Supporting information

for

Impact of ultrasonic dispersion on the photocatalytic activity of titania aggregates

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Details for the reaction rate model and experimental setup

Determination of reaction rate constant in the experimental setup based on a plug flow reactor

Nomenclature

| Symbol | Definition |
|--------|------------|
| $C_{\text{init}}, C_0$ | concentration of species A prior to the reaction and at time $t$, [mol/m$^3$]. |
| $k$ | reaction rate constant of the reactor, [s$^{-1}$]. |
| $K$ | overall degradation constant, [s$^{-1}$]. |
| $n$ | moles of species A, [mol]. |
| $\dot{n}$ | molar flow rate of species A, [mol/s]. |
| $r$ | reaction rate, [mol/m$^3$s]. |
| $t$ | time, [s]. |
| $V$ | volume, [m$^3$]. |
| $R,T,M$ | the subscripts designate for the plug flow reactor, tubing, and the mixing tank. |
| $\dot{\nu}$ | flow rate, [m$^3$/s]. |
| $\vartheta$ | stoichiometric coefficient of species A, dimensionless. |

Assumptions

The model development is based on the following assumptions:

- There is no axial batch mixing in the plug flow reactor (PFR). Variations only exist along the length of the reactor.
- In the PFR, the process is assumed as a steady-state isothermal reaction.
- Since the reaction is slow and dominates over the mass transfer, the kinetic of PFR is considered by means of a pseudo-homogenous model.
- Reaction occurs only in the PFR where photocatalyst is activated by absorbing photon energy of UV-irradiation and it is a first-order reaction

\[ A \overset{\text{cat.}}{\rightarrow} B \]

- There is no reaction in the mixing tank.
- The mixing in the tank is assumedly ideal.

**Modeling**

Consider a volume element of species A in the PFR, the material balance follows

\[ \frac{dn}{dV} = \vartheta r \]  

(S1)

Since the reaction is first-order, \( \vartheta = -1 \), and \( r = kC \). The integral gives the solution as

\[ C_0(t) = C_0(t) - t e^{-kt} \]  

(S2)

Material balance for species A in the mixing tank is described as

\[ \frac{dn_0}{dt} = -n_0 + n_2 \]  

(S3)

By substituting with the concentrations of species A and letting \( \tau = t + t_R \), the material balance in the whole setup becomes a linear delay differential equation

\[ \frac{dC_0}{dt} = -C_0(t) + C_0(t - \tau) e^{-kt} \]  

(S4)

Try the general exponential solution \( C_0(t) = Ae^{-kt} \), Eq.(S4) is derived as

\[ 1 - Kt = e^{K\tau - kt} \]  

(S5)
Eq. (S5) is the characteristic equation and the number of characteristic solutions is determined by looking for the intersection(s) of plotting curves. For positive $t_m$ and $\tau$, there is one intersection (Figure S1), correspondent with one single solution $K$ equaling to $C_0 = Ae^{-Kt}$.

![Graph showing characteristic equation](image)

**Figure S1:** Solution of the characteristic equation.

The boundary condition is determined at $t = 0, C_0(t) = C_{ini}$. Accordingly, the conversion of species A follows

$$C_0(t) = C_{ini} e^{-Kt} \quad (S6)$$

and the reaction rate constant $k$ is investigated as

$$k = \frac{K(t_r + t_m) - \ln(1 - Kt_m)}{t_g} \quad (S7)$$
Calibration curve of methylene blue measured by UV–vis spectroscopy

Methylene blue (MB) (Merck KGaA) 3.126 mM was used as the stock solution for the calibration. The eight concentrations ranging from 0.537–12.344 µM were prepared. The absorbance of solutions was scanned in the wavelength of 200–800 nm through 10 mm optical path length by a Varian Cary 100 Bio spectrometer. The maximum absorbance at wavelength λ = 664 nm was picked out from the whole UV-Vis spectra. All measurements were repeated three times. Analysis of the values along with MB concentrations were shown in Figure S2, where standard deviations of each point are too small to be observed, lower and upper CI respectively show the 95% confidence intervals of the linear fit.

