display relatively good stability in the acidic range (pH comprised between 2 and 4) except for TiO<sub>2</sub> A displaying instability from pH 5 until 2. These results on TiO<sub>2</sub> indicate it could have been possible to formulate a stable suspension in acidic media for TiO<sub>2</sub> B, C, D and E but the best zeta potential values are obtained for pH comprised between 10 and 12 (under – 30 mV). SiO<sub>2</sub> and ZnO materials revealed to be unstable in acidic conditions. So, for practical aspects, it was chosen to prepare basic colloidal suspensions for subsequent TEM.

#### Sample grids

To prepare the TEM grids, the “grid on drop” method detailed in De Temmerman *et al*<sup>9</sup> was used. Briefly, the colloidal suspensions were prepared applying the formulations obtained previously with the zeta potential study. Then, the grids (Cu 400 Mesh Carbon film Agar Scientific) were pre-treated with Alcian Blue Solution 1%. The grids were deposited on drops of Alcian Blue Solution 1% set on a parafilm band (figure S4). The grids floated 10 minutes on the drops before three to five rinsing with MilliQ water drops. Then, the same “grid on drop method” was applied with the colloidal suspension. The treated grids floated 1 minute before a new rinsing. The grids were finally stocked in a special TEM grid box after drying at room temperature and ambient pressure.



**Figure S4** : TEM grids floating on Alcian Blue Solution 1%.

To establish the number size distributions after particles counting with ImageJ software (Java version 1.8.0), the number of classes and the intervals for the histograms were determined according to the equations (2) and (3) respectively:

$$K = N^{0.5} \quad (2)$$

K represents the number of classes and n the number of particles counted.

$$I = S/K \quad (3)$$

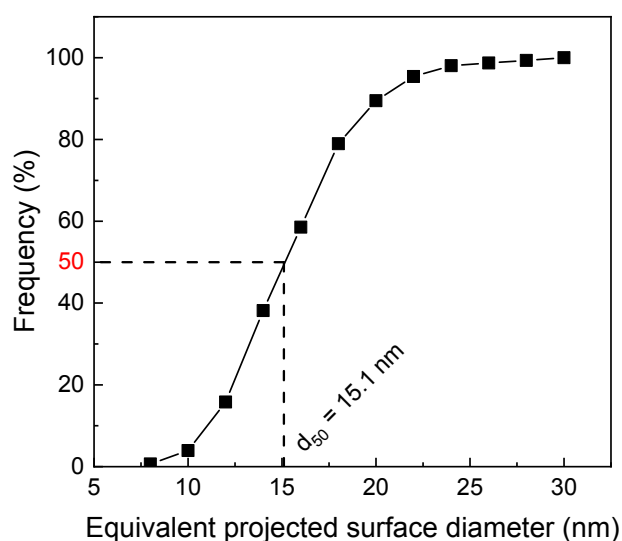
S is the span between the highest and smallest dimension measured and K the number of classes previously determined.

Then the particles were ranked in the different classes depending on their equivalent projected surface area diameter.

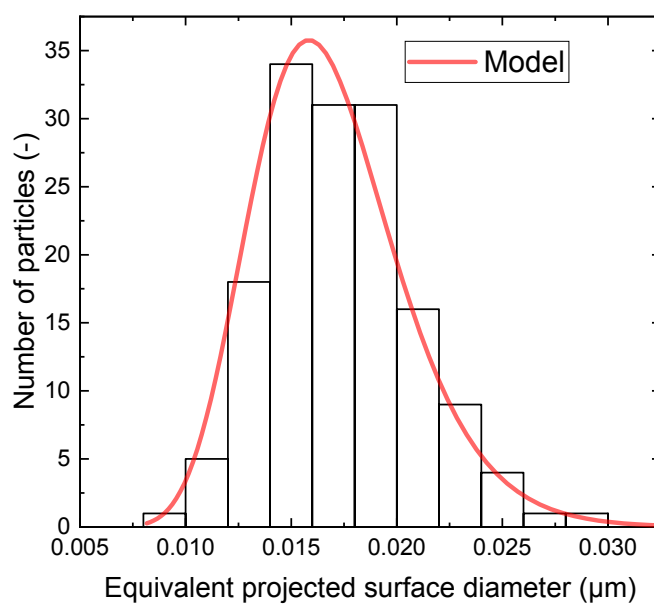
Two types of representations for number size distributions can be obtained: cumulated graph (figure S5) and histogram graph (figure S6).

Cumulated number size distribution lets evidence rapidly the median  $D_{50}$  diameter which is the reference value to compare with the recommendation of European Commission <sup>10</sup> for nanomaterial classification based on the size parameter.

Histogram gives more information as the size mode, mean, median diameters and the polydispersity of the powder. A model can be adjusted (lognormal distribution for instance) on the histogram to determine the monomodal or bi modal nature of the distribution.



