Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

Hansen parameters evaluation for titania photocatalysts characterization using particle size distributions and combinatorics

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Section S1: Material properties – Probe liquids (PLs)

Ten PLs were chosen based on their Hansen solubility parameters (HSPs) to cover large number of solvents in the three-dimensional Hansen space as shown in Figure 2 of the manuscript. The HSPs of the chosen solvents, so called probe liquids, are given in Table 1 of the main text.[1]

Table S1: Probe liquid HSP values and properties.

Probe liquid	δD / $MPa^{0.5}$	δP / $MPa^{0.5}$	δH / $MPa^{0.5}$	Density / kgm^{-3}	Viscosity/mPa·s (20 ℃)	Refractive index /- (20℃)	Purity / %	CAS #	Manufacturer
1,4 Dioxane (Diox)	19.0	1.8	7.4	1304	1.200	1.422	99	123-91-1	VWR
Ethyl Acetate (EA)	15.8	5.3	7.2	902	0.428	1.372	99	141-78-6	VWR
Acetone (Ace)	15.5	10.4	7.0	784	0.360	1.359	99	67-64-1	VWR
Ethanol (EtOH)	15.8	8.8	19.4	789	1.144	1.361	99	64-17-5	VWR
N-Methyl-2-Pyrrolidone (NMP)	18.0	12.3	7.2	1030	1.800	1.465	99	872-50-4	VWR
Diacetone Alcohol (DAA)	15.8	8.2	10.8	931	3.400	1.424	99	123-42-2	VWR
Dimethyl formamide (DMF)	17.4	13.7	11.3	944	0.920	1.431	99	68-12-2	VWR
Acetonitrile (ACN)	15.3	18.0	6.1	780	0.369	1.344	99	75-05-8	Alfa Aesar
Dimethyl Sulfoxide (DMSO)	18.4	16.4	10.2	1100	1.990	1.479	99	67-68-5	VWR
Propylene carbonate (PC)	20.0	18.0	4.1	1205	2.400	1.421	99	108-32-7	VWR

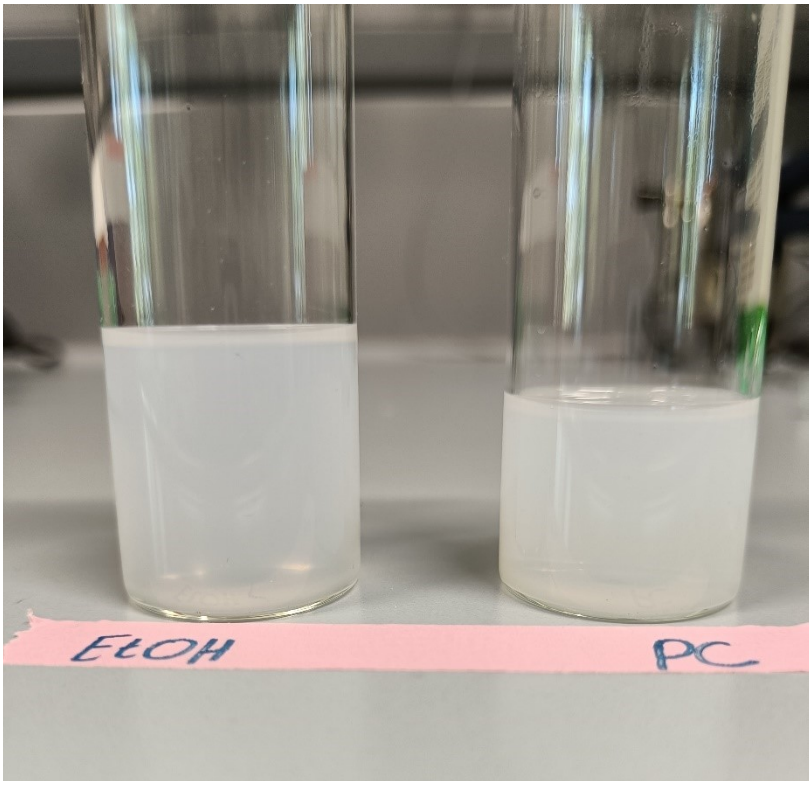

Figure S1: Dispersions of titania P25 in EtOH (left) and PC (right). Visual inspection of the dispersions revealed less optically opaque dispersions for EtOH in comparison to PC.

