TIO_2 Nanoparticle Coated Hollow Glass Microspheres; Fabrication and Analysis

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ABSTRACT

The use of titanium dioxide (TiO_2) nanoparticles has gained increased interest due to their unique photocatalytic capabilities. The immobilization of nanoparticulate TiO_2 on engineered microparticles such as hollow glass microspheres (HGMs) can create a new material combination which offers the unique abilities of nanoscale materials in a safe and scalable form for use in real world applications.

Many of the nanoparticle film applications (particularly photocatalysis) are linked to coating morphological properties such as surface area through the requirement that a gas or liquid media have easy ability to flow in and out of the coatings pore structures in order to access the high surface area.

The unique challenges of depositing nanoparticle surface films on microparticles have limited the ability of researchers to optimize the coating morphology to application. This work utilizes a novel sol-gel nanoparticle formation and deposition technique, which produced a controlled alteration of coating thickness which has secondary effects on surface area, porosity, and coating mechanical stability.

The final coating thickness targets which were attained for thin and thick coatings were 62.25 ± 14.88 nm and 203.08 ± 29.62nm respectively. Particularly strong relationships are established between coating thickness and coating pore volume. Relationships are also defined between the thermal treatment utilized to crystallize the thin film coatings and both surface area or average pore size.

OBJECTIVES

The primary goal of this research is to establish the relationships between the microstructural properties of titanium dioxide (TiO_2) coatings applied to hollow glass microspheres (HGMs). In order to do this, the following specific objectives needed to be accomplished:

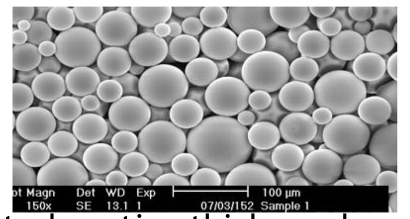
➢Develop a reliable, controllable technique for coating microparticles with TiO_2 nanoparticulates.

➢Analyze basic coating microstructural properties such as thickness, mechanical stability, and pore structure.

