

# Enhanced Light Scattering from Hollow Polycrystalline TiO<sub>2</sub> Particles in a Cellulose Matrix

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Hollow and core–shell rutile particles were synthesized, and their opacifying power in a cellulose matrix was compared with that of commercial solid rutile particles. It was found that the opacifying power of hollow polycrystalline rutile particles was superior to that of a commercial rutile pigment in a highly pressed bleached fiber matrix, depending on cavity size, whereas the opacifying power of silica–rutile titania core–shell particles was found comparable to that of commercial rutile at constant titania loading. The light scattering efficiency of titania core–shell particles was also shown to be dependent on the light scattering efficiency of the core material. The light scattering efficiency of the polycrystalline silica cores was found to depend on calcination temperature and crystal structure.

## Introduction

Characterization of the scattering of light by titanium dioxide particles has been the subject of significant research for many decades, as TiO<sub>2</sub>'s many technological applications often depend on its high light scattering efficiency. Because of its exceptionally high refractive index and whiteness, titanium dioxide is used to impart opacity to a wide variety of products including coatings, paints, plastics, paper, rubber printing inks, synthetic fibers, ceramics, cosmetics, and even toothpaste.<sup>1</sup> Increasing global demand growth, coupled with raw material supply constraints, has led to increasing prices for an already exceptionally expensive pigment. The introduction of novel, even more efficient light scattering TiO<sub>2</sub>-based pigments can help manufactures limit costs while maintaining the required optical properties of their product. One approach to increasing the efficiency of TiO<sub>2</sub> is to create unique pigment morphologies designed to scatter light more effectively than conventional TiO<sub>2</sub> pigments. Modifying pigment structure to enhance light scattering is not a new concept. Pigment suppliers offer several varieties of "structured and engineered pigments" including highly structured or calcined clay, TiO<sub>2</sub>/clay aggregates, and hollow plastic pigments.<sup>2</sup> Uniform, hollow latex plastic pigments enhance opacity by incorporating large amounts of air into coatings. Unlike solid particles whose optical performance depends on the surrounding media, the hollow spheres have a large air/particle shell interface on their interior surface that is always available to scatter light, no matter what media surrounds the outer surface of the particle.<sup>3</sup> From experimental studies, the optimal particle size and void volume for the hollow spheres are 1060 nm and 50%, respectively.<sup>4</sup>

A recently developing field of practical and scientific interest is the synthesis of novel inorganic pigment structures using sophisticated techniques borrowed from the fields of nanotechnology and interfacial science. Although such particles have

wide applicability across many fields, for papermaking they are designed to offer enhanced optical and physical performance. Ideally these particles should have high opacity and provide high bulk and minimal impact on paper strength. As a result of these requirements, many these novel fillers have a highly porous or hollow structure, designed to minimize material usage and density and enhance light scattering. Several research groups have synthesized hollow calcium carbonate particles ranging from 0.5 to 300  $\mu\text{m}$ .<sup>5–13</sup> Enomae and Tsujino prepared spherical hollow particles of precipitated calcium carbonate (PCC) between 0.5 and 2  $\mu\text{m}$  in diameter using interfacial reaction in a water-in-oil (W/O) emulsion.<sup>8</sup> The shell is composed of aggregated crystals between 50 and 300 nm in mixed crystal forms of calcite and vaterite. These particles give higher specific light scattering coefficient than conventional ground calcium carbonate for both paper filler and coating applications. Also, when compared to hollow plastic pigments, hollow PCC gives higher light scattering, presumably due to PCC's higher refractive index. Researchers have also synthesized hollow silica<sup>14,15</sup> and clay particles.<sup>15,16</sup> Many reports have been published on the synthesis of spherical core–shell<sup>17,18</sup> and hollow<sup>19–38</sup> titania particles.

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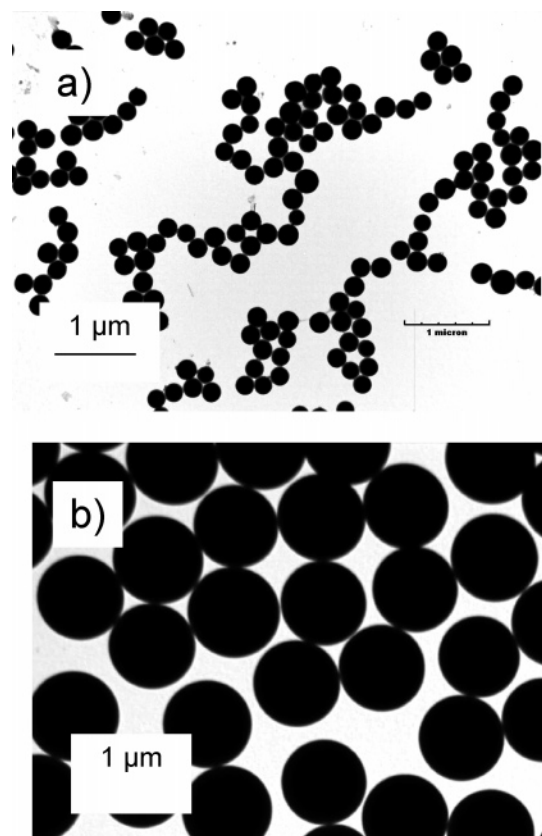
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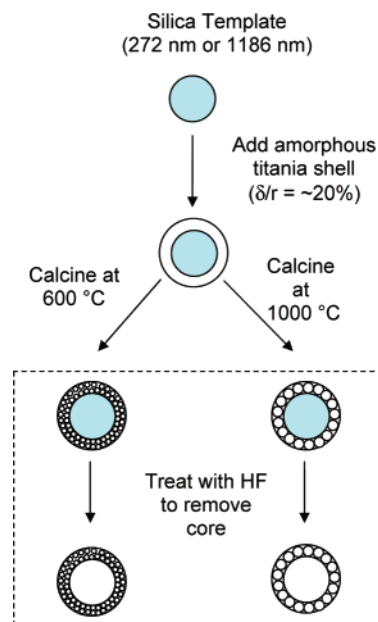
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**Figure 1.** TEM images of the monodisperse silica cores with average diameters of (a) 272 and (b) 1186 nm.

