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Zinc oxide tetrapods as efficient photocatalysts for organic pollutant degradation

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ABSTRACT

Bisphenol A (BPA) and other organic pollutants from industrial wastewater have drawn increasing concern in the past decades regarding their environmental and biological risks, and hence developing strategies of effective degradation of BPA and other organic pollutants is imperative. Metal oxide nanostructures, in particular titanium oxide (TiO_2) and zinc oxide (ZnO), have been demonstrated to exhibit efficient photodegradation of various common organic dyes. ZnO tetrapods are of special interest due to their low density of native defects which consequently lead to lower recombination losses and higher photocatalytic efficiency. Tetrapods can be obtained by relatively simple and low-cost vapor phase deposition in large quantity; the micron-scale size would also be advantageous for catalyst recovery. In this study, the photodegradation of BPA with ZnO tetrapods and TiO_2 nanostructures under UV illumination were compared. The concentration of BPA dissolved in DI water was analyzed by high-performance liquid chromatography (HPLC) at specified time intervals. It was observed that the photocatalytic efficiency of ZnO tetrapods eventually surpassed Degussa P25 in free-standing form, and more than 80% of BPA was degraded after 60 min. Photodegradation of other organic dye pollutants by tetrapods and P25 were also examined. The superior photocatalytic efficiency of ZnO tetrapods for degradation of BPA and other organic dye pollutants and its correlation with the material properties were discussed.

Keywords: Zinc oxide, tetrapods, photodegradation

1. INTRODUCTION

Organic pollutants from industrial wastewater have long been a worldwide concern. Organic dyes form a common class of pollutants. In addition, endocrine disruptors, typically bisphenol A (BPA), have resulted in increasing risks for both marine environment and public health.[1] Hence, efficient photocatalysts for degradation of the above pollutants are demanded. Titanium dioxide (TiO_2) has been extensively studied over the decades for its photocatalytic activity. It has been demonstrated that TiO_2 is capable of degrading a wide range of organic pollutants in aqueous environment, including BPA.[2, 3] In addition to the two principal crystal phases, anatase and rutile, another commercially available form of TiO_2, Degussa P25, has been widely applied for degradation of BPA and various organic dyes.[3, 4] P25 consists of approximately 80% anatase and 20% rutile phase, and it exhibits higher photocatalytic activity than either pure phase.[4] With the universally high photocatalytic activity, P25 is commonly used as a standard for photocatalytic studies. [2-4]

In addition to TiO_2, other semiconducting materials such as zinc oxide (ZnO) have drawn attention as potential candidates for high efficient photocatalysts. ZnO tetrapods exhibit unique structural and photocatalytic properties among various ZnO morphologies.[5, 6] ZnO tetrapods can be synthesized by relatively simple and low-cost method in large quantity. Moreover, though with micron-scale morphology and inferior surface-to-volume ratio, ZnO tetrapods are reported to possess outstanding photocatalytic efficiency for degradation of several organic dyes.[5, 6] In this study, we compared the photocatalytic performance of ZnO tetrapods and TiO_2 P25 for degradation of BPA and selected dyes. The tetrapods exhibited better performance in all conditions studied. The attribution of superior photocatalytic performance of ZnO tetrapods was discussed in detail.

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2. EXPERIMENTAL

2.1 Material preparation and characterization

Degussa P25 was purchased from Evonik Industries. ZnO tetrapods were synthesized through a vapor-phase approach described as follows.[5-7] 0.2 g of zinc powder (99.995%, Sigma Aldrich Co.) were placed in a quartz crucible inside a horizontal quartz tube and evaporated at 950 ^{o}C under 0.2 Lpm humid argon flow. The white material was deposited on the downstream inner wall of the quartz tube and manually collected for further characterization. To examine the crystal and surface properties of ZnO tetrapods, high resolution transmission microscopy (HRTEM) and selected area electron diffraction (SAED) were performed using a JEOL JEM-2100F Field Emission Electron Microscope STEM. X-ray diffraction (XRD) patterns of ZnO tetrapods and Degussa P25 were measured with a Bruker D8 advance diffractometer (Cu Kα radiation (λ = 0.154184 nm) as the X-ray source). Fourier transform infrared spectroscopy (FTIR) measurements of the samples were performed using a SHIMADZU IRAffinity-1S Fourier Transform Infrared Spectrophotometer. For FTIR measurements, samples were well mixed into KBr (FT-IR grade, Sigma Aldrich Co.) and pressed to form transparent pellets using a 13 mm pellet-forming die. Background measurement was taken with a pellet of KBr only.