- Establish key relationships which can be used for future coating optimization

MATERIALS AND METHODS

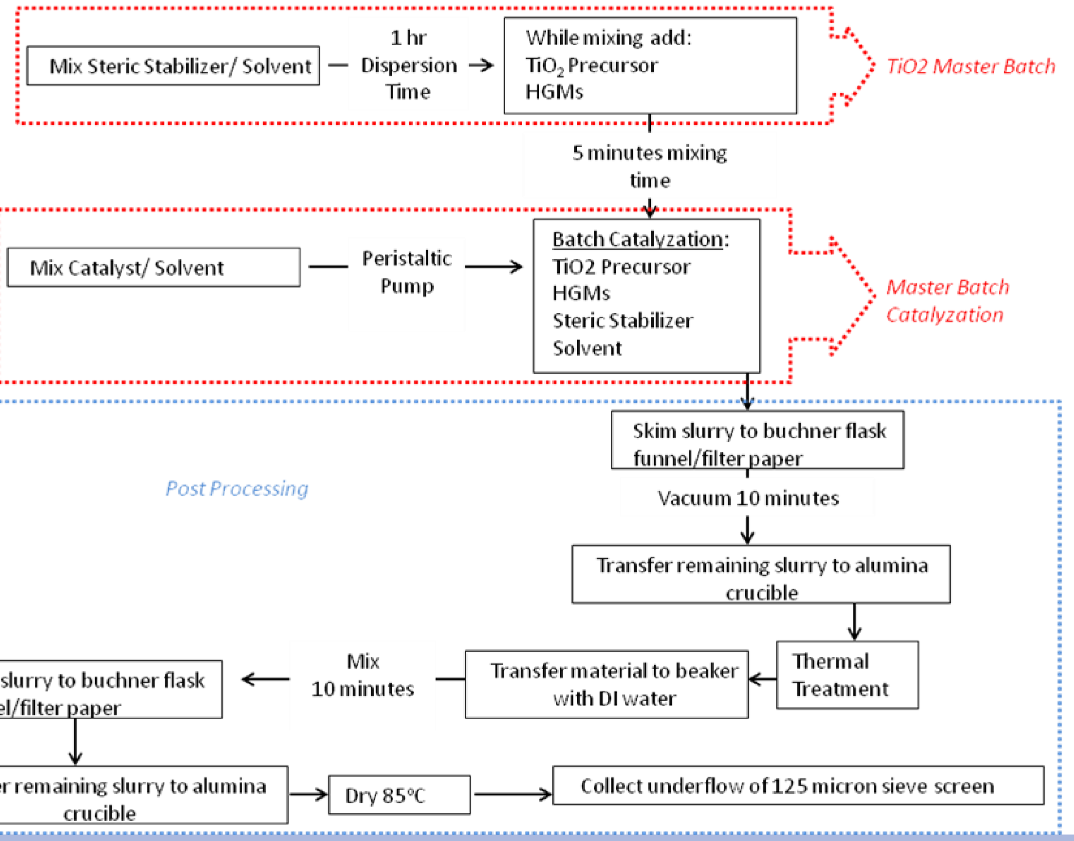
FABRICATION



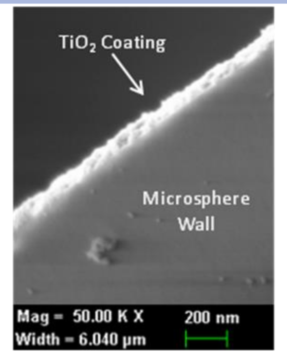
This work utilizes Trelleborg Offshore Boston "SI 200" grade borosilicate HGMs. The SI 200 HGMs has a mean particle size of approximately 50 microns with a density of 0.2 g/cc.

Several common processing parameters necessary to control coating thickness have been researched and utilized to produce a cross-section of samples having a variety of coating thicknesses.

2 coating thickness targets were chosen and thermally treated at 3 temperatures, for a total of 6 individual coating procedures. The film fabrication parameters for all 3 samples within each target thickness domain were identical with the exception of thermal treatment.



ANALYTICAL METHODS



Thickness measurements were taken by fracturing the HGMs and imaging the coating cross-sections. HGMS were fractured by placing them upon carbon tape adhered to a SEM sample stub. A second stub was then brought into contact in a parallel plate scenario and twisted several times.

Smart-Tiff® software was used to make estimates of 20 microsphere coating thicknesses.

Gas adsorption data was collected on a Micrometerics Gemini 2375 V5.01 gas adsorption unit with Nitrogen as the adsorbate

- Total Surface Area (m^2/g)- BET monolayer method
- Average Pore Size (nm) – Volume adsorption method
- Specific Pore Volume (cm^3/g)- Total gas volume adsorbed

TiO_2 coating content and process yield were calculated using thickness measurements under a concentric sphere coating assumption with specific pore volume measurements used to normalize for the coating pore content.

Crystallite phase and size measurements were taken on an Scintag XDS 2000 with a CuK source.

FILM THICKNESS, AND CRYSTAL PHASE

The process yielded samples with a clear distinction between the thin and thick coatings.

XRD analysis was performed on the thickly coated samples only. The large volume of the low density hollow particle catalyst support results in a large amount of sample volume with a comparatively low TiO_2 content. As a result the thinly coated samples produce results with insufficient intensity to be properly analyzed. The x-ray results show that the anatase crystal phase is found in all samples regardless of thermal treatment.

