

Optical and photocatalytic properties of photoactive paper with polycrystalline TiO_2 nanopigment for optimal product design

SEONGHYUK KO, PAUL D. FLEMING, MARGARET JOYCE, AND PNINA ARI-GUR

ABSTRACT: We investigated the effect of the crystalline phases of titanium dioxide nanopigment to optimize the optical properties and photocatalytic activity for synthesizing a photoactive paper. Six different ratios of anatase to rutile were prepared. Phase change and particle size were characterized using X-ray diffraction and transmission electron microscopy. Optical properties including opacity and brightness were tested. Photocatalytic activity was evaluated by measuring toluene decomposition, using gas chromatography. A specific ratio between two different crystallites of titanium dioxide showed relatively better optical and photoactive properties. The optimal anatase-to-rutile ratio was found to be 0.52:0.48.

Application: The effect of titanium dioxide crystalline phases on optical properties and photocatalytic activity is useful in designing photocatalytic paper with optimal printing quality, photoactivity, and marketability.

Titanium dioxide (TiO_2) has been largely used as an opacifying pigment and photocatalytic agent [1]. Due to its unique optical properties of high refractive index and whiteness, TiO_2 has long been incorporated in applications requiring high opacity and brightness, such as in paper coatings, paints, plastics, ink, and paper [2]. During the past two decades, nanocrystalline TiO_2 has drawn attention as a photocatalytic semiconductor material because it is photosensitive, inexpensive, nontoxic, and chemically stable [3–6]. These benefits have led to its wide application in solar cells [7,8], optical sensors [9], and hygienic products [10], as well as in extensive environmental cleanup for both air pollutants [11,12] and wastewater contaminants [13,14].

Among the various TiO_2 applications, there is growing interest in extending the range of applications of photocatalytic paper—defined as paper with a light-activated catalytic function that decomposes organic pollutants and kills pathogens [15]. Since the first photoactive TiO_2 -containing paper was introduced by Matsubara et al. in 1995 [16], a number of publications and patents have been issued [15]. Tanaka's research group [17–19] successfully prepared different types of photocatalytic paper composites with a dual polymeric retention system using TiO_2 supported by inorganic fibers. These papers were found to remove the hazardous chemicals of bisphenol A from wastewater, as well as indoor air pollutants such as acetaldehyde and toluene. Kinetic studies of ketone photooxidation over TiO_2 -containing paper were carried out in the presence of water vapor [20]. Fukahori et al. investigated the effect of microvoids of TiO_2 paper on acetaldehyde decompo-

sition [21]. It was reported that microscale voids, formed from a layered fiber network, improved the adsorption affinity of gaseous acetaldehyde and thereby improved adsorption capacity synergistically, contributing to the increased performance of photocatalysis. Recently, we have successfully prepared high-performance photocatalytic paper composite using nanotitania combined with a natural zeolite. Our previous study showed high photocatalytic activity for organic compounds due to the increase of TiO_2 retention rate and adsorption capacity of organic contaminant by natural zeolite and subsequent photodecomposition of adsorbate by TiO_2 particles [22,23].

Titanium dioxide is well known to have three main crystalline structures with different optical and physical properties; namely anatase, brookite, and rutile [1]. Due to its larger surface area and higher capacity of radicals ($\text{OH}\cdot$ and $\text{O}_2\cdot^-$) generation, anatase has higher photoactivity than rutile and brookite. Anatase transforms to rutile with an increase in temperature because the Gibbs free energy is minimized to become thermodynamically stable; therefore, rutile is the most stable of the three main phases at high temperature [24].

