Titanium Oxide Nano Colloids for Dye Sensitized Solar Cells and other Applications

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Executive Summary

G24 Power produces and markets colloidal Titanium dioxide (TiO_2) nanoparticles with tunable particle sizes from 18 to 30 nm. Characteristics of our TiO_2 include high anatase purity, variable light trapping characteristics with transparent or opaque coating options. Also, formulations can be targeted to achieve the tunable pore volume needed for emerging solid state solar cells based on Perovskite and other light absorbers.

TiO_2 from G24 Power is well suited for the creation of Dye Sensitized Solar Cells (DSSC) due to its high purity (>99.8% based on trace metal analysis), and ability to form good coating from environmentally benign aqueous fluids with improved solar conversion efficiency. G24 Power has ability to produce high quality anatase nanoparticles with size less than 10 nm for cosmetic applications and coating fluids for Solid Oxide Fuel Cell electrodes.

Background

TiO_2 is a wide band gap inorganic semiconductor substance that is thermally stable, non-flammable, insoluble, and not classified as hazardous by Globally Harmonized System of Classification and Labeling of Chemicals (GHS). It has been used extensively in a wide range of industrial and consumer applications including water splitting for the creation of hydrogen, gas sensing, coated fabrics and textiles, catalyst systems, ceramics, floor coverings, roofing materials, corrosion protective coating, optical coating, biocompatible coatings in orthopedic implants, varistors, and as pigments in paints, cosmetics and in paper industry. Nanostructured titanium oxides are used in lithium ion batteries, electrochromic devices, solid oxide fuel cells and photovoltaics. In 2013 the annual production of TiO_2 was more than 5 million tones, with an addressable market of over $10 billion.[1]

Commodity grade TiO_2 nanoparticles are very cheap as they are made from inexpensive minerals using chloride or sulfate