**Figure S2**: Calibration of methylene blue.
Ultrasonic dispersion of P25 aggregates

The 1 g/L P25 suspensions were disintegrated by ultrasonication. Aggregate sizes were examined as a function of energy density $E_V$ (Table S1–Table S6). The size properties were measured by the photon correlation spectroscopy (PCS) Malvern HPPS-ET, including intensity-weighted harmonic mean size $x_{\text{cum}}$, polydispersity index $PDI$, the median of the intensity-, number- and volume-weighted distribution function $x_{50,\text{int}}$, $x_{50,0}$, and $x_{50,3}$. The cumulative sizes $x_{\text{cum}}^{(*)}$ comparable to measurement by PCS Malvern Nano S90 were converted from $x_{\text{cum}}$ as

$$x_{\text{cum}}^{(*)} = 1.01 \times x_{\text{cum}} \times t^{0.027}$$

(S7)

where parameters were determined by correlating measurements along with time $t$ by two instruments (HPPS-ET and Nano S90).

Table S1: Ultrasonic dispersion of 200 mL P25 suspensions by Hielscher UP100H with a generating power of 10 W.

| No | $E_V$, J/mL | $x_{\text{cum}}$, nm | PDI, - | $x_{50,\text{int}}$, nm | $x_{50,0}$, nm | $x_{50,3}$, nm | $x_{\text{cum}}^{(*)}$, nm |
|----|------------|----------------------|--------|----------------|--------------|---------------|----------------|
| 1  | 9          | 383                  | 0.499  | 446           | 131          | 530           | 392           |
| 2  | 15         | 351                  | 0.437  | 397           | 131          | 702           | 366           |
| 3  | 27         | 326                  | 0.389  | 369           | 113          | 435           | 347           |
| 4  | 39         | 305                  | 0.370  | 326           | 112          | 352           | 328           |
| 5  | 63         | 279                  | 0.337  | 300           | 99           | 219           | 304           |
| 6  | 93         | 263                  | 0.300  | 277           | 93           | 181           | 290           |
| 7  | 123        | 242                  | 0.295  | 262           | 121          | 179           | 269           |
| 8  | 153        | 244                  | 0.241  | 268           | 98           | 149           | 273           |
### Table S2: Ultrasonic dispersion of 200 mL P25 suspensions by Hielscher UP100H with a generating power of 30 W.

| No | EV, J/mL | \(x_{\text{cum}}\), nm | PDI, - | \(x_{50,\text{int}}\), nm | \(x_{50,0}\), nm | \(x_{50,3}\), nm | \(x_{\text{cum}}(*)\), nm |
|----|----------|----------------|--------|----------------|----------------|----------------|----------------|
| 1  | 18       | 329            | 0.419  | 357            | 114            | 482            | 337            |
| 2  | 36       | 298            | 0.397  | 311            | 105            | 367            | 311            |
| 3  | 108      | 249            | 0.270  | 262            | 108            | 187            | 268            |
| 4  | 180      | 229            | 0.249  | 248            | 93             | 141            | 250            |
| 5  | 252      | 216            | 0.240  | 225            | 110            | 145            | 238            |
| 6  | 324      | 209            | 0.224  | 222            | 102            | 135            | 231            |
| 7  | 396      | 204            | 0.222  | 216            | 99             | 135            | 227            |
| 8  | 468      | 197            | 0.181  | 214            | 91             | 122            | 220            |

### Table S3: Ultrasonic dispersion of 200 mL P25 suspensions by Topas UDS751 with a generating power of 33 W.

| No | EV, J/mL | \(x_{\text{cum}}\), nm | PDI, - | \(x_{50,\text{int}}\), nm | \(x_{50,0}\), nm | \(x_{50,3}\), nm | \(x_{\text{cum}}(*)\), nm |
|----|----------|----------------|--------|----------------|----------------|----------------|----------------|
| 1  | 10       | 333            | 0.396  | 370            | 111            | 597            | 335            |
| 2  | 30       | 276            | 0.373  | 304            | 118            | 255            | 286            |
| 3  | 50       | 252            | 0.296  | 260            | 130            | 205            | 265            |
| 4  | 69       | 242            | 0.277  | 249            | 127            | 218            | 256            |
**Table S4**: Ultrasonic dispersion of 200 mL P25 suspensions by Topas UDS751 with a generating power of 70 W.