It would not be an overstatement to say that photocatalytic paper could have innovative applications, for example, antimicrobial food packaging, bioactive conjugated catalytic paper, and toxin passivation and deodorizing. Most previous attempts to demonstrate its utility [17–21] have been performed by using exclusively anatase TiO_2 because of its strong photooxidation activity compared to rutile and brookite. Rutile TiO_2 has the relative advantage of optical and photosensitivity because of its exceptionally high refractive index and

smaller band gap energy [24], which provide better visible light absorption efficiency. Furthermore, the mixture of these two polymorphs enhances photocatalytic activity at a specific ratio due to the special electronic states of the two crystal structures, which allows for a semiconductor-semiconductor junction. In other words, a space-charge region forms at the rutile-anatase interface where the charge-transfer process occurs because of the difference in the band gap between rutile and anatase. Photoexcitation generates electron-hole pairs in anatase particles and then the holes transfer into the rutile phase. Bickley et al. [25] have proposed that a mixture of approximately 20%–25% rutile and 75%–80% anatase may be an optimal blend for photocatalysis.

Interestingly, the study of optical properties against photocatalytic activity for use of the bicrystalline TiO_2 pigment in photocatalytic paper applications is hardly reported in the literature. Similar works focused only on photoactivity [26–28]. We explored the optimum combination of TiO_2 crystalline phases to impart opacity and brightness, while maintaining the high photocatalysis function in a photocatalytic paper. To date, such an investigation of the simultaneous effect of photoactivity and optical properties on a paper substrate is unavailable in the literature.

In the present study, we investigated the properties of photocatalytic paper using bicrystalline TiO_2 . We examined the effect of the ratio of crystalline phases of polycrystalline TiO_2 nanoparticles on optical properties, such as opacity and brightness, and on photocatalytic activity. Six kinds of TiO_2 nanoparticles, with varied fractions of anatase and rutile, were applied to a paper substrate. The physical and optical properties were measured and the photocatalytic activity evaluated by measuring toluene decomposition. We determined the range of crystalline phase fraction for optimizing both optical properties and photocatalytic activity.

EXPERIMENTAL

Sample preparation

Nanocrystalline Degussa P25 TiO_2 (Evonik Degussa; Parsippany, NJ, USA) was used for this study. The P25 TiO_2 has a bicrystalline structure of 70% anatase and 30% rutile phase (surface area = 50 m^2/g). Crystalline phase modulation was accomplished by sets of heat treatments, which transformed anatase into the more thermodynamically stable rutile phase because of the thermal energy provided to overcome the activation energy. The heat treatment (calcination) of the TiO_2 powder was performed in air for 4 h at temperatures ranging from 500°C to 800°C. As a result, six different kinds of TiO_2 nanoparticles with varying fractions of crystal structures were obtained.

Titanium dioxide powder deposition was performed with a filler-free base paper prepared in the laboratory as follows. Filler-free handsheets of approximate 100 g/m^2 of basis weight were prepared with a diameter of 11.29 cm, then cut to 7 cm in diameter for use in vacuum filtering system. For the deposition of TiO_2 powder, an aqueous suspension was prepared by

mixing 0.1 g of TiO_2 in 50 mL of deionized water under vigorous stirring for 30 min. The solution was then sonicated for 1 h to minimize the presence of large aggregates. After sonication, the TiO_2 particles were immediately applied to a base paper, which contained no fillers, using a vacuum filtration system and dried at 80°C for 2 days. Finally, a well-dispersed TiO_2 filter cake formed on the top side was obtained. The coat weight calculated was about 26.0 g/m^2 based on the amount of TiO_2 used (0.1 g) and size of base paper (7 cm in diameter).

Characterization of TiO_2

To investigate the phase transition in the samples, X-ray diffraction (XRD) was performed with a Diano Diffractometer (Diano; Woburn, MA, USA) at room temperature using 20 kW Cu-K α radiation ($\lambda = 0.154$ nm). The average crystallite size of the samples was calculated from the X-ray line broadening, using the Scherrer equation [29], as follows in Eq. (1):

$$\tau = 0.9\lambda / \beta \cos\theta_b \quad (1)$$

where:

τ = the mean diameter of the particle, nm

λ = the wavelength of X-ray used, nm

β = the full width of diffraction lines at half of maximum intensity, radians

θ_b = the diffraction angle corresponding to the maximum peak

The crystalline phase fraction was also calculated by the formula [30] in Eq. (2):

$$W_R = 1 / [1 + 0.8(I_A/I_R)] \quad (2)$$

where:

W_R = the percentage of rutile phase

I_A = the intensity of anatase (101) diffraction peak

I_R = the intensity of rutile (110) diffraction peak

These peaks were chosen because they were the strongest lines in each phase; anatase (ICDD 21-1272) and rutile (ICDD 21-1276). In each calculation, the background was subtracted from the peak intensities and the lowest-intensity value of each series was taken to be the background for that sample.

The morphology and size of TiO_2 particles were determined with transmission electron microscopy (TEM) (JEM-1230 from JEOL; Tokyo, Japan). The samples for TEM imaging were prepared by dropping a small amount of TiO_2 dispersed in 2-propanol on a Formvar/carbon-coated copper grid (01814F from Ted Pella; Redding, CA, USA). Three typical regions of each sample were imaged at 300,000X magnification.

The optical properties of the TiO_2 deposited onto the paper were characterized with respect to opacity and brightness. Each optical property was tested using a BNL-2 Opacimeter (Diano) and a Micro S-5 BrightMeter (Technidyne; New Albany, IN, USA), respectively. Ten measurements were taken

for each sample and the average values were calculated and reported.

Evaluation of photocatalysis

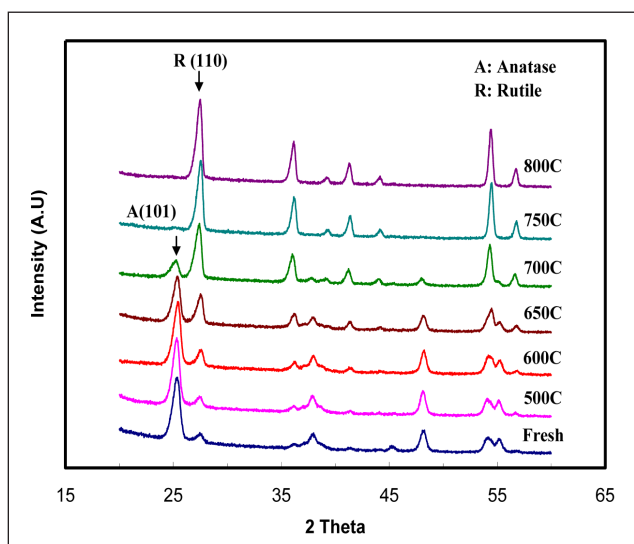
To evaluate the photoreactivity, the photocatalytic decomposition of gas-phase toluene was carried out at room temperature in a 1-L glass photoreactor under ultraviolet (UV) light irradiation (blacklight lamp, 4W, $\lambda = 365$ nm from Eiko North America; Shawnee, KS, USA). The initial concentration of toluene was 73.1 ppm (v/v). Titanium dioxide powder was deposited onto the paper substrate with a diameter of 7 cm. The distance from the lamp was maintained at about 10 cm. For the quantitative analysis of toluene concentration during the UV irradiation process, gas samples were withdrawn from a sampling port attached to the reactor and injected into the gas chromatograph (SRI 8610C from SRI Instruments; Torrance, CA, USA) equipped with a flame ionization detector (FID) and a 30-m $\times$ 0.25-mm fused silica capillary column (Quadrex; Woodbridge, CT, USA).