Table S2: Material properties and analytical centrifugation processing conditions.

Material	Density / kgm^{-3}	Particle size / nm	Centrifugal speed / rpm	Relative centrifugal acceleration / ms^{-2}	Concentration / wt%
Titania Aeroxide (P25)	4230	20	1600	300	0.02
Solvothermal titania (T1)	3880	10	500	30	0.07
Sol-gel Er-doped titania (T2)	3880	15	500	30	0.27

Section S2: Heating characteristics of the ultrasonic homogenizer

Temperature measurements were taken while heating a known mass of water, insulated to avoid heat losses (according to NANoREG D4.12 SOP). The Bandelin sonicator (HD 2200.2 with TT13 sonotrode tip) was used. It was assumed that there were negligible losses to surroundings during the heating and that all the acoustic energy generated in the sonotrode was transferred to the water. The acoustic power (P) can be calculated according to:

$$P = c_p \cdot m \cdot \frac{\Delta T}{\Delta t} \quad \text{(S1)}$$

Where c_p is the specific heat capacity of the liquid (water = 4.18 J kg^{-1} K^{-1}), m is the mass of the liquid and $\Delta T/\Delta t$ is the slope of the regression curve. The heating characteristics were measured at 20 % and 70 % amplitude of the sonicator. The resulting heating curves are plotted below in Fig. S2. According to the equation and the data from the heating curves, the delivered acoustic power was calculated as 22 J/cm^3 and 47 J/cm^3 at 20 % and 70 % amplitude, respectively.

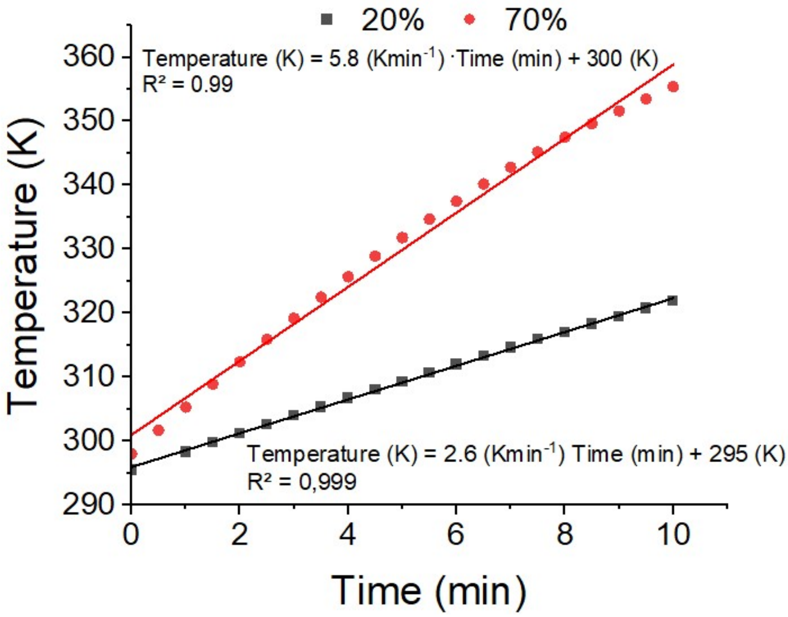

Figure S2. Heating curves at 20 % and 70 % amplitude of the Bandelin sonicator with TT13 tip.

Section S3: Calculation of permutations according to the HSP reporting framework

Details of the Hansen reporting framework as introduced by Bapat et al. are summarized in the main manuscript.[2] Here, we shortly introduce the equations needed to calculate the permutations for the HSP reporting framework. To calculate the total number of permutations, Eq. S2 is used. The equation includes total permutations (2^N) with the forbidden cases subtracted from them. These include the case of just one poor PL, all poor PLs and just 1 good PL.

$$Q_N = 2^N - {}^{N}_{0}C - {}^{N}_{N}C - {}^{N}_{1}C \qquad \text{(S2)}$$

The number of permutations can be calculated based on the number of PLs designated good '*M*' (Eq. S3) and poor '*L*' (Eq. S4). If both the good and poor PLs are known, Eq.S5 can be used to give the total evaluable permutations directly.