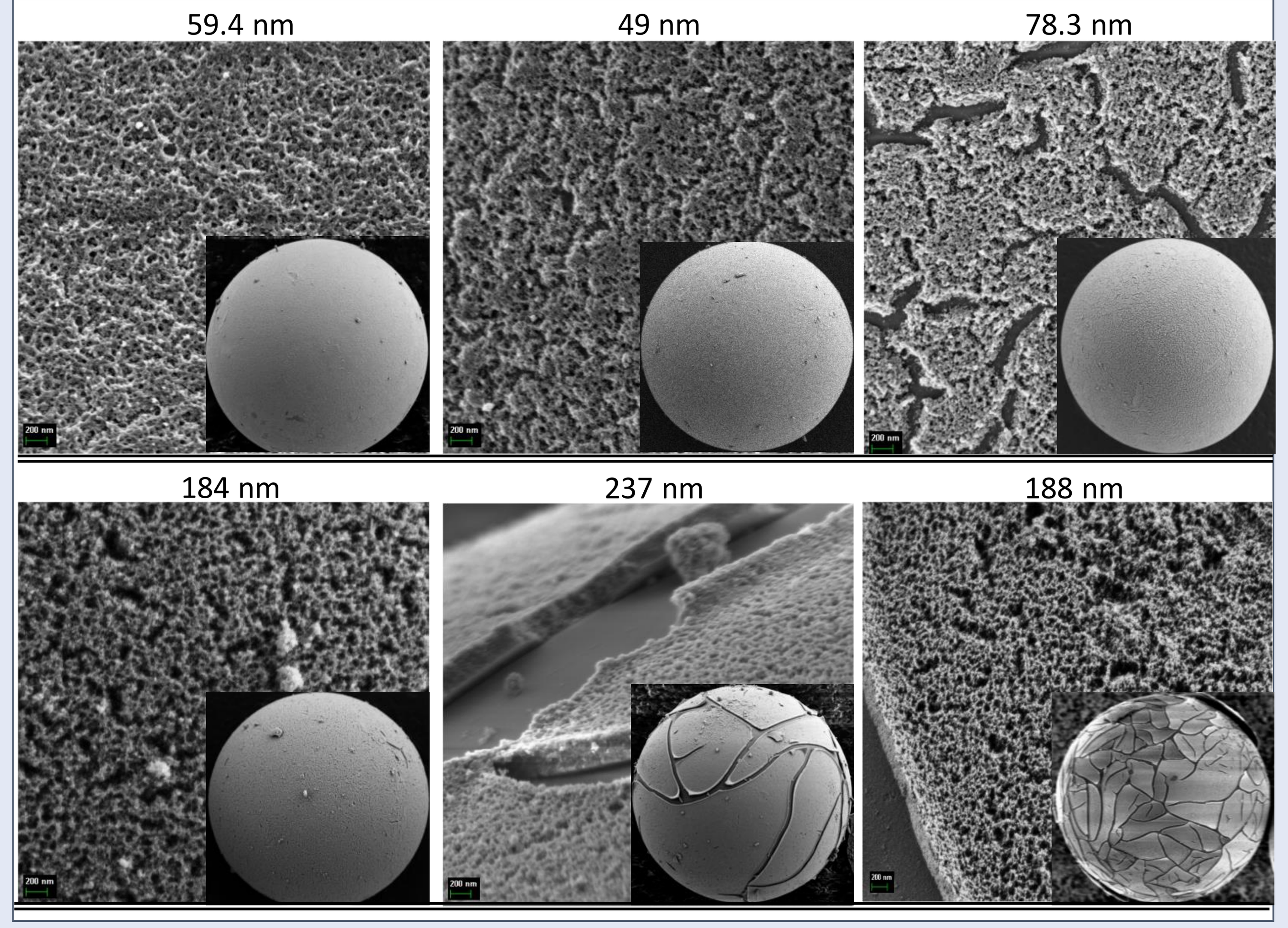
Target Thickness	Annealing Temp. (°C)	Thickness (nm)	Standard Deviation of Coating Thickness (nm)	Calculated TiO_2 content (wt%)	Calculated Process Yield (%)	Crystallite Size (nm)
Thin	400	59.4	16.3	2.04	17.07	-
	500	49	16.3	0.42	3.56	-
	600	78.35	26.01	4.26	29.09	-
Thick	400	184	45	11.55	55.66	12.26
	500	237.2	44.7	16.70	85.98	12.44
	600	188.03	27.9	14.50	69.13	14.80

FILM QUALITY

Immediately obvious is the growth of long thin fissures approximately 50 - 200 nm wide and extending all the way through the coating to the glass substrate. In these more thinly coated samples there does not seem to be any obvious impacts on the films adherence to the substrate.