If hollow plastic and calcium carbonate pigments, with low shell refractive near 1.59, enhance light scattering as light is refracted between the shell and the air-filled core, one can easily anticipate even more light scattering from a titania shell with a refractive index of 2.72. Hsu et al. were the first group to experimentally and theoretically investigate the hiding power of core-shell titania particles.<sup>39</sup> They coated monodispersed spherical silica with titania and evaluated hiding power in a cellulose matrix as a function of core diameter (0.2–1.3  $\mu\text{m}$ ) and titania shell thickness. Optimum opacity was obtained for core-shell particles with an overall diameter of  $\sim 1.0 \mu\text{m}$  and a shell thickness of 50 nm, corresponding to about 40 wt %  $\text{TiO}_2$ . This powder gave an opacity comparable to that of a commercial rutile powder when incorporated into an Avicel matrix at constant mass loadings of 17%, 37%, and 50% filler. These experimental results were supported by theoretical light scattering calculations using the well-known BHCOAT computer program developed by Bohren and Huffman<sup>40</sup> based on Mie theory. Several years after this study, researchers from DuPont Titanium Technologies



**Figure 2.** Illustration of the synthesis method for preparation of core-shell and hollow titania morphologies.

**Table 1.** Reactant Concentrations for Synthesis of Titania-Coated Silica Core-Shell Particles

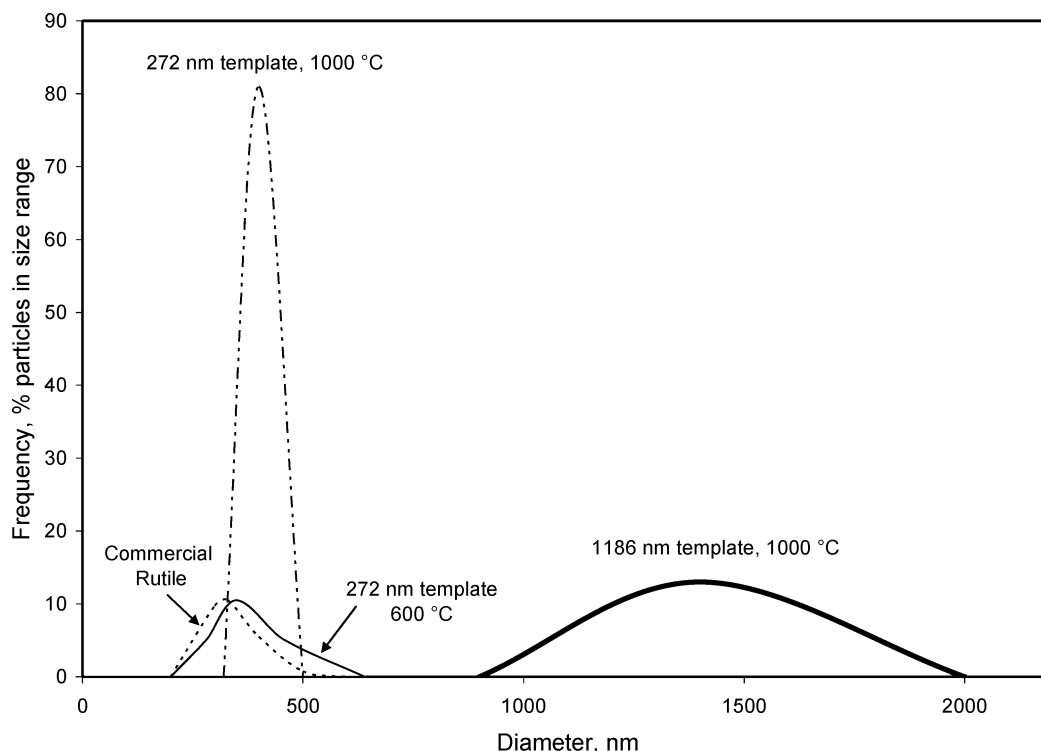
silica diameter, nm	272	1186
silica, g	0.075	0.075
PVP, g	0.06	0.06
ethanol, mL	50	50
TBT (96 wt %), g	0.224	1.1228
water	0.512	2.56

published a rebuttal based on theoretical light scattering calculations using the program BHCOAT modified to incorporate the asymmetry parameter, which accounts for the direction of light scattered from a particle.<sup>41</sup> The researchers argue that the theoretical calculations performed by Hsu et al.<sup>39</sup> for an isolated particle cannot be used to anticipate the light scattering of  $\text{TiO}_2$  in actual films where multiple light scattering occurs between the large numbers of particles present. The opacity of a film depends on the ability of the pigment to scatter light back in the direction from which it came. A single particle efficiently scatters light, but typically for small spherical particles only a small portion is scattered in the backward direction. However, light scattered by multiple particles is bent a sufficient number of times to achieve a backward direction. Thus in practical applications, the reflectance of light by a film (opacity) depends on the predominant direction in which the pigments scatter light and the number of times the light is scattered by other particles. The asymmetry parameter includes the scattering angle to give a scattering parameter that is meaningful to correlate with the value of a pigment for opacification in real applications. Their calculations show that core-shell pigments are substantially less efficient light scattering materials than pure rutile.<sup>41</sup> However, this conclusion is questionable because the shell used in their calculation consists of only one crystal. Actually, polycrystalline rutile particles were actually found in most hollow  $\text{TiO}_2$  obtained experimentally. Therefore, how a hollow-structured polycrystalline rutile particle affects the opacity needs to be studied.