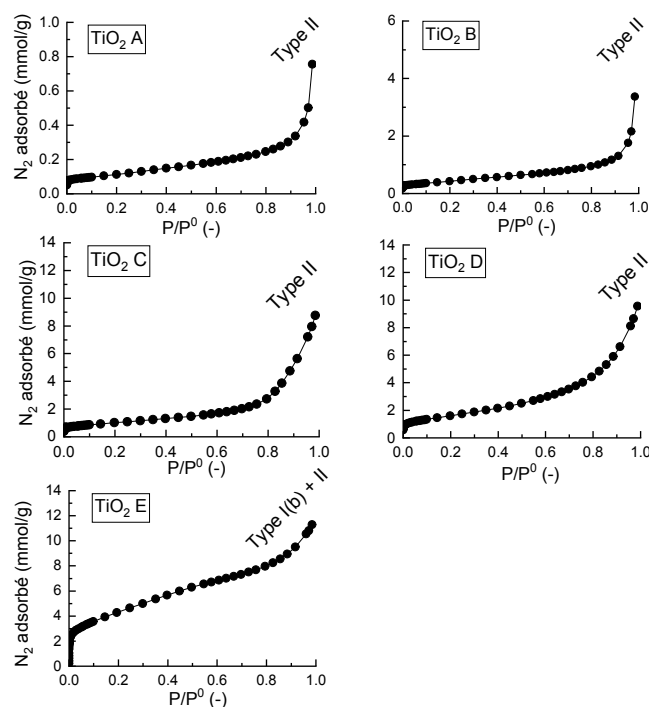
**Figure S5** : Example of a monomodal cumulated number size distribution of primary powder particles.



**Figure S6 :** Example of a monomodal number size distribution with fitting model.

## Part 3 : Supplementary results

The typical  $N_2$  adsorption isotherms obtained on the 15 powders are presented in figure S7.



**Figure S7 :**  $N_2$  adsorption isotherms obtained in Lab A for the powders studied in this work.

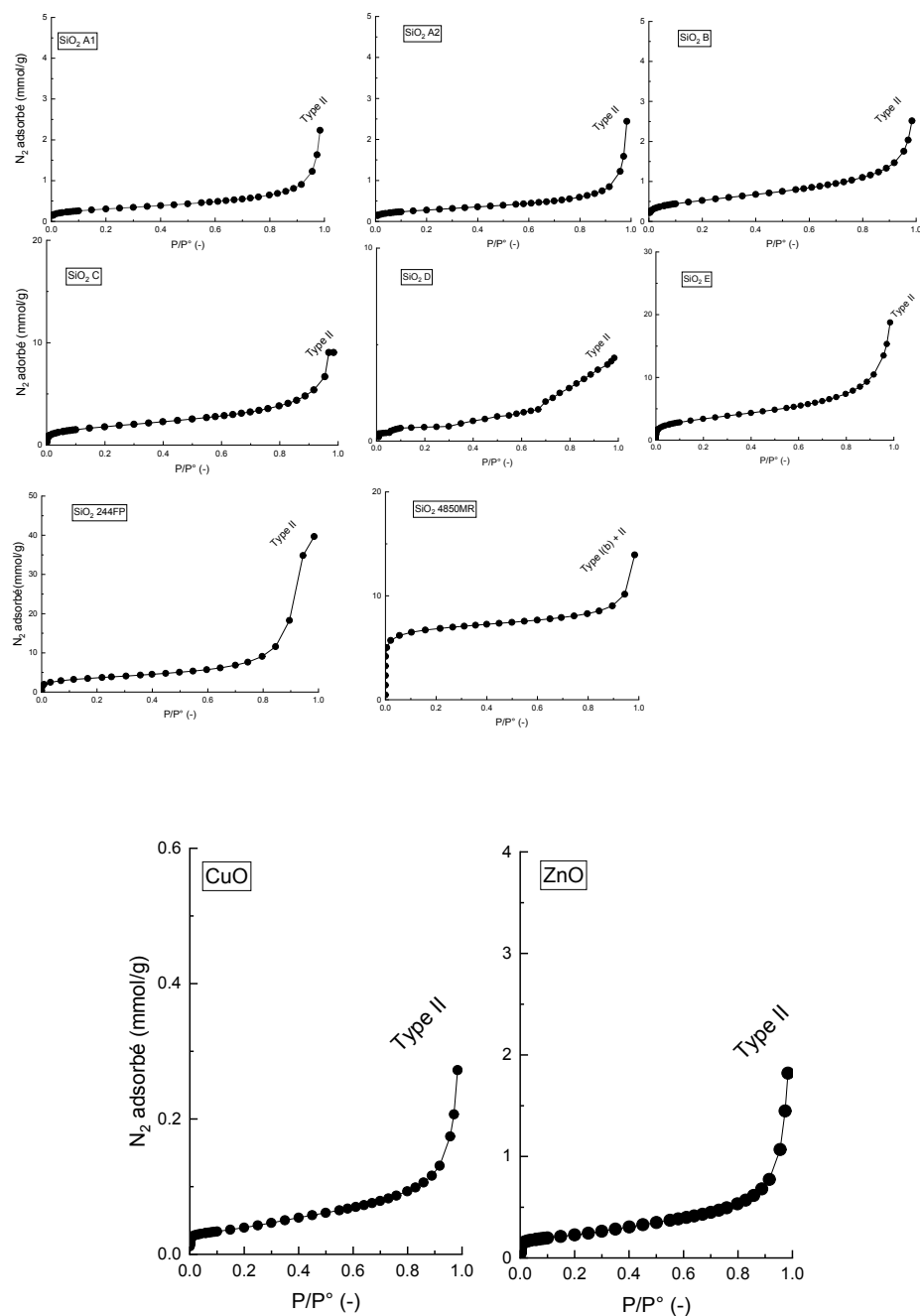


Figure S7 (continue)

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