Supporting information

Surface Modification of TiO₂ for Obtaining High Resistance against Poisoning during Photocatalytic Decomposition of Toluene

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Supporting information 1

Experimental set-up for the batch-type reactor



Supporting information 2 (a)UV-Vis DRS (UV-Vis diffuse reflectance spectrometer) spectra and (b) the Kubelka-Munk plot $((hvF)^{1/2} vs hv)$ of each spectra are displayed. The optical band gap energy of each TiO₂ sample (bare TiO₂ and h-TiO₂) was calculated from the intercept in the X-axis of the extrapolated straight line of each Kubelka-Munk plot $((hvF)^{1/2} vs hv)$. At 365 nm, no notable absorbance difference between the samples was observed, whereas the difference became larger as wavelength increased. In h-TiO₂, there was additional light absorption in visible light region. This can be explained by generation of intermediate energy levels between intrinsic band gap of TiO₂ as result of generation of oxygen vacancies in TiO₂ lattice. During the process of vacuum annealing, oxygen from TiO₂ lattice.



Supporting information 3 Changes of CO₂ concentration under dry condition (initial toluene concentration of 66 ppm) over bare TiO₂ and h-TiO₂ as function of UV irradiation time are displayed. Photo-catalytic decomposition experiment was repeated without changing the sample 3 times.



Supporting information 4 The gas mixture inside the reactor after the photocatalytic decomposition of toluene with the presence of h-TiO₂ catalysts was analyzed by TD-GC/MS in order to identify the by-products of toluene decomposition (upper spectrum). The dimethylacetamide was identified which corresponds to the second peak found in GC spectrum beside CO₂ peak. The TD-GC/MS spectrum of dimethylacetamide is shown in the bottom for comparison, which was taken from the library of TD-GC/MS software (Search library Database/W9N08.L)

a) Bare TiO₂



Supporting information 5 Changes of toluene and CO₂ concentration under humid condition over (a) bare TiO₂ and (b) h-TiO₂ as function of UV irradiation time are displayed. Each reaction proceeded under humid condition (33.6 % of relative humidity) and initial toluene concentration of 66 ppm. Photo-catalytic decomposition experiment was repeated without changing the sample 2 times.



Supporting information 6 Changes of toluene and CO_2 concentration under humid condition over (a) bare TiO₂ and (b) h-TiO₂ as function of UV irradiation time are displayed. Each reaction proceeded under humid condition (25.2 % of relative humidity) and initial toluene concentration of 442 ppm. Photo-catalytic decomposition experiment was repeated without changing the sample 3 times.



Supporting information 7 we compared the dispersity of two samples (bare TiO_2 and h- TiO_2) in a bi-layer heterogeneous mixture of toluene-water solution (please see a photographic picture in the above). The two particles (TiO_2 and h- TiO_2) were dispersed into a bi-layer heterogeneous mixture consisting of a non-polar solvent (toluene, upper part) and a polar one (water, bottom part). Bare TiO_2 particles were well-dispersed in both solvents, however, h- TiO_2 particles were mostly dispersed in water, which indicates the higher hydrophilicity of h- TiO_2 than that of bare TiO_2 . **Supporting information 8** Details on the calculation process of toluene concentration and CO₂ concentration are described below. For our photocatalysis experiments, an evacuated batch-type reactor with total volume of 5.3 L was used. The vacuum reactor was filled with gas mixture (total pressure of 760 torr) containing 50 mtorr of toluene. We regarded all gases in the reactor as the ideal gases for simplicity, thus the concentration of toluene could be expressed with the partial pressure of toluene divided by the total pressure of gas mixture (760 torr), which is ~ 66 ppm (P_{toluene}/P_{total} = $n_{toluene}/n_{total}$).

If the initial concentration of toluene is ~66 ppm (calculated by the aforementioned method), this means that 66 μ mol of toluene molecules are present in 22.4 L of volume under the standard state. Since the total volume of our reactor is 5.3 L, we multiplied 5.3/22.4 to 66 μ mol to calculate the number of toluene molecules in the reactor, which gave us the value of ~15.6 μ mol as the number of toluene molecules in the reactor at the initial stage. If the initial toluene concentration decreased by 50% under certain conditions of experiments, this means ~7.10 μ mol of toluene molecules were removed during the reaction.

The number of CO₂ molecules present in the reactor was calculated based on a linear relationship between the number of carbon atoms that existed in an injected gas and FID peak intensity of GC. The relationship was determined by measuring FID peak intensity of CO₂ by injecting the standard CO₂ gas with known CO₂ concentration.