This paper presents an experimental solution to the problem of light scattering by well-dispersed polycrystalline core-shell and hollow titania particles in an optically uniform, transparent, pore-free cellulose nanowhisker matrix. The effects of shell crystal

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**Figure 3.** Particle size distributions of synthesized and commercial TiO<sub>2</sub> obtained from light scattering.

structure, core structure, and core/cavity size on the opacifying power of the synthesized pigments are investigated and compared with those of a commercial rutile pigment.

### Experimental Section

**Materials.** Cotton pulp (Procter and Gamble Cellulose) and rutile titanium dioxide (Tiona RCS-P, Millennium Chemicals) were donated and used as received. Commercial dry lap bleached Kraft pulp (1:1 softwood/hardwood) was refined to a Canadian standard freeness of 400. Sulfuric acid (96.5%, EM Science), poly(acrylic acid, sodium salt) (PAA, MW 5100, Aldrich), poly(ethylene glycol (PEG, MW = 8000, Aldrich), poly(vinylpyrrolidone) (PVP, MW = 55 000, Aldrich), titanium(IV) butoxide (TBT, 97%, Aldrich), tetraethyl orthosilicate (TEOS, 98 wt %, Aldrich), ammonia (29 wt %, VWR), hydrofluoric acid (48%, Aldrich), and ethanol (anhydrous, VWR) were used without further purification. Water was obtained from a Nanopure ultrapure water system with a resistivity of about 18 MΩ cm.

**Preparation.** As shown in the TEM images of Figure 1, monodispersed silica particles with diameters of 272 and 1186 nm were prepared by hydrolysis of TEOS in ethanol in the presence of water and ammonia. Particles with a diameter of 272 nm were prepared following the methods of Hsu et al. and Giesche.<sup>17,42</sup> Water (53.307 g) and ammonia (29 wt %, 26.441 g) were added to 330 mL of ethanol and heated to 40 °C under reflux. TEOS (98%, 26.573 g) was also heated to 40 °C in a separate, closed container. TEOS was then added to the ethanol solution under vigorous stirring. Fifteen seconds later, the stirring was reduced to low and continued for 1 h at 40 °C. The resulting solids were isolated by three centrifugation and ethanol washing cycles at 25 900 RCF (relative centrifugal force) for 2.5 min and freeze-dried.

Silica particles with a diameter of 1186 nm were prepared following the method of Barder and DuBois.<sup>43</sup> The synthesis requires (a) 312 mL of TEOS (98%) and (b) 651 mL of a solution containing ethanol (11.3 wt %), ammonia (10.6 wt %), and water (78 wt %). In step 1, 12 mL of solution a are combined with 50 mL of solution b at room temperature and stirred gently for 5 min. The same amounts

of solutions a and b are then added to the reaction every 5 min for 1 h for a total of 12 additions. In step 2, the same amounts of solutions a and b are added to the reaction every 3.5 min for 2 h and 15 min for a total of 39 additions. The resulting solids were isolated by three centrifugation and ethanol washing cycles at 25 900 RCF for 2.5 min and freeze-dried.

To study the effect of calcination on the polycrystalline composition of the silica particles, both silica powders were calcined at 600 and 1000 °C. Prior to calcination the titania particles were mixed with dispersed cellulose particles in water with a ratio of 1 to 5 to prevent interparticle sintering. The dispersion was then sonicated (Heat Systems—Ultrasonics W-385 probe sonicator) for about 5 min. The mixture was dried under vacuum at 120 °C and then calcined at different temperatures for 1.5 h. The cellulose powder was prepared by grinding hardened, ashless filter paper (Whatman, 541) in a Wiley mill (Arthur H. Thomas Co.) to pass through a 1 mm mesh. This specialty filter paper was used because of its extremely low inorganic ash content (0.017%).

The freeze-dried 272 and 1186 nm silica templates were coated with an amorphous titania shell using the sol–gel synthesis methods of Hanprasopwattana et al. and Liu et al.<sup>44,45</sup> Table 1 gives the concentrations of reactants used for each template to obtain an amorphous shell thickness that is approximately 20% of the core–shell radius. Using the 272 nm template case as an example of the general synthesis method, 0.075 g of the silica powder was first added to 10 mL of ethanol along with 0.06 g of PVP dispersant, and the mixture was sonicated for up to 45 min (5 min for the 1 μm template) to completely disperse the particles. The remaining 40 mL of ethanol was added to the suspension along with 0.224 g of TBT solution (96%). Under moderate stirring at room temperature, 0.512 g of water was added to the system at a rate of 0.003 g/min. The resulting solids were isolated by three centrifugation and ethanol washing cycles at 25 900 RCF for 2.5 min and vacuum-dried at 60 °C.