| No | $E_V$, J/mL | $x_{\text{cum}}$, nm | PDI, - | $x_{50,\text{int}}$, nm | $x_{50,0}$, nm | $x_{50,3}$, nm | $x_{\text{cum}}^{(*)}$, nm |
|----|-------------|----------------------|--------|--------------------------|---------------|---------------|-------------------------|
| 1  | 42          | 267                  | 0.277  | 292                      | 105           | 216           | 274                     |
| 2  | 84          | 244                  | 0.271  | 260                      | 114           | 171           | 255                     |
| 3  | 126         | 226                  | 0.245  | 245                      | 103           | 144           | 239                     |
| 4  | 168         | 217                  | 0.216  | 238                      | 88            | 133           | 231                     |
| 5  | 252         | 202                  | 0.197  | 219                      | 99            | 131           | 217                     |
| 6  | 336         | 194                  | 0.190  | 205                      | 108           | 133           | 210                     |
| 7  | 420         | 186                  | 0.182  | 200                      | 98            | 125           | 203                     |
| 8  | 588         | 183                  | 0.168  | 194                      | 103           | 128           | 201                     |
| 9  | 756         | 175                  | 0.149  | 187                      | 103           | 124           | 194                     |
**Table S5:** Ultrasonic dispersion of 1000 mL P25 suspensions by Topas UDS751 with a generating power of 97 W.

| No | E<sub>v</sub>, J/mL | x<sub>cum</sub>, nm | PDI, - | x<sub>50,int</sub>, nm | x<sub>50,0</sub>, nm | x<sub>50,3</sub>, nm | x<sub>cum</sub> (*) , nm |
|----|-------------------|------------------|--------|-----------------|-------------|----------------|-----------------|
| 1  | 7                 | 342              | 0.485  | 345             | 107         | 319            | 350             |
| 2  | 14                | 316              | 0.388  | 337             | 106         | 338            | 330             |
| 3  | 27                | 277              | 0.354  | 288             | 106         | 251            | 295             |
| 4  | 51                | 245              | 0.268  | 260             | 96          | 152            | 265             |
| 5  | 76                | 229              | 0.255  | 246             | 98          | 142            | 251             |
| 6  | 104               | 220              | 0.232  | 237             | 96          | 134            | 243             |
| 7  | 125               | 212              | 0.209  | 232             | 96          | 131            | 235             |
| 8  | 156               | 204              | 0.199  | 225             | 89          | 124            | 228             |

**Table S6:** Ultrasonic dispersion of 1800 mL P25 suspensions by Topas UDS751 with a generating power of 97 W.

| No | E<sub>v</sub>, J/mL | x<sub>cum</sub>, nm | PDI, - | x<sub>50,int</sub>, nm | x<sub>50,0</sub>, nm | x<sub>50,3</sub>, nm | x<sub>cum</sub> (*) , nm |
|----|-------------------|------------------|--------|-----------------|-------------|----------------|-----------------|
| 1  | 8                 | 370              | 0.446  | 379             | 111         | 323            | 379             |
| 2  | 17                | 322              | 0.418  | 323             | 114         | 417            | 336             |
| 3  | 28                | 297              | 0.398  | 290             | 98          | 206            | 316             |
| 4  | 51                | 266              | 0.328  | 293             | 93          | 152            | 288             |
| 5  | 78                | 250              | 0.291  | 272             | 100         | 151            | 274             |
| 6  | 104               | 241              | 0.256  | 264             | 78          | 144            | 266             |
| 7  | 119               | 230              | 0.237  | 247             | 105         | 149            | 255             |
| 8  | 136               | 225              | 0.231  | 248             | 89          | 131            | 251             |
| 9  | 186               | 220              | 0.219  | 241             | 104         | 138            | 247             |
Stability of dispersed suspensions

The stability of the P25 titania suspensions (at room temperature) were examined by monitoring the size parameters over a time period of three days. Their aggregate sizes measured by PCS Malvern Nano S90 including $x_{\text{cum}}$, $PDI$, $x_{50,int}$, $x_{50,0}$, and $x_{50,3}$ (Table S7) show that a stable suspension can be achieved by ultrasonication, while the re-aggregation of the colloids is induced by a conventional stirring.

