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Anatase and rutile in evonik aeroxide P25: Heterojunctioned or individual nanoparticles?

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ABSTRACT

Evonik Aeroxide P25 (formerly Degussa P25) is a flame-made multiphasic TiO_2 nanoparticles containing anatase and rutile, as well as a small amount of amorphous TiO_2. The past decades have witnessed the wide applications of P25 as a benchmark material for studying photocatalytic mechanism, materials and process. However, controversy remains regarding the microstructure of anatase and rutile: do they interwoven forming heterojunction structure or exist individually? To clarify it, we selected a medium alkaline, LiOH to erode bare P25 under a mild hydrothermal condition. Since rutile presents much higher resistances towards dissolution by LiOH than anatase, it is reasonable to find during hydrothermal reaction that the ratio of anatase to rutile (A/R) gradually decrease if they exist individually. Reversely, the A/R value gradually increases at the beginning of the hydrothermal reaction, implying that rutile shows high activity towards dissolution and phase transformation to lithium titanate. As calculated, around 15% rutile nanoparticles more likely exist on the surface of anatase with the formation of a heterojunction structure, although isolated nanoparticles with sole rutile phase coexist. In addition to XRD analysis, TEM measurement shows that the Moiré fringes frequently present, which further manifests that some anatase particles are covered with rutile clusters or thin overlayers.

1. Introduction

Semiconductor photocatalysis and the associated photoactive materials have attracted numerous interests that aims to efficiently convert solar energy to chemical energy for various technologically important applications, such as environmental remediation, solar fuel production, photocatalytic organic synthesis, etc. Owing to its outstanding physicochemical characteristics, e.g. suitable band position, non-toxicity, low cost, chemical inertness, photostability, and biocompatibility, TiO_2 has been demonstrated to be one of the most viable photocatalysts [1–5]. Given the superior functionality, TiO_2 nanoparticles have been commercially produced in large scale and brought a widespread success in practical applications. As estimated by Robichaud et al. [6], the market of TiO_2 will be dominated by the nanosized TiO_2 by 2025 with an annual global production of 14 million tons.

A representative TiO_2 nanoparticle product is Evonik (formerly Degussa) AEROXIDE® TiO_2 P-25 (denoted as P25). Manufactured via a proprietary Aerosil process, namely, $TiCl_4$ vapor-fed flame pyrolysis process, P25 was initially produced for chemical industry. Academic studies on P25 as a semiconducting metal oxide photocatalyst serendipitously appeared in early 1980s, and surged in 1990s following the rapid development in semiconductor photochemistry. Up to now P25 has been undoubtedly the most commonly used commercial TiO_2 for studying photocatalytic processes. Specifically, P25 is also the most widely employed referential photocatalyst to evaluate the photocatalytic activity of new materials. Several remarkable properties account for the uniqueness of P25: high chemical purity, relatively broad light absorption, low aggregation, excellent dispersion especially in liquid media, and high quantum efficiency and photocatalytic activity for various photocatalytic reactions [4,7,8].

Interestingly, although P25 has been widely employed, controversy remains regarding the microstructure of P25. As widely revealed by

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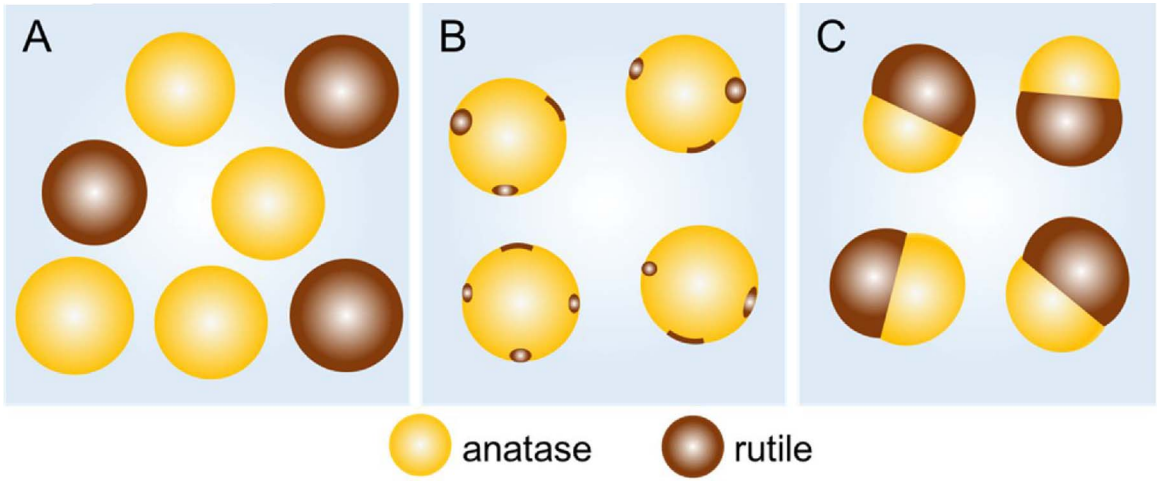

Fig. 1. The possible microstructures of anatase and rutile in P25: free naonparticles (A); heterojunction structure consisting of rutile clusters and thin overlayers on anatase nanoparticles (B); and inter-particles (C).