RESULTS AND DISCUSSION

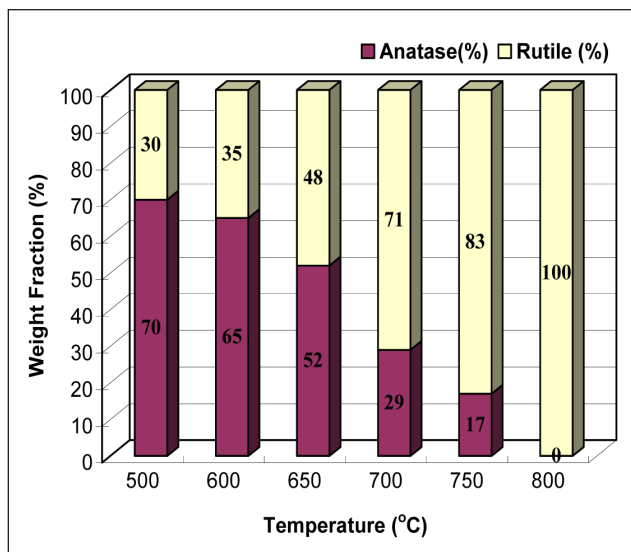
X-ray diffraction patterns and crystalline phase transition

Figure 1 shows the XRD patterns for the P25 TiO₂ nanoparticles calcined at different temperatures. Diffraction peaks correspond to reference patterns (anatase: ICDD 21-1272, rutile: ICDD 21-1276) of crystalline TiO₂. It is evident that P25 comprises anatase and rutile phases and the crystallite structure gradually transforms to rutile from anatase along with heat treatment. As shown in Fig. 1, nothing happens to the crystalline phase at a temperature of 500°C. The diffraction intensity of the rutile phase increased at 600°C and the anatase phase completely disappeared after being heat treated at 800°C.

Figure 2 shows the change in phase fraction at the different calcination temperatures. Using the strongest intensity



1. X-ray diffraction patterns of phase-modulated P25 titanium dioxide (TiO₂) nanoparticles.



2. Crystallite fractions of TiO₂ nanoparticles calcined at varied temperature.

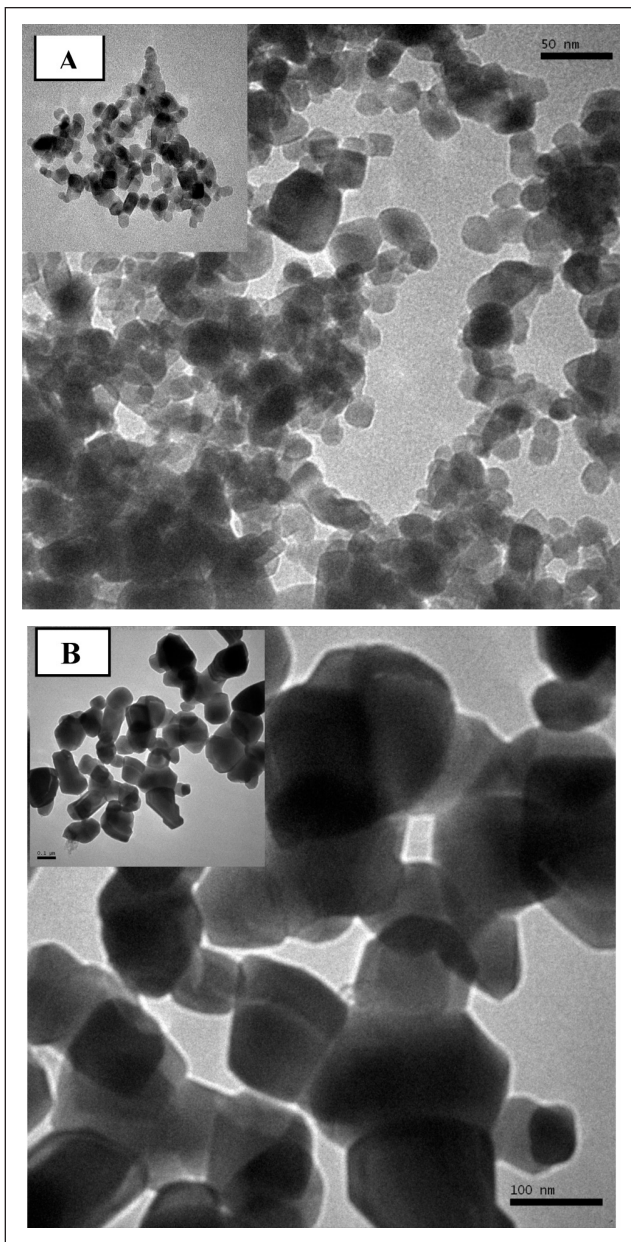
of each diffraction peak, the phase fraction was numerically determined and was found to be in the range of 30%–100% rutile phase. On the basis of the Scherrer equation, Eq. (1), which was used to estimate the size of nanoparticles, the average particle size of anatase remained about 25 nm in diameter. The particle size of the rutile phase was about 40 nm in diameter throughout the entire range of the heat treatments.