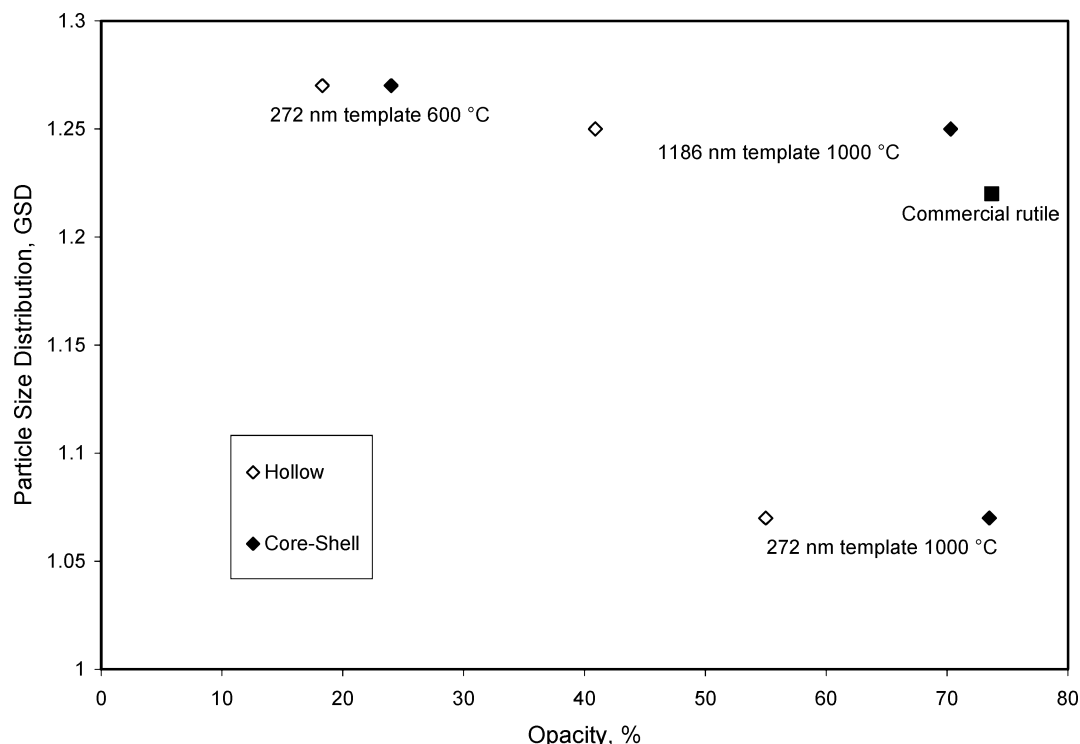
The particles were then calcined in a cellulose matrix at either 600 or 1000 °C for 1.5 h to obtain anatase or rutile polycrystalline shells, respectively. Half of the calcined core–shell powder was

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**Figure 4.** Relationship between GSD and opacity for the synthesized and commercial rutile powders.

**Table 2.** Synthesized and Commercial TiO<sub>2</sub> Particle Characterization and Corresponding Opacity for a 70  $\mu$ m Thick Cellulose Film Loaded with 3 wt % Titania

		crystal phase	crystallite size, nm	particle size, nm	shell thickness, nm	shell thickness, $\delta/r$	opacity at 70 $\mu$ m
272 nm template 600 °C	core-shell hollow	anatase	$19.9 \pm 1.5$	357	43	24%	24.0 18.3
272 nm template 1000 °C	core-shell hollow	rutile	$82.3 \pm 1.2$	400	64	32%	73.5 55.0
1186 nm template 1000 °C	core-shell hollow	rutile	$158.9 \pm 5.4$	1425	120	17%	70.3 40.9
commercial		rutile	210	336	N/A	N/A	73.7

then treated with hydrofluoric acid overnight to dissolve the silica core and obtain hollow polycrystalline particles. Excess acid was removed by dialysis (Spectra/Por membrane, MWCO 50K) against water for several days until the water achieved a neutral pH. Figure 2 illustrates the four different particle types synthesized for each silica template size. However, the titania shell of the 1  $\mu$ m core-shell and hollow particles calcined at 600 °C did not remain intact during synthesis, and these powders were discarded. The possible reason for these particles not remaining intact is that the size of the crystals synthesized at 600 °C is much smaller ( $\sim 20$  nm) than other particles synthesized at high temperatures (82 and 159 nm at 1000 °C, Table 2). Also the thickness of the sample synthesized at 600 °C is only 43 nm, which is much thinner than those synthesized at high temperature, 64 and 120 nm. Therefore, the mechanical integrity between the tiny crystallites is poor, which could not hold the shell during the calcinations.

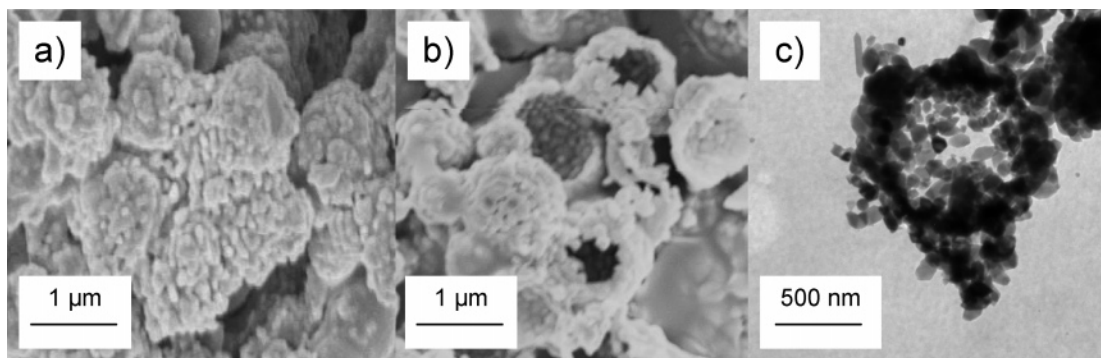
In order to compare the opacifying power of the synthesized nanoparticles with that of commercial rutile titania, the powders were distributed throughout two different types of cellulose-based films. The first film matrix composed of nanosized cellulose whiskers and PEG was chosen because these materials form a uniform, pore-free, transparent film, ideal for evaluating the opacifying power of the commercial rutile and core-shell pigments. This matrix is nonideal for evaluating the opacifying power of hollow pigments, since the liquid PEG can fill the hollow interior of the particles, thereby negating the light scattering that occurs in the air-filled cavity. To evaluate the opacifying power of the hollow titania particles, a second cellulose film matrix composed of highly pressed

bleached fibers was chosen. Although this matrix is nontransparent and so less ideal, the highly pressed cellulose fibers uniformly conform around the hollow particles, leaving the air-filled cavity intact. For a typical experiment utilizing the cellulose whiskers matrix, 0.04 g of pigment powder was dispersed in approximately 10 mL of water along with 0.004 g of PAA dispersant, and the mixture was sonicated (or minivortexed in the case of hollow particles) for 10 min. The solutions were then allowed to rest for about 2 min. During this time, oversized particles that could not be dispersed into primary particles during sonication, either because of agglomeration or sintering during calcination, quickly settle to the bottom while fully dispersed primary particles remain in the supernatant. The supernatant was then removed from the settled solids, and the settled solids were dried under vacuum and weighed. The supernatant was also weighed such that the exact concentration of the solution could be determined.