Table S7: Aggregate size of P25 photocatalyst in MB solution with and without ultrasonic dispersion after three day in room conditions.

| No | dispersion       | time, day | $x_{\text{cum}}, \text{ nm}$ | PDI, - | $x_{50,int}, \text{ nm}$ | $x_{50,0}, \text{ nm}$ | $x_{50,3}, \text{ nm}$ |
|----|------------------|-----------|-------------------------------|--------|--------------------------|------------------------|------------------------|
| 1  | magnetic stirring | 0         | 390                           | 0.396  | 476                      | 198                    | 892                    |
| 2  | magnetic stirring | 1         | 447                           | 0.480  | 395                      | 229                    | 834                    |
| 3  | magnetic stirring | 2         | 418                           | 0.432  | 484                      | 199                    | 790                    |
| 4  | magnetic stirring | 3         | 432                           | 0.390  | 518                      | 228                    | 866                    |
| 5  | ultrasonic dispersion | 0       | 219                           | 0.166  | 240                      | 129                    | 238                    |
| 6  | ultrasonic dispersion | 1       | 220                           | 0.175  | 237                      | 144                    | 258                    |
| 7  | ultrasonic dispersion | 2       | 233                           | 0.177  | 257                      | 140                    | 365                    |
| 8  | ultrasonic dispersion | 3       | 223                           | 0.190  | 243                      | 133                    | 252                    |
Color removal of MB in P25 suspensions

The photocatalytic properties of P25 were examined by the discoloration of MB. Photocatalyst aggregate sizes were measured by PCS Malvern Nano S90 including $x_{\text{cum}}$, $PDI$, $x_{50,\text{int}}$, $x_{50,0}$, and $x_{50,3}$. The 90% quantile of intensity-weighted cumulative distribution $x_{90,\text{int}}$ calculated as Eq. (7) is considered as agglomerate size of photocatalyst. The apparent reaction rate constant $K$ in the whole setup and the intrinsic reaction rate constant $k$ in the reactor are calculated as Eq. (3) and Eq.(4). Data are given in Table S8 and Figure S3.

Table S8: Data of MB discoloration in 1 g/L P25 suspensions.

| No | $x_{\text{cum}}, \text{nm}$ | PDI, - | $x_{50,\text{int}}, \text{nm}$ | $x_{50,0}, \text{nm}$ | $x_{50,3}, \text{nm}$ | $x_{90,\text{int}}, \text{nm}$ | $K, \text{min}^{-1}$ | $k, \text{min}^{-1}$ |
|----|-----------------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1  | 245             | 0.218  | 265             | 102             | 343             | 478             | 0.096           | 0.140           |
| 2  | 250             | 0.229  | 264             | 120             | 446             | 494             | 0.096           | 0.140           |
| 3  | 272             | 0.258  | 278             | 169             | 340             | 564             | 0.091           | 0.133           |
| 4  | 275             | 0.249  | 287             | 112             | 386             | 562             | 0.092           | 0.134           |
| 5  | 293             | 0.285  | 307             | 148             | 431             | 631             | 0.095           | 0.139           |
| 6  | 308             | 0.352  | 319             | 149             | 360             | 708             | 0.096           | 0.140           |
| 7  | 315             | 0.340  | 338             | 109             | 404             | 743             | 0.106           | 0.155           |
| 8  | 320             | 0.353  | 335             | 123             | 400             | 754             | 0.108           | 0.158           |
| 9  | 336             | 0.341  | 369             | 125             | 499             | 780             | 0.100           | 0.146           |
| 10 | 345             | 0.386  | 334             | 156             | 581             | 845             | 0.100           | 0.146           |
| 11 | 374             | 0.368  | 386             | 160             | 601             | 845             | 0.081           | 0.118           |
| 12 | 391             | 0.431  | 401             | 185             | 729             | 1006            | 0.079           | 0.115           |
Figure S3: Dependency of MB discoloration in 1 g/L P25 suspensions on the photocatalyst agglomerate size achieved by ultrasonic dispersion and magnetic stirring (experiments were repeated twice, error bars indicate the span between the minimum and maximum values, and the upper and lower bands indicate the t-confidence intervals of 95%).