Titanium dioxide morphology and particle size

Transmission electron microscopy images of the P25 TiO₂ powder are shown in **Fig. 3** (no calcination and calcined at 800°C). Two different grain sizes were observed. The smaller particles appeared to be approximately 20 nm in diameter and the larger particles appeared to be about 40 nm. These were in agreement with the calculations based on the XRD measurements. Because the anatase phase is dominant in the XRD pattern (Fig. 1), it may be concluded that the smaller particles are anatase and the larger particles are rutile, which is compatible with the observations of others [31]. In addition, the rutile phase TiO₂ in Fig. 3 showed that the majority of the TiO₂ particle sizes were within the range of 40–50 nm in diameter. This also suggests that two phases in P25 TiO₂ coexisted in close proximity and the photocatalytic activity of P25 TiO₂ was mainly being contributed by the anatase phase.

Optical properties

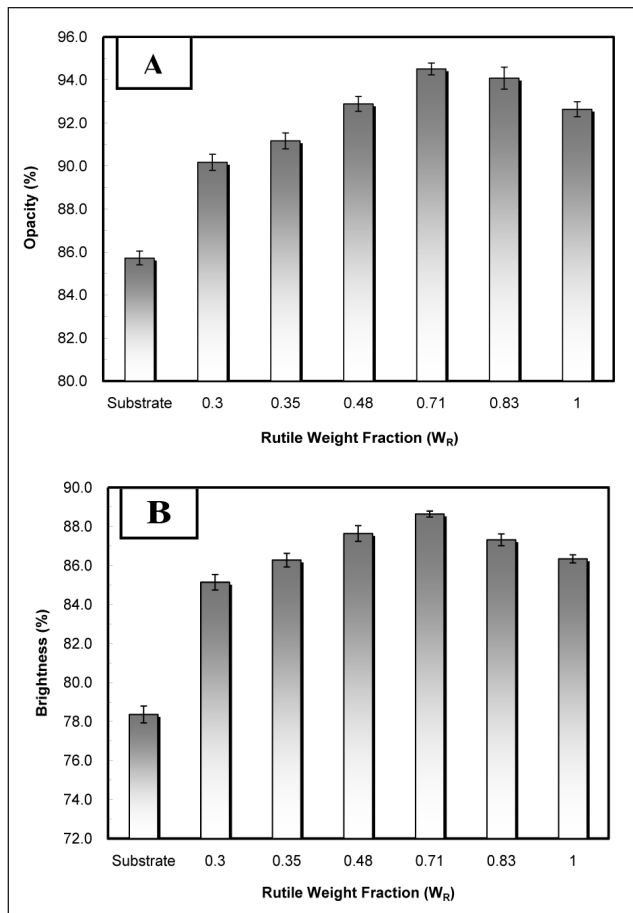
Transmission electron microscopy results revealed that primary single particle size ranged between 25 nm and 50 nm in diameter, which was essentially transparent in the visible light region (400–700 nm wavelengths). However, the P25 TiO₂ tended to aggregate in aqueous media, although it was treated with sonication and formed secondary agglomerated larger particles with the range of 300–500 nm. It is well known that particle size must be larger than a half of the light wavelength ($> \lambda/2$) to reflect light. Therefore, due to the agglomerates of



3. Representative transmission electron microscopy images of P25 TiO₂ nanoparticles: (A) no calcination, mixture of anatase and rutile phase, scale bar = 50 nm and (B) calcined at 800°C, rutile phase only, scale bar = 100 nm.

nanoparticles, nanosized TiO₂ used in this study showed some optical properties in the visible region.