The thickly coated samples which were annealed to 500 and 600ºC show severe fissuring. The fissures have grown to several microns in width and are interconnected, typically running all the way around the circumference of the microspheres. The coating delamination seems to be localized around the crack edges, and triple points. There is little evidence of large scale coating loss. The film seems to have simply pulled away and retracted revealing the substrate below

400ºC	500ºC	600ºC



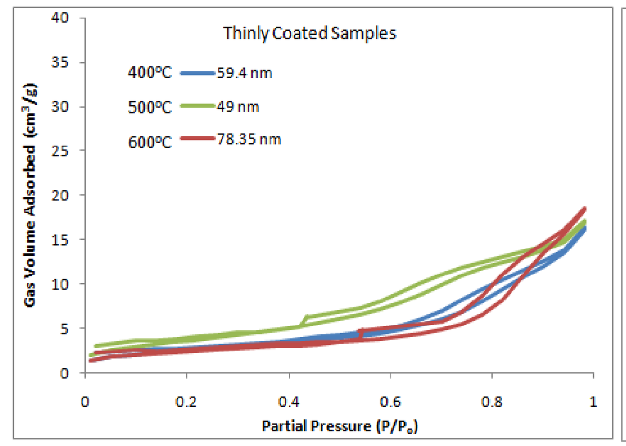
RESULTS

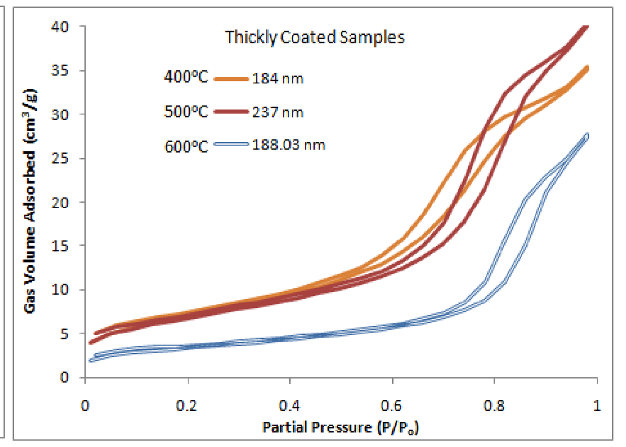
FILM MICROSTRUCTURAL ANALYSIS

The gas adsorption isotherms show the expected shape for nanoparticulate materials with hysteresis loops indicating gas condensation inside the pore structure. However, there are notable differences in shape between the thinly and thickly coated samples.

The thickly coated samples show an apparent lifting (from a horizontal to vertical orientation) and narrowing of the hysteresis loop with increased annealing temperature. These curves show highly organized meso and microporosity which are common to agglomerates of spherical particles (G.Leofantia,1998).

The 400 and 500ºC thinly coated samples show a long horizontal hysteresis indicating a high level of disorganization in pore geometry and size. The 600ºC thinly coated sample appears to be in a much clearer transition to a more regular mesoporous structure.

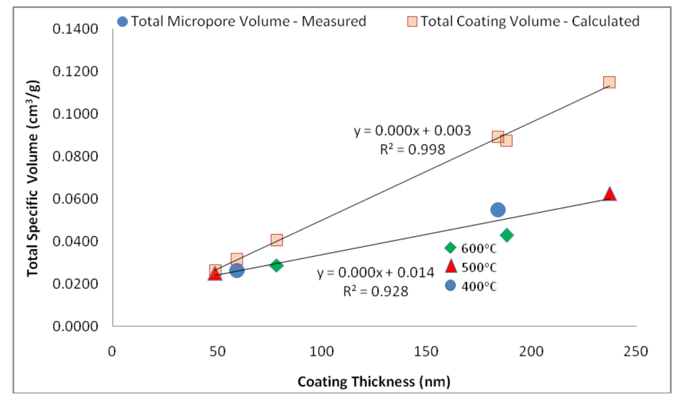




There are several microstructural relationships which appear to have significant linear correlations to either coating thickness or thermal treatment:

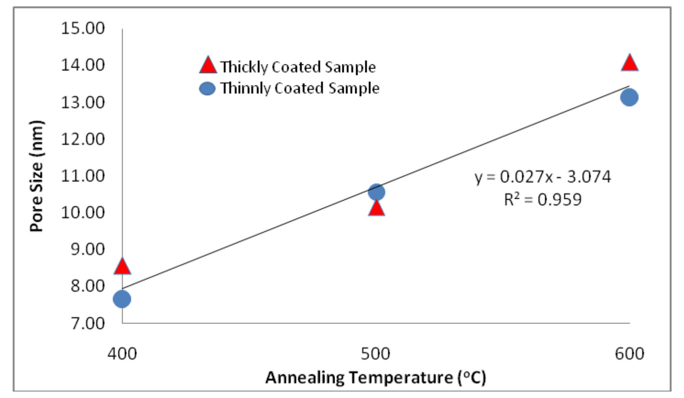
➢Total coating pore volume and coating thickness

- The volume percentage of the coating made up by its pore structure is decreases as thickness increases.



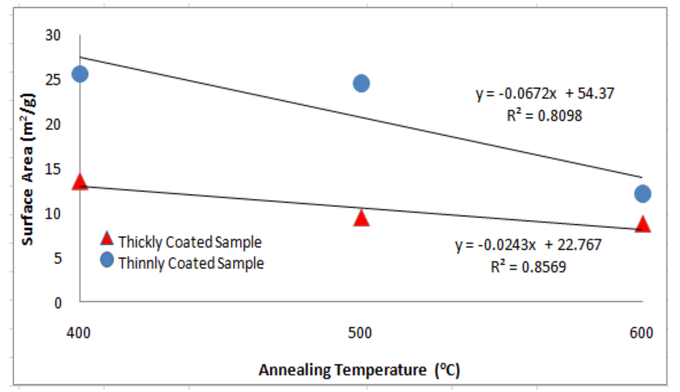
➢ Average pore size and annealing temperature

- The average pore size show a very regular growth with increasing thermal treatments, but no relationship to coating thickness.



➢ Surface area and annealing temperature

- The surface area loss with increased annealing temperature appears to be accelerative with increased coating thickness.



CONCLUSIONS

The HGMs coating procedure outlined was able to produce a system of thinly and thickly microparticles. Although, the deviation in coating thicknesses was large ranging from 14.8% to 33.2% (on a microsphere-to-microsphere basis), the process did deliver good differentiation between thin and thick coatings. The thickly coated samples showed 2 – 3 times the thickness of the thinner coatings.

The ability to produce a nanoparticulate coating on a microparticle in a safe scalable batch system and reliably target coating thicknesses to within ~20 nm (thin coatings 60±15nm, thick coatings 200nm ± 20) is unique. Furthermore, the equipment and chemicals utilized to fabricate the coated HGMs are readily available in most laboratories and at low cost.

Several coating microstructural properties have been and analyzed and strong morphological relationships established.

The average pore size and surface area generated by the application of the nanoparticulate coating appears to show a very regular growth with the application of increasing thermal treatments, but no relationship to coating thickness. Conversely the total pore volume appears to be sensitive only to coating thickness.

The ability to manipulate one or two of the coating microstructural properties while having only minor impacts on the others makes these materials ideal for optimization.

REFERENCES

G. Leofantia M. Padovanb, G. Tozzolac, B. Venturellic; Surface area and pore texture of catalysts : Catalysis Today, 1998. - 1-3 : Vol. 41.

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