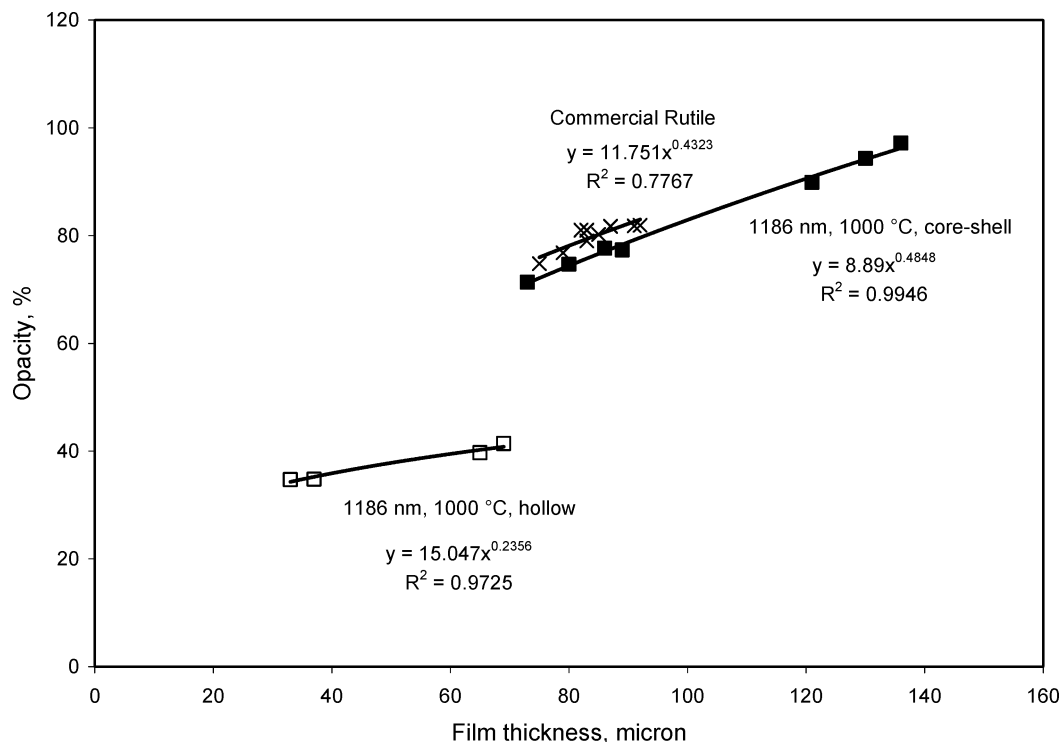
Cellulose films with a known weight concentration of uniformly distributed particles were then obtained by combining the well-dispersed filler suspension prepared above with PEG (whose role will be discussed below) and a gel-like solution of cellulose whiskers. This gel-like mixture was allowed to dry on a transparency within a 1.25 in.  $\times$  1.25 in. area framed by Scotch tape. For the typical film with a particle concentration of 3 wt %, 3.9105 g of cellulose whiskers solution (8.27 wt %) was combined with 0.1386 g of PEG and the filler suspension containing 0.01429 g titania. This mixture was then pipetted onto four separate 1.25 in.  $\times$  1.25 in. area films. The cellulose nanowhiskers were prepared as outlined previously.<sup>46</sup>

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**Figure 5.** SEM images of synthesized (a) core-shell and (b) hollow titania particles with a 1186 nm core calcined at 1000 °C and (c) TEM image of corresponding hollow particles.



**Figure 6.** Opacity of cellulose films loaded with 3 wt % 1186 nm template core-shell and hollow particles calcined at 1000 °C.

Since the hollow titania particles have a porous shell, the effect of air entrapped in the core on light scattering (and opacifying power) is negated when embedded in the cellulose/PEG film, since the liquid PEG fills the center cavity. Thus, in order to compare the hiding power of the hollow particles with the corresponding core-shell particles and with commercial rutile, the fillers were incorporated into a matrix composed of bleached fibers. This matrix was then highly pressed to remove air pores. Experimentally, the pulp was concentrated to a consistency of 5.47% such that only water bound to the pulp solids remained. The pulp (4.57 g) was then combined with 0.773 g of 1 wt %  $\text{TiO}_2$  solution containing 0.1 wt % PAA dispersant and minivortexed. The resulting paste was then spread onto a metal platen in a 4 in.  $\times$  1 in. square and vacuum-dried at 120 °C until slightly damp and pressed at 50 psi at 105 °C for 2 min using an automated pressing apparatus (P. Bonk and Co.). The resulting paper sheet was cut into four samples for optical testing.