2.2 Photodegradation of Bisphenol-A

Bisphenol A (BPA, Sigma Aldrich Co.) was dissolved in deionized water at a concentration of 40 mg/L. 50 mg of the catalysts were mixed with 50 ml of BPA solution in a Petri dish and stirred in dark for 30 min to reach equilibrium. The mixture was then subjected to UV illumination (365 nm, 66.2 mW/cm^2, Blak-Ray® B-100 AP Lamp). The BPA concentration was measured after specified exposure time (0, 15, 30, 45, 60 min) using a nanoscale reversed-phase high-performance liquid chromatography (HPLC, Agilent Technologies, Santa Clara, CA). The suspension was prefiltered with a Millex-FH PTFE filter (0.45 μm pore size) to obtain a clear solution for HPLC measurements.

2.3 Photodegradation of organic dyes

5 common organic dyes were selected for photocatalytic experiments, including acid red 88 (International Lab USA), tropaeolin O (Acros Organics), cresyl violet acetate, naphthol blue black, and sunset yellow (Sigma Aldrich Co.). The dyes were dissolved in deionized water at a concentration of 10 mg/L. 50 mg of the catalysts were mixed with 50 ml of dye solution in a Petri dish and stirred in dark for 30 min, following by exposure to UV illumination. Absorption spectra were measured using a PerkinElmer Lambda Bio 40 UV/VIS spectrometer immediately before exposure to UV illumination and at specified time intervals during UV exposure. For each measurement, 3 ml of the suspension was withdrawn and filtered to obtain a clear solution.

3. RESULTS AND DISCUSSION

The high-resolution TEM image and SAED pattern of a tetrapod leg in **Figure 1** illustrate excellent crystal properties of the material. The legs have a wurtzite structure with a growth direction along [0001] and $(10\bar{1}0)$ terminating facets. It is noted that the nonpolar $(10\bar{1}0)$ surface has been reported to exhibit the highest photocatalytic activity and stability among different crystallographic orientations of the ZnO crystal.[8] The XRD patterns in **Figure 2** also confirm the high crystallinity of the ZnO tetrapods. The sharp diffraction peaks in the XRD pattern of tetrapods match the characteristic ZnO wurtzite structure, with no other crystal phases observed, in agreement with literature.[5, 6]

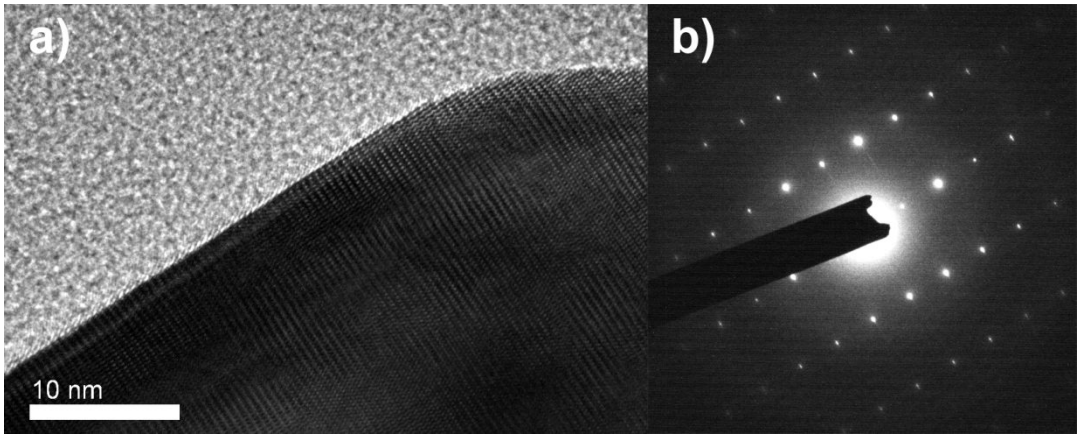

Figure 1. a) HRTEM image and b) SAED pattern of ZnO tetrapods.

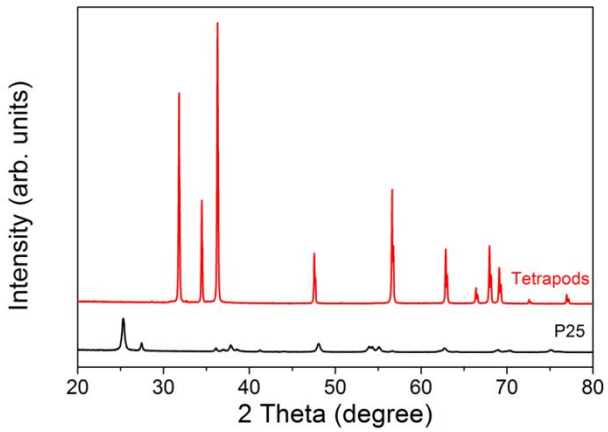

Figure 2. XRD patterns of ZnO tetrapods and Degussa P25.