$$Q_M = \begin{cases} 2^{N-M}, & |M > 1 \\ 2^{N-M} - {}^{N\,M}_{N\,M}C - {}^{N\,M}_{0}C, & |M = 1 \end{cases} \qquad \text{(S3)}$$

$$Q_L = 2^{N-L} - {}^{N-L}_{0}C - {}^{N-L}_{1}C \qquad \text{(S4)}$$

$$Q_{LM} = \begin{cases} 2^{N-M-L}, & |M > 1 \\ 2^{N-M-L} - {}^{N\ M\ L}_{N\ M\ L}C, & |M = 1 \end{cases} \tag{S5}$$

Section S4: Combinatorics application to uncertain PLs in case of T1 and T2

The combinatorics method was applied to T1 and T2. The blue cells show the permutations chosen for providing the HSP ranges while the gray cells are reported as outliers.

Table S3: HSP reporting summary of T1.

NMP	DMSO	Ace	EtOH	δD ($MPa^{1/2}$)	δP ($MPa^{1/2}$)	δH ($MPa^{1/2}$)	R/MPa	Poor PLs in sphere	Good PLs out of sphere
1	1	1	1	15.4	18.8	14.4	11.2	0	0
1	1	0	1	16.5	16.3	14.6	9.0	0	0
1	0	1	1	14.4	15.3	14.1	8.9	1	2
0	1	1	1	14.8	18.4	14.4	11.0	0	0
1	1	1	0	16.5	14.5	8.0	4.8	0	0
1	1	0	0	16.8	15.5	7.8	4.2	0	0
1	0	1	0	16.2	14.5	7.8	4.4	0	0
1	0	0	1	14.4	15.8	14.5	9.0	1	2
0	1	1	0	16.0	14.7	9.4	5.1	0	0
0	1	0	1	15.3	16.1	14.6	8.8	0	0
0	0	1	1	13.1	17.7	14.5	11.5	0	0
0	0	0	1	14.5	15.9	14.7	9.0	0	0
0	0	1	0	16.1	14.4	8.0	4.4	0	0
0	1	0	0	16.5	16.2	8.8	4.1	0	0
1	0	0	0	16.6	15.2	7.8	4.2	0	0
0	0	0	0	16.4	15.7	8.5	4.0	0	0

Table S4: HSP reporting summary of T2.

NMP	DMF	EA	EtOH	δD ($MPa^{1/2}$)	δP ($MPa^{1/2}$)	δH ($MPa^{1/2}$)	R/MPa	Poor PLs in sphere	Good PLs out of sphere
1	1	1	1	13.2	13.3	11.4	10.4	1	3
1	1	0	1	14.2	15.7	14.1	9.1	1	3
1	0	1	1	11.9	11.8	11.9	11.0	1	3
0	1	1	1	11.9	11.6	12.0	11.0	1	3
1	1	1	0	16.5	11.6	5.0	6.9	0	0
1	1	0	0	11.7	12.6	4.1	10.4	0	2
1	0	1	0	15.5	11.5	5.0	6.6	0	0
1	0	0	1	12.1	17.7	14.6	12.6	2	1
0	1	1	0	13.8	12.9	4.2	9.2	2	1
0	1	0	1	13.0	17.6	14.5	11.6	0	0
0	0	1	1	12.4	11.3	11.7	10.9	2	0
0	0	0	1	12.0	15.5	14.4	11.3	1	1
0	0	1	0	14.7	11.4	5.2	6.8	0	0
0	1	0	0	16.0	14.5	8.1	4.4	0	0
1	0	0	0	16.2	14.3	6.4	4.2	0	0
0	0	0	0	15.5	14.3	7.0	3.9	0	0

Section S5: Effect of PL list, expemplified by removing DMSO and Ethanol on the HSP range of T1

The choice of a comprehensive PL list chosen for the HSP determination is paramount. In a nutshell, they should be well spread out over the Hansen space. Thus, PLs with high polar, hydrogen and dispersive contributions should be included. Here we show the effect of removing first DMSO and then ethanol from the PL list on the HSP range determined for T1.