XRD analysis, P25 is of mixed-phase TiO_2 mainly containing anatase and rutile, the two most common crystal phases of TiO_2. However, attempts made to understand the exact state of anatase and rutile phases, as summarized in Fig. 1, have unfortnately led to contestable results, despite different characterization techniques used and a variety of persuasive evidences provided. For example, based on transmission electron microscopy (TEM), Ohno et al. [9] and Datye et al. [10] observed individual anatase- and rutile-phase TiO_2 particles that were separated without forming a heterojunction structure (Type A in Fig. 1), while Bickley et al. [11] observed that some individual particles were a mixture of amorphous TiO_2 with either anatase or rutile phased TiO_2, and the other particles, which were mostly anatase, covered by a thin overlayer or of rutile (Type B in Fig. 1). Thus, the intimate contact among the amorphous, anatase, and rutile TiO_2 was believed to improve the magnitude of the space-charge potential due to the efficient charge carrier separation, leading to a much higher photocatalytic activity than that of sole-phase TiO_2, either anatase or rutile. Such a synergetic effect was demonstrated by using electron paramagnetic resonance (EPR) spectroscopy by Hurum et al. [12] and Macdonald et al. [13,14]. By irradiating an aqueous P25 suspension with visible light ($>$ 400 nm) at an extremely low temperature of 10 K to exclude interparticle charge transfer, they detected the electron transfer from rutile to anatase, implying the presence of chemically bonded clusters [12]. On the contrary, Otahni et al. [15,16] isolated the anatase nanoparticles from P25, and found that P25 showed a lower photocatalytic activity in most photocatalytic processes than single-phase anatase due to the presence of less active rutile phase in P25. The absence of synergetic effect, as they concluded, was thus associated with the fact that P25 was a simple mixture of anatase and rutile without any electrical interactions. Very recently, Ide et al. [17] claimed that the synergetic effect and the superior photocatalytic activity of P25 are originated from the anatase-rutile interparticle contact (Type C in Fig. 1). Different from Type B with a smaller size rutile, Type C possesses similar size anatase and rutile that are fused together tightly. The interface of anatase-rutile nanoparticles, like the heterojunction structure, is beneficial to the charge carrier separation and consequently the efficiency of photocatalysis [18,19]. The interparticle structure of P25, as further demonstrated by Ide et al., can be improved by hydrothermal treatment due to the aggregation and crystallization [17].

A comprehensive understanding of P25 microstructure is of particulate importance for designing efficient TiO_2-based photocatalyst for various photochemical applications since the phase composition and microstructure have significant influences on the resulting properties and performances of the photoactive materials. Using single characterization technique seems to be insufficient to provide solid evidences, which, instead, might lead to the inconsistent results as mentioned above. Normally “direct” characterization of polymorphic P25 at the nanoscale is of huge difficulty. Taking TEM as an example, the inhomogeneity of P25 makes the observation somewhat contingent and ambiguous. Herein a novel “indirect” tactic has been developed to ease the analyses of the composition and microstructure of P25. Different from previous studies, chemical corrosion of P25 by LiOH at hydrothermal conditions reveals as an effective means to discriminate the crystal phases of P25. Based on their different reaction kinetics with LiOH, the states of anatase and rutile are well understood with the aids of X-ray diffraction (XRD) and TEM techniques.

2. Experimental section

2.1. Hydrothermal reaction between P25 with LiOH

All the chemicals were purchased from Aldrich and used as received unless otherwise stated. P25 (1.0 g) was dispersed in 30 ml of LiOH solution (1.0 mol/L). The milk-like suspension was stirred for 15 min before transferred to a Teflon-lined autoclave to conduct the hydrothermal reaction in an electronic oven with a temperature of 90 °C. After keeping in oven for different time of 0.5–8 h, the autoclave was cooling down and the collected powdered samples were washed with water for three times.

2.2. Materials characterization

Powder wide-angle XRD measurement was performed on a Bruker D8 Advance X-ray diffractometer with a monochromated high-intensity CuKα radiation (λ = 1.5418 Å). Quantitative analysis of the obtained XRD patterns was implemented according to the Rietveld refinement technique with the aid of X'Pert HighScore Plus (HSP) and MAUD (Materials Analysis Using Diffraction) programs [20,21]. The morphology and microstructure of P25-based nanoparticles were observed by a JEOL JEM-2010 transmission electron microscope. Nitrogen adsorption-desorption isotherms were obtained using a Micromeritics ASAP 2020 surface area, and Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area from adsorption data obtained at P/P_0 = 0.01–0.30.

3. Results

3.1. Phase composition of P25

Fig. 2a shows a representative XRD pattern of P25, which matches