Figure 3 shows the FTIR spectra of ZnO tetrapods and P25 nanoparticles. Except the broad resonance at ~3200-3600 cm^{-1} corresponding to OH group vibration and the peak at ~1630 cm^{-1} assigned to the scissoring mode of the molecular water,[9] there is no significant peak identified in the spectra for both samples, indicating negligible presence of organic surface adsorbates.

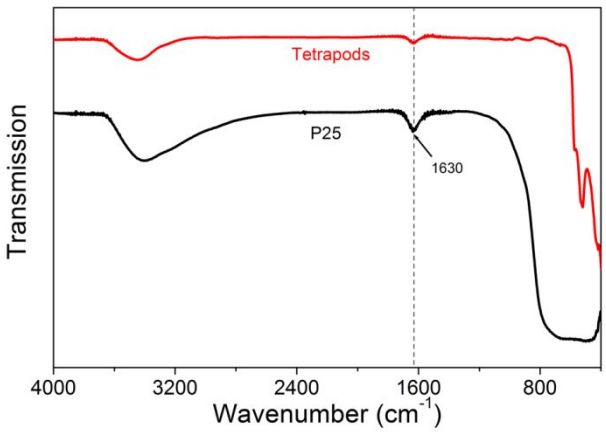

Figure 3. FTIR spectra of ZnO tetrapods and Degussa P25.

Figure 4 shows the photodegradation of BPA by ZnO tetrapods and P25. Despite that P25 exhibits faster degradation rate during the initial 20 min, the photocatalytic performance of ZnO tetrapods eventually surpasses P25 as the UV exposure time increases. After 60 min of UV irradiation, more than 80% of BPA is degraded with tetrapods as the photocatalyst, indicating excellent photocatalytic efficiency of tetrapods towards BPA. **Figure 5** summarizes the photodegradation curves of different organic dyes by ZnO tetrapods and P25. For all dyes selected, tetrapods result in comparable or higher photocatalytic performance over P25, which provides a support to the universal remarkable photoactivity of ZnO tetrapods.

The results in this study, together with other reports in the literature,[5, 10] demonstrate the superior photocatalytic performance of ZnO tetrapods for a variety of organic pollutants compared to Degussa P25 which is commonly regarded as a standard, highly efficient photocatalyst. Such high performance of tetrapods may stem from their intrinsic material properties. It has been reported that ZnO tetrapods exhibits excellent optical properties, for instance long photoluminescene (PL) lifetime at specified growth temperature, high UV-to-defect emission ratio, or even with the absence of visible defect emission in the room temperature photoluminescence.[7] ZnO tetrapods also possess excellent crystal quality with relatively low native defect concentration.[5-7] Native defects have been reported to play a hindering role in the photocatalysis reaction since they serve as the recombination center of the photogenerated electron-hole pairs and hence lead to recombination losses.[5] Thus lower native defects would contribute to higher photocatalytic efficiency. On the other hand, smooth, clean surfaces with negligible surface adsorbates, as well as a higher ratio of smooth $(10\bar{1}0)$ facets which exhibit high photocatalytic activity,[8] all these morphological advantages favor photocatalytic efficiency of ZnO tetrapods. One point worth noticing is that ZnO tetrapods have a micron-scale size and siginificantly lower surface area compare to Degussa P25 nanoparticles and other nanostructured photocatalysts. High surface area is conventionally considered as a crucial factor enhancing photocatalytic efficiency.[11] However, in the case of ZnO tetrapods, superior performance is observed over a range of different ZnO and TiO_2 nanoparticles with higher surface area than tetrapods. This may indicate that the excellent crystal and structural properties rather than surface area play a more determining role in the photoactivity of ZnO tetrapods.

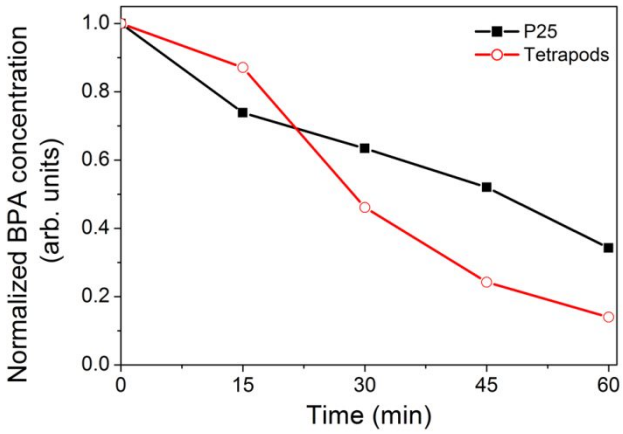

Figure 4. Photodegradation curve of BPA aqueous solution by ZnO tetrapods and Degussa P25.