The removal of ethanol has a more considerable effect on the HSP range than DMSO. This is because ethanol has a higher hydrogen bonding contribution (19.4 $MPa^{1/2}$) than DMSO (10.2 $MPa^{1/2}$). Inclusion of ethanol in the list of PLs therefore is important and is recommended as a test for probing the interaction of the material being under investigation with a hydrogen bonding rich PL. In case for some reason Ethanol cannot be used, the authors recommend using isopropanol or another PL with a similarly high hydrogen bonding contribution.

Table S5: HSPs along with the total combinations and outliers for T1 with all 10 PLs, T1 without DMSO and T1 without EtOH.

Material	**T1**	**T1 (no DMSO)**	**T1 (no EtOH)**
Disperse interactions δD ($MPa^{1/2}$)	13.1 - 16.8	14.7 - 16.5	15.9 - 16.7
Polar interactions δP ($MPa^{1/2}$)	14.4 - 18.8	14.4 - 18.8	14.4 - 16.1
Hydrogen bonding δH ($MPa^{1/2}$)	7.8 - 14.7	7.8 - 14.6	7.8 - 9.4
Sphere radius ($MPa^{1/2}$)	4.0-11.5	4.0 - 11.2	4.0 - 5.1
Total combinations possible	1024		
Combinations chosen for HSP	14 out of 16	16 out of 16	16 out of 16
Outliers	2	0	0

Section S6: Factors affecting the HSP prediction accuracy

While HSPs have great potential for understanding surface-driven particle behavior with their surroundings, it is imperative that their determination is done properly and the following effects are considered.

Table S6: Factors affecting HSPs and their prediction of VOC adsorption with ways to avoid them

Factors of instability	Effect on method's predictability of VOC adsorption	How to avoid them?
Processing of dispersion	Inadequate processing will directly affect subsequent dispersion behavior during the measurement. This is true for any measurement done for particle characterization such as dynamic light scattering, electron microscopy or analytical centrifugation.	It is important to note how the sample was processed. It is recommended that comparative studies (between methods, samples, experimenters) be done when comparing photocatalysts or any materials and any processing done should be kept same across them.
Changes of the sample during processing, e.g., by high energy input during dispersion	During dispersion, depending on the investigated material, it is possible that the energy input into the system to disperse may be too high and end up changing the surface. This may in particular occur for carbon-laden photocatalysts.	Start with low energy input devices such as sonication bath before moving on to higher energy devices. Check the literature for material specific dispersion parameters so as to preserve the surface. Check the material surface properties before and after dispersion via surface sensitive techniques especially in case of photocatalysts with graphene/carbon hybrids.
Choice of Probe liquid list	In case too few PLs are chosen, or the ones chosen result in several uncertain PLs (such that most have similar dispersion behavior),	Start with a reasonable number of PLs well spread out over the Hansen space. Try to choose PLs with a variety of surface groups as well as

	the determined HSPs will have a high degree of uncertainty.	molecular sizes to have dispersion sedimentation behavior well spread out so as to have a range of product ratios. This will help in clustering the PLs properly.
Choice of dispersion concentration during AC measurement	PSD derivation via analytical centrifuge requires the concentration of the dispersions to be in the Lambert-Beer range and absence of zone sedimentation. Similarly, very low concentrations will also not work since the CCD detectors of the analytical centrifuge will not measure any extinction. Concentrations out of the stipulated range will have erroneous PSDs and, by extension, erroneous HSPs.	Perform trial experiments with one material in all PLs of choice and try to find a concentration which has all the PLs forming dispersions that do not exceed the Lambert Beer range of extinctions higher than 1. Similarly, there should be initial turbidity in the dispersion for the system to measure it and there should be more than 20 % difference between the initial and final transmission profile.
Photocatalyst storage	Photocatalysts, especially those with carbon hybridizations, have the tendency to degrade if kept for a long time or near sources of radiation.	Keep photocatalysts strictly stored in a dark, cool place and take care that any carbon/graphene additions are still existing to accurately quantify useful HSPs.