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The influence of crystallite size and crystallinity of anatase nanoparticles on the photo-degradation of phenol



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1. Introduction

ABSTRACT

Crystallite size and crystallinity have been recognized as important parameters that influence the photocatalytic performance of pristine TiO_2 nanoparticles. But how these two parameters individually affect the photo-reactivity of TiO_2 remains unclear and debated due to the difficulties in preparing well-controlled TiO_2 photocatalysts that vary crystallite size and crystallinity independently. Here, we have studied the effect of crystallite size and crystallinity on phenol photo-decomposition using well-defined anatase nanoparticles synthesized under supercritical water–isopropanol conditions. The photo-reactivity was found to increase with increasing crystallite size but to be independent of the crystallinity. By tracking the evolution of phenolic intermediates, we explored the reaction kinetics and demonstrated that an increase in the crystallite size of anatase nanoparticles can significantly suppress undesired hydroquinone–benzoquinone redox reactions and thus promote the full decomposition of phenol and phenolic compounds.

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Titanium dioxide (TiO_2) has attracted great attention in heterogeneous photocatalysis applications due to its high reactivity, strong oxidizing power, long-term stability, and non-toxicity [1,2]. It has been found that the recombination kinetics, charge separation, charge trapping efficiency, and optical properties of TiO_2 nanoparticles are governed by their size, shape, polymorph composition, crystallinity, and impurity concentration [3–6]. Fine tuning of these parameters is expected to impact the photo-reactivity strongly [7–9].

Anatase is considered to be the most active polymorph of TiO_2 due to its high adsorption affinity for organic molecules [10] and low recombination rate [5]. The crystallite size has been recognized as an important factor that influences the photo-reactivity because it dictates many physical properties of the pristine anatase nanoparticles (i.e., surface area, surface energy, light absorptivity, and lattice distortion) [11,12]. Anpo et al. first reported the size effect of anatase on the photocatalytic hydrogenation of propyne [13]. It has been pointed out that the energy of photo-generated

radicals increases by reducing the crystallite size due to the quantum confinement effect, which improves the performance of the photocatalyst. This effect has been further supported by other authors who have studied various other photo-reactions [2,14,15]. Additionally, a reduction in the crystallite size leads to larger surface areas thus improves the adsorption of reactants and subsequently enhances the photo-reactivity [16,17]. However, contradictive reports also exist [18-20], which claims that the quantization effect alters the electric field gradients and reduces the separation of electron-hole pairs [21]. Almquist and co-workers reported that the photocatalytic performance of anatase nanoparticles increases upon an increase in the crystallite size due to the optimization of the optical property and charge carrier dynamics [22]. Interestingly, there are also reports suggesting that the optimum crystallite size is in the range of 7-15 nm for various photocatalytic reactions [23-26].

Crystallinity is believed to be another critical parameter that affecting the photocatalytic performance of anatase. Ohtani et al. showed that amorphous titania plays a role as a recombination center, and it exhibits negligible reactivity in several photocatalytic reactions [27]. Even though reports suggesting that hydrated amorphous titania can be photo-reactive exist [28], it is generally accepted that the photo-reactivity can be enhanced by improving the crystallinity [29–36]. This may be attributed to the enhanced



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electron transport from the conduction band of TiO_2 to the surface adsorbed molecules [37]. However, it is very difficult to interpret these data as the degrees of crystallinity have been estimated indirectly from the annealing temperatures, and the absolute values are missing in most studies.

The general approach of tuning the crystallite size and crystallinity is by heat treatment of either the amorphous phase or of small anatase nanoparticles in previous studies [12,13,16–26,28– 33,35,37–47]. Unfortunately, anatase nanoparticles prepared *via* conventional synthesis routines normally exhibit a broad distribution of crystallite sizes [48]. Moreover, the calcination process produces variations in crystallite size and crystallinity simultaneously. These drawbacks render any clear conclusion about the individual impact of crystallite size and crystallinity impossible. Despite the large interest in this topic, no previous studies where pure anatase nanoparticles with tuneable crystallite size and crystallinity but otherwise identical properties have been evaluated for their photocatalytic activities exist.

Here, we have prepared a series of crystallite size and crystallinity controlled anatase nanoparticles by supercritical flow synthesis. The crystallite size series ranged from 6 nm to 27 nm with a fixed crystallinity of ~84%, whereas the crystallinity series varied the absolute crystallinity from 12% to 82% with a fixed crystallite size of ~9 nm. Thus, it was possible to directly correlate the photocatalytic performance of anatase nanoparticles to the crystallite size and crystallinity. The photo-reactivity of these catalysts was systematically evaluated using phenol as the probing molecule. The influence of crystallite size and crystallinity of the anatase nanoparticles on the degradation of phenol was studied by tracking the evolution of the phenolic intermediates and the reaction kinetics.