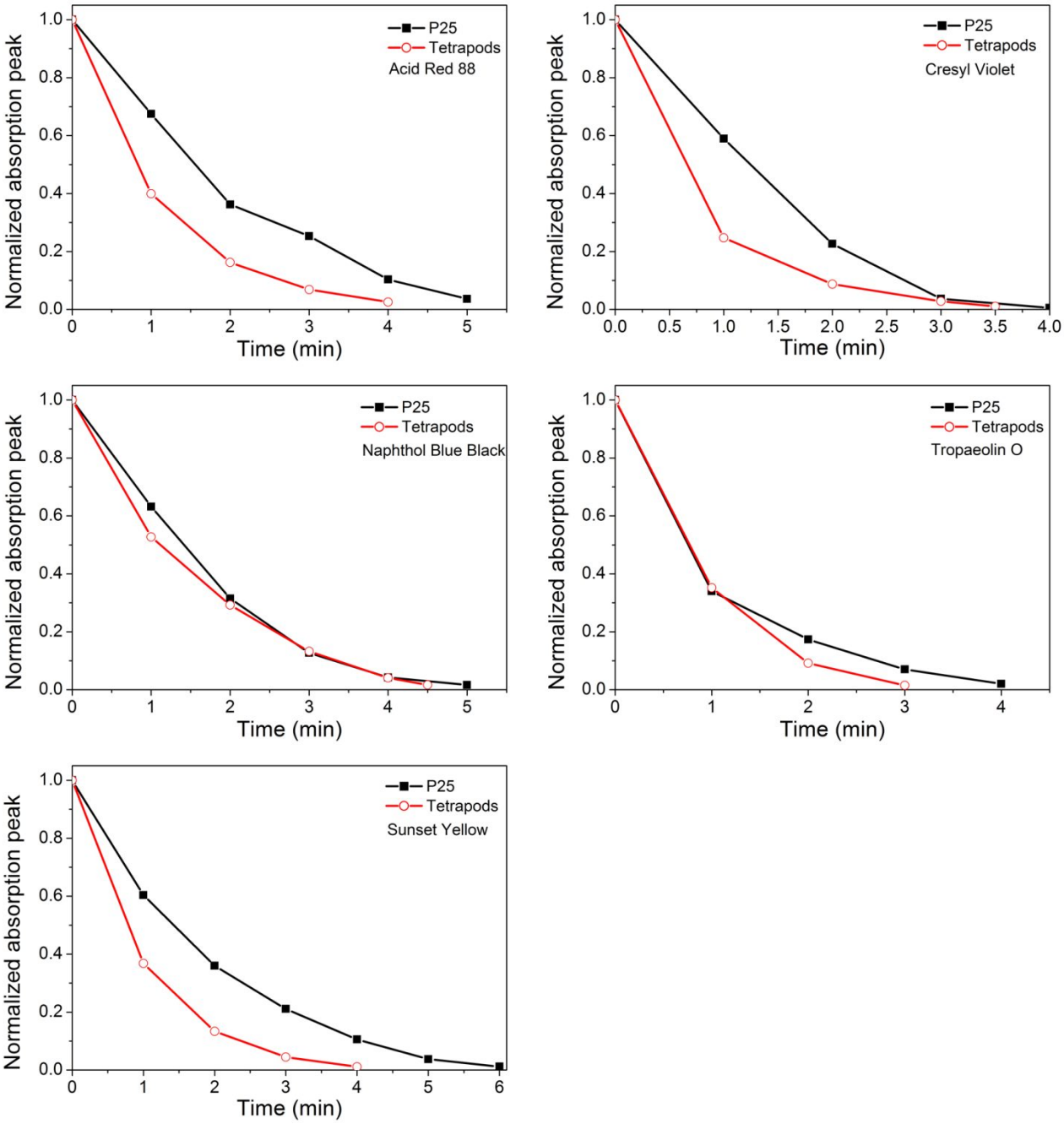

Figure 5. Photodegradation curves of different dyes by ZnO tetrapods and Degussa P25.

4. CONCLUSION

In this study we examined the photocatalytic activity of vapor-phase synthesized ZnO tetrapods compared with commercially available Degussa P25 TiO_2 nanoparticles as the standard catalyst. ZnO tetrapods exhibit higher performance in photodegradation of bisphenol A and various organic dyes than P25. The high crystallinity, smooth surface with specific photoactive terminating facets, as well as the negligible presence of surface adsorbates contribute to the superior photocatalytic activity of ZnO tetrapods.

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