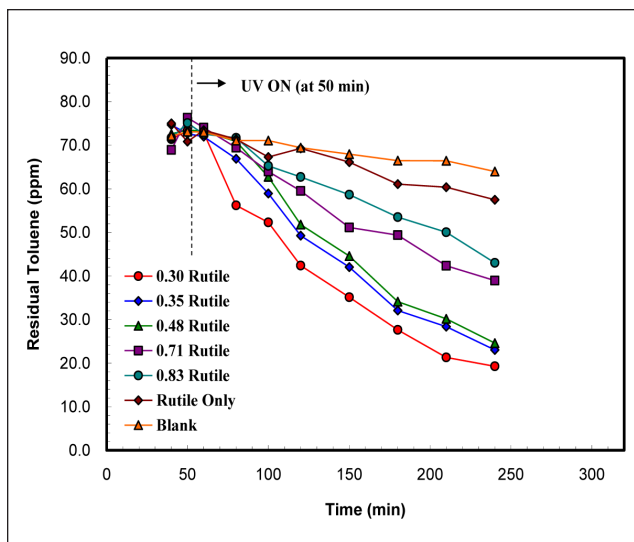
Figure 4 shows the change in opacity and brightness with the weight fraction of rutile. In general, it was highly expected that the pure rutile phase would give the best opacity and brightness, due to its higher refractive index and better ability to reflect radiation in comparison to anatase. As seen in Fig. 4, an optimal ratio between the two crystalline forms, anatase and rutile, exists. Specifically, the optimal fraction of the two crystalline phases occurred near the 0.29 anatase and 0.71 rutile ratio for both opacity and brightness. Because both



4. Optical values of TiO₂ nanoparticles according to different rutile fractions: (A) opacity and (B) brightness.

anatase and rutile crystals are highly birefringent due to the large difference in their ordinary (n_o for radiation polarized in the x or y direction) and extraordinary (n_e for radiation polarized in the z-axis) refractive indices, there will be a significant discontinuity of the refractive index (Δn) at the grain boundaries. It is known that at the two bordering anatase and rutile particles, refraction or bending of light across a grain boundary increases as Δn increases. Therefore, a different ratio of crystalline phase gives different Δn , and optical properties of TiO₂ particles vary from the ratio of phase.

Notably, for paper sheets, opacity is a function of refractive index relative to the air. The greater the difference is in refractive index, the higher the amount of light scattering. It is also known that light scattering occurring from particles is also attributed to direct reflection and diffraction [2]. Nelson and Deng [32] recently reported that light-scattering efficiency of a biphasic pigment increased by reflection and refraction of light at the grain boundaries between crystals of different phases, which have different refractive indices. From the fact that anatase has the more sensitive phase in terms of UV reflectance with high surface area, it is understood that combinations of anatase could strengthen optical properties because of synergetic effects of refraction, reflection, and



5. Photodegradation of toluene with varied crystalline phase of TiO_2 nanoparticles under ultraviolet irradiation.

diffraction between the two phases in light scattering.

Photocatalytic activity

For the photocatalytic activity, toluene was used as a model compound to investigate the effect of phase transformation. **Figure 5** shows toluene removal with TiO_2 nanoparticles as a function of rutile contents from 0.3 to 1.0 weight fraction. As shown in Fig. 5, residual toluene increased gradually by small steps to 0.48 rutile fraction, while efficiency of toluene removal dropped rapidly at 0.71 rutile; only 25% of initial toluene was removed using rutile phase only. A similar effect of the rutile phase on photodecomposition rate has been observed by others [26–28]. It is highly probable that rutile TiO_2 has a low photooxidation capability because it has low-level conduction band energy, which does not have enough reducing potential to produce a superoxide ($\text{O}_2^{\bullet-}$) from molecular oxygen (O_2). It has been found that the superoxide is as important as the holes and hydroxyl radicals in breaking down organic compounds [1]. As a result, photocatalytic activity is strongly dependent on the anatase phase.