**Characterization.** Transmission electron microscopy (TEM) was performed using a Hitachi HD-2000 field emission gun (FEG) microscope at 200 kV. X-ray diffraction (XRD) was carried out using an X'Pert Pro Alpha-1 diffractometer with an incident beam monochromator allowing only the  $\text{K}\alpha_1$  component of Cu radiation. XRD spectra were analyzed using JADE 7 software from Materials Data. It is well-known that the width of a peak in a diffraction pattern results from instrument optics and crystallite microstrain and size. With the use of the JADE software, the effect of instrumental

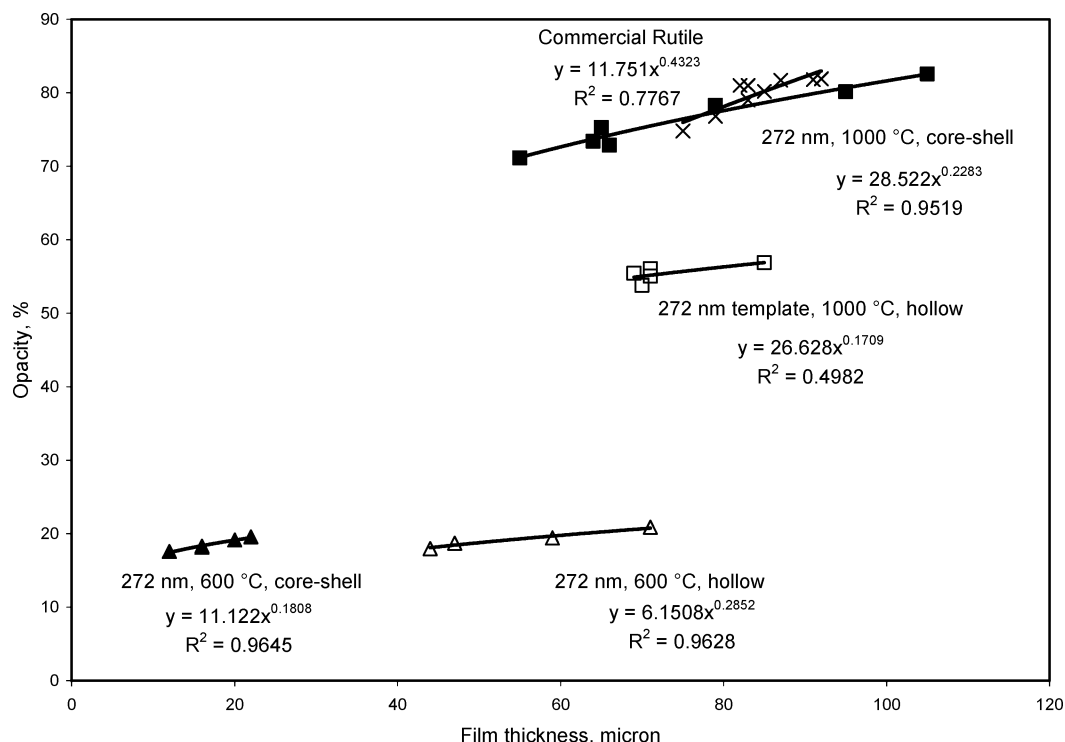
broadening was removed by calibration with the standard  $\text{LaB}_6$  (NIST, 660 SRM), and crystallite strain was calculated to be zero. Thus, crystallite size was calculated from peak broadening using classical Williamson-Hall plots.<sup>47</sup> The plots were constructed for all nonoverlapping peaks occurring for  $2\theta$  values between 20° and 80°. Pigment average particle size and particle size distributions were obtained with a Malvern 3000 Zetasizer. The width of the particle size distribution, or geometric size distribution, GSD, was calculated from the particle size distributions shown in Figure 3 using the equation

$$\text{GSD} = (d_{84}/d_{16})^{0.5}$$

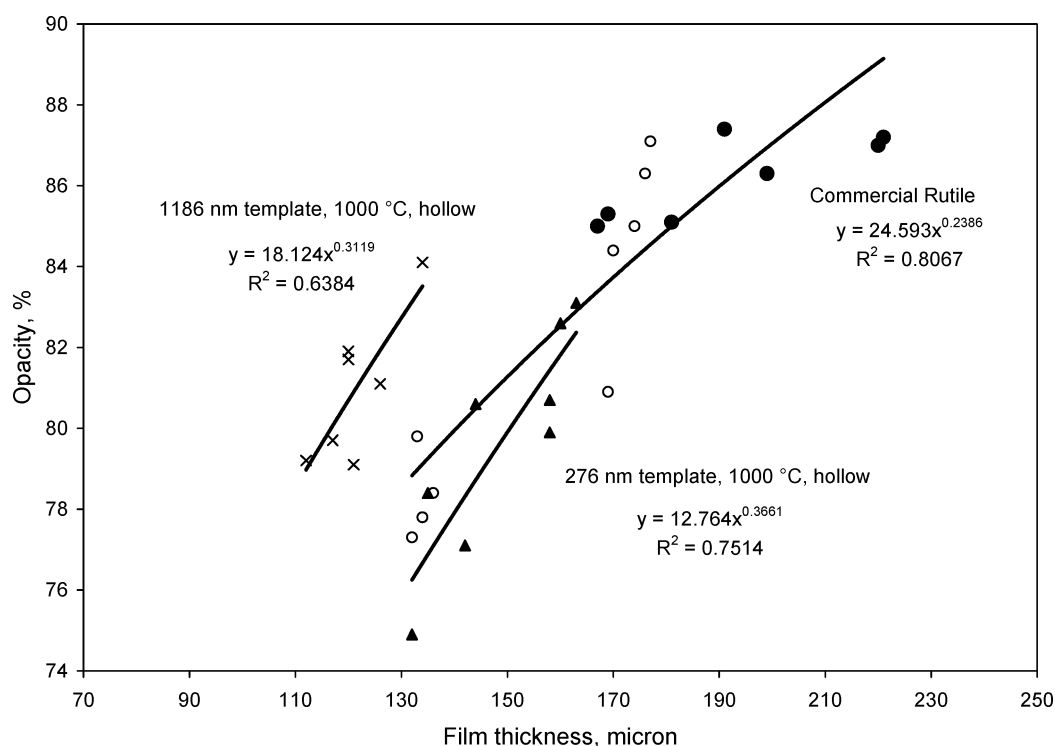
where  $d_{84}$  = diameter for 84% finer and  $d_{16}$  = diameter for 16% finer.