2. Materials and methods

2.1. Sample preparation

 TiO_2 nanoparticles were prepared by supercritical synthesis using a continuous flow reactor [48–50]. The supercritical synthesis method is featured by a rapid mixing of the cold reactant solution with the superheated solvent stream in a continuous process, which results in a high degree of super-saturation and thus a rapid nucleation that facilitates the formation of primary crystallites in large quantities. The crystallite size and crystallinity depend on temperature, pressure, and the synthesis and quenching time (flow rates of the reactant and solvent). The supercritical solvent was isopropanol mixed with deionized (DI) water, and the reactant was titanium isopropoxide (TTIP) (ACROS, 98%). Pure TiO₂ nanoparticles in the polymorph of anatase with a precise control of crystallite size and crystallinity were synthesized by varying the concentration of TTIP, the composition of the solvent, flow rate, temperature, and pressure, as shown in Table 1 in detail. The asprepared anatase nanoparticles in suspension were centrifuged, washed in DI water, and subsequently dried overnight at 120 °C. The crystallite size series (crystallinity controlled) and crystallinity series (size controlled) are labeled as S1–S6 and C1–C5, respectively.

Fig. 1 shows the absolute crystallinity as a function of crystallite size of the as-prepared anatase nanoparticles. Clearly, the as-synthesized anatase nanoparticles showed well-defined crystallite size and crystallinity [51]. The crystallite size of anatase with a crystallinity of ~84% could be adjusted from ~6 nm to ~27 nm, whereas the crystallinity could be tuned independently from ~12% to ~82%, respectively.

2.2. Characterization of physical properties

X-ray diffraction (XRD) was employed to examine the crystallite size and crystallinity of the nanoparticles using a powder X-ray diffractometer (PXRD, Stadi P, Stoe) with Cu K α 1 radiation from a curved Ge (111) monochromator. The crystallinity of the sample was evaluated by comparing the integrated areas of the diffraction peaks of anatase (101) with 100% crystalline CaF₂ (111) in a mixture with a weight ratio of 1:1 using the following equation [43,51]:

 $crystallinity = 0.763 \times A_{anatase(101)} / A_{CaF_2(111)} \times 100\%$ (1)

In practice, Rietveld refinement was applied to all diffraction patterns to determine the peak area and the crystallite size [52]. Xray photoelectron-emission spectroscopy (XPS, AXIS Ultra, Kratos) was utilized to analyze the chemical composition of the samples and the oxidation states of the containing elements. A monochromatic Al Ka source was operated at 10 mA emission current at an accelerating voltage of 15 kV. Survey scans and high-resolution spectra were collected using a pass energy of 160 eV and of 40 eV, respectively. The binding energy scale was calibrated using the C 1s binding energy of 285 eV of adventitious carbon. Microscopic features of the anatase nanoparticles were characterized using a transmission electron microscope (TEM, CM20, Philips). The surface area was determined by Brunauer-Emmett-Teller (BET) method using a Quantachrome NOVA 2000 surface area analyzer with N₂ as adsorbate at 77 K [53]. The samples were degassed 3 h at 423 K in a vacuum oven before measurements.

2.3. Photo-reactivity measurement

The photo-induced decomposition of phenol was carried out under ambient conditions to evaluate the photocatalytic performance of the catalysts. All samples were UV irradiated for 2 h to remove the surface adsorbed organic molecules prior to the measurements. Catalysts with a loading of 0.5 g/L were added into

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Parameters	for s	unthesis	of anatas	- nanona	rticles	with	various	crystallite	size ar	nd cry	stallinity
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Label ^a	S1	S2	S3	S4	S5	S6	C1	C2	C3	C4	C5
[TTIP] ^b (M)	0.5	0.5	0.5	0.5	0.5	0.5	1.0	0.5	1.0	1.0	1.0
H_2O^{c} (%)	100	100	10	5.44	3.47	2.55	11	10	12	14	18
Flow (g min ⁻¹)	2.5	5	5	5	5	2.5	10	5	10	10	10
Temp. (°C)	400	350	350	350	350	300	255	225	265	275	350
Pressure (MPa)	30	30	30	30	30	30	25	30	25	25	25
d_{XRD}^{d} (nm)	6.6	8.9	11.3	15.9	20.4	26.6	9.3	7.8	9.2	9.2	9.3
Cry. ^e (%)	74.2	82.8	82.3	82.6	89.2	86.3	12.6	53.8	60.3	75.5	82.0

^a S1–S6 and C1–C5 denote the crystallite size series and crystallinity series.

^b The molar concentration of titanium isopropoxide in the isopropanol–water solvent.

^c The volume concentration of water in the isopropanol-water solvent.

^d The volume averaged crystallite size determined from XRD patterns.

^e The absolute crystallinity derived from XRD patterns.

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