CONCLUSIONS

The results of our studies of optical properties and photocatalytic activity allowed us to design a photoactive paper using TiO_2 nanopigment with unique principal crystal structures of anatase and rutile. Six different fractions of crystal structure of TiO_2 with anatase to rutile ratios in the range of 0.7:0.3–0:1 (100% rutile) were prepared. The 0.29 anatase:0.71 rutile phase composition of TiO_2 was significantly better for the optical properties of opacity and brightness than that of the other fractions, even though pure rutile has a higher refractive index. The photocatalytic activity in toluene decomposition gradually decreased with a decrease in anatase phase and its removal efficiency greatly decreased beyond the 0.48 rutile ratio. Accordingly, there was an optimal range of anatase and

rutile crystalline phases that provided better optical properties and photocatalytic activity. The optimal ratio of the two TiO_2 phases was determined to be 0.52 anatase:0.48 rutile.

We have been successful in implementing the effects of different phase ratios of nanocrystalline TiO_2 in optical and photocatalytic activities. Previous work has suggested [1] that when TiO_2 is present next to fiber in the form of very fine particles within 20 nm in diameter, the hydrogen bonds between fibers are broken by photocatalysis and the paper loses strength. In contrast, when TiO_2 aggregates on the fiber it has less photocatalytic effect on breaking hydrogen bonds and the paper strength can be maintained at a satisfactory level even when the paper is exposed to light. However, none of these studies performed coating with some additive binders and none had different crystalline phases of TiO_2 as we reported. The effect of size distribution and crystalline phase ratios of TiO_2 mixed with organic materials such as coating binders is a topic for further work to establish correlation between loss of paper or coating strength and photocatalytic activity when the paper is irradiated.

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ABOUT THE AUTHORS

Titanium dioxide (TiO₂) has been widely used for two major purposes: as an opacifying pigment and as a photocatalysis agent. Because of its unique optical properties (i.e., high refractive index and whiteness), TiO₂ has long been used in applications requiring those properties, such as coatings, paints, plastics, inks, and paper. To most researchers who are working in the area of photocatalysis, it is probably true that TiO₂ is one of the most well-known photocatalysis materials. In general, however, many paper engineers and scientists are much more likely to consider TiO₂ as white pigment only. The use of TiO₂ as a photocatalyst and its application for a new type of paper product is still quite unknown in the field of paper engineering and industry.

Our research was quite new. As either pigment or photocatalyst, technical application of TiO₂ has a very wide spectrum for an industrial standpoint. Whereas previous work was focused on the synthesis of nano-TiO₂ and testing of its photocatalytic properties, our research tried to use TiO₂ nanomaterials to develop a new pulp and paper product area, photocatalytic paper.

The most challenging aspect of this research was the deposition of TiO₂ nanoparticles on the paper substrate. To reduce particle aggregation, particle solution was sonicated for a long time, followed by immediate vacuum suction through the substrate.

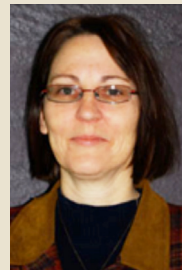
This research started with a question: Will be there tradeoff point between different crystalline phases of



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Fleming



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TiO₂ in optical properties and photocatalytic activity? We found that there is an optimum ratio of rutile and anatase TiO₂ that provides better printing quality and photoactivity when the photocatalytic paper is used.

Paper mills can use the information and results obtained in this research to produce photocatalytic paper having different optical properties and photoactivity according to the application.

The TiO₂ used in our research was UV-only activated. The next step will be the development of a visible light-responsive TiO₂-based photocatalyst, which can more effectively use indoor light or sunlight, and its use in photoactive paper.

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