The TAPPI opacity of the pigment-filled cellulose films was measured using a Technidyne BNL-3 opacimeter with a quartz-tungsten-halogen lamp filtered for illumination at 572 nm. Film thickness was measured using a hard caliper instrument (AB Lorentzen and Wettre).

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**Figure 7.** Opacity of cellulose films loaded with 3 wt % 272 nm template core-shell and hollow particles calcined at 1000 °C.



**Figure 8.** Opacity of pressed fiber films loaded with 3 wt % hollow titania particles.

### Results and Discussion

The first part of this study evaluates the light scattering power of core-shell and hollow titania particles in an optically uniform cellulose/PEG film. A cellulose matrix was chosen to evaluate the light scattering performance of synthesized TiO<sub>2</sub> particles for two reasons: (1) papermaking represents an important technological application of TiO<sub>2</sub> and (2) there is an established debate in the literature on the relationship between morphology

and TiO<sub>2</sub> opacifying power in a cellulose matrix.<sup>17,41</sup> The light scattering power of TiO<sub>2</sub> in pigment applications depends on several factors including the severity of particle flocculation, the refractive index of the medium in which the pigment is dispersed, the wavelength of incident light, particle size distribution, particle size, and pigment concentration.<sup>48</sup> In order to experimentally evaluate the effects of pigment composition and morphology on

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TiO<sub>2</sub> opacifying power, care must be taken to fix these variables. In this study, cellulose whiskers were used as the matrix because they easily form a uniform, transparent cellulose film upon casting and drying. In addition, the cellulose whiskers are discrete rod-shaped nanomaterials, with dimensions of  $8 \times (100\text{--}300)$  nm, whose size allows even distribution, or spacing, of the TiO<sub>2</sub> particles. To remove the potential effect of small pores on the scattering of light within the film, low molecular weight PEG, with an index of refraction (1.47) which closely matches cellulose (1.53), was added to the aqueous solution of whiskers and pigment prior to casting the film. PEG remains a liquid at room temperature and can effectively fill possible small pores in the film. When the TiO<sub>2</sub> filled cellulose/PEG films were removed from the transparency upon which they were dried, the surface in contact with the transparency was very smooth and uniform. For all films, this surface was placed in contact with the fixed wavelength (572 nm) light source during opacity measurements. It is well-known that pigments with a broad size distribution centered around the optimal size have less opacifying power than a corresponding monodisperse distribution.<sup>48,49</sup> Pigment manufacturers report the width of the particle size distribution as geometric size distribution, GSD. Typically, as GSD increases for a given pigment, opacifying power is lower. Figure 3 shows the particle size distributions of the synthesized and commercial rutile TiO<sub>2</sub> powders. The widths of distribution are similar for all powders except the one synthesized from the 272 nm template and calcined at 1000 °C. Figure 4 shows that even though this synthesized sample has a significantly lower GSD than the other particles, it does not give the highest opacity. Thus, some other over-riding factor must explain the difference in opacity among the samples. This report attempts to identify this more dominate factor affecting opacity.

Particle sizes under investigation were chosen based on previous work by Hsu et al. who showed experimentally that opacifying power of titania-coated silica particles depends on the silica core diameter and titania shell thickness. Optimum opacifying power was observed for silica cores  $\sim 1.0$   $\mu\text{m}$  in diameter and for the maximum titania thickness that they could achieve,  $\delta/r \sim 10\%$ , where  $\delta$  is shell thickness and  $r$  is the diameter of the core-shell particle. In order to confirm these results, silica cores with diameters of 272 and 1186 nm were chosen. The sol-gel coating method used in this study allows deposition of uniform amorphous titania shells with any thickness. The amorphous titania shell thickness target was fixed at  $\delta/r \sim 20\%$  for this study. Upon crystallization of the shells during calcination, the density and thickness of the shell changes, depending on calcination temperature and titania crystal phase formed. Table 2 lists the post calcination particle sizes and shell thicknesses.

The phase composition and crystallite size of the titania shell are dependent upon calcination temperature. X-ray analysis showed the titania shells for the particles calcined at 600 and 1000 °C to be composed of pure anatase and rutile, respectively (XRD spectra are given in Supporting Information Figure S-1). As shown in Table 2, for both coated templates calcined at 1000 °C, the average rutile crystallite size determined by XRD and the shell thickness estimated from light scattering data agree closely: 82 and 64 nm for the 272 nm template and 159 and 132 nm for the 1186 nm template, respectively. The close agreement of these values suggests that the rutile shell is one rutile crystal thick. The particle morphologies of the synthesized hollow and core-shell particles are shown in the TEM and SEM images of Figure 5 and Supporting Information Figures S-2 and S-3.

**Table 3. Synthesized Silica Particle Characterization and Corresponding Opacity for a 70  $\mu\text{m}$  Thick Cellulose Film Loaded with 3 wt % Pigment**

	crystalline phase	crystallite size	opacity
250 nm			
no heat	cristobalite low	$1.4 \pm 0$	15.8
	cristobalite high	$2 \pm 1$	
600 °C	cristobalite low	$<1$	18.1
	cristobalite high	$49.2 \pm 1.3$	
1000 °C	cristobalite low	$34.9 \pm 2.6$	41.1
	quartz	$51.0 \pm 1.4$	
1 $\mu\text{m}$			
no heat	cristobalite low	$1.7 \pm 0$	14.9
	cristobalite high	$2 \pm 1$	
1000 °C	cristobalite low	$27.6 \pm 0.5$	28.2
	quartz	$24 \pm 2$	
commercial TiO <sub>2</sub>	rutile	210	73.7

Whereas the 600 °C shell is smooth and uniform, the 1000 °C samples have a rough and irregular shell.

The opacifying power of the synthesized polycrystalline core-shell and hollow TiO<sub>2</sub> particles in a cellulose film was investigated experimentally and compared to that of a commercial rutile TiO<sub>2</sub> pigment. Figures 6 and 7 compare the opacity of cellulose whisker/PEG films filled with the synthesized particles at a titania loading of 3 wt %, while Table 2 lists the corresponding opacity values for a film thickness of 70  $\mu\text{m}$ . It is important to note that due to the porous nature of the hollow particles, their interior in this matrix is filled with liquid PEG rather than air. Since the refractive index of air is 1 compared to 1.467 for PEG, the refraction of light going from the TiO<sub>2</sub> shell to the interior cavity, and therefore it is expected that hollow particle performs better than commercial TiO<sub>2</sub> fillers if the interior cavities of the hollow particles are filled by air rather than PEG. This will be confirmed and further discussed below. Figures 6 and 7 and Table 2 show that, at equal titania loading, (a) the opacifying power of the titania core-shell particles with a silica template size of 272 nm calcined at 1000 °C is equal to that of commercial rutile and (b) the titania-silica core-shell pigments have significantly more opacifying power than the hollow titania particles filled with PEG.

The only difference between the titania-silica core-shell pigments and the hollow titania particles filled with PEG is the core material. This is an interesting finding since the refractive index of PEG is 1.467 and that of precipitated silica is reported to be in the same range depending on the silica crystalline phase. We investigated the effect of calcination temperature on the light scattering efficiency of the silica cores. Table 3 shows that the opacifying power of the silica templates dispersed in the cellulose/PEG matrix increases dramatically upon calcination. Table 3 gives the results of XRD analysis of the crystal structure of the silica powders (XRD spectra are given in Supporting Information Figures S-4 and S-5). Unlike liquid PEG, the silica particles are polycrystalline in nature and the opacifying power increases as the character and phase composition of the crystals changes upon calcination. Thus, it is concluded that the increased opacifying power of the silica-titania core-shell particles over the same titania shells filled with PEG results from light scattering taking place within the polycrystalline silica cores. No light scattering is expected to take place in the optically uniform liquid PEG core.

In order to investigate the light scattering properties of air-filled hollow titania particles, the hollow particles calcined at 1000 °C were dispersed in a bleached fiber matrix which was highly pressed to remove air pockets. As shown in Figure 8 and Table 4 the hollow particles with the 1186 nm cavity size provide about 6% more opacity than commercial rutile, whereas the hollow

(49) Thiele, E. S.; French, R. H. *J. Am. Ceram. Soc.* **1998**, *81* (3), 469.

**Table 4. Opacity for a 135  $\mu\text{m}$  Thick Bleached Fiber Matrix Loaded with 3 wt % Hollow Pigment**

	structure	opacity at 135 nm
272 nm template 1000 °C	hollow polycrystalline rutile	76.9
1186 nm template 1000 °C	hollow polycrystalline rutile	83.7
commercial	rutile	79.2

particles with the 272 nm cavity provide about 3% less for a film thickness of 135  $\mu\text{m}$ .

These results contradict the theoretical light scattering results calculated by Johnson et al. for hollow titania spheres in a cellulose matrix.<sup>41</sup> Johnson et al. used the well-known program BHCOAT which calculates the light scattering efficiency of isolated core-shell particles based on Mie theory.<sup>40</sup> Their results show that the light scattering efficiency for a hollow titania particle with a shell thickness of 10% of the particle radius is dramatically less than that for a solid optimally sized rutile particle, regardless of cavity size. However, there is a decisive difference between the hollow titania particles considered in this study and those modeled using Mie theory. Mie theory assumes an optically uniform titania shell characterized by a single refractive index throughout and lack of any inclusions including pores, crystals, and grain boundaries. However, the hollow titania shells synthesized here are composed of many birefringent rutile crystals, and the TEM and SEM images (Figure 5 and Supporting Information Figure S-3) suggest the presence of pores. The strong birefringence of the rutile crystal is characterized by two different refractive indexes at a given wavelength depending on the direction of propagation and polarization of incident light. Thus, when a polycrystalline material is composed of randomly oriented crystallites (as is the case here), light propagating in a particular direction will pass through many crystals with different indexes of refraction and light scattering will occur through reflection and refraction. A similar phenomenon results in the presence of pores. The complex light scattering patterns that result in the polycrystalline shell through the multitude of reflections and

bendings of the light path at grain boundaries are expected to become even more complex and substantial as the many light paths reflect and refract upon entering the air-filled core and bounce around. The reason why the  $\sim 1\ \mu\text{m}$  cavity size gives more light scattering than the  $\sim 250\ \text{nm}$  size is not fully understood at this point.

### Conclusion

Polycrystalline titania-silica particles were synthesized with varying titania and silica phase compositions. Hollow titania particles were synthesized by dissolution of the silica core. The light scattering efficiency of hollow and silica-titania core-shell pigments was evaluated by measuring the opacity of optically uniform cellulose nanowhisker/PEG films loaded with pigments containing 3 wt % titania. The opacifying power of the rutile titania core-shell particles was found to be superior to that of the PEG-filled hollow particles at equal *titania* loadings in the film. The light scattering efficiency of the polycrystalline silica cores was found to depend on calcination temperature and crystal structure. It is suggested that the increased opacifying power of the silica-titania core-shell particles over the same PEG-filled titania shells results from light scattering taking place within the polycrystalline silica cores. Hollow rutile titania particles with a 1186 nm cavity size provide about 6% more opacity than commercial rutile, whereas hollow particles with 272 nm cavity provide about 3% less in a highly pressed bleached fiber matrix.

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**Supporting Information Available:** XRD data of hollow  $\text{TiO}_2$  particles synthesized using 272 and 1186 nm templates and calcined at 600 and 1000 °C, respectively; SEM images of synthesized core-shell and hollow titania particles with a 272 nm core calcined at 600 and 1000 °C; silica templates (1186 nm) calcined at 600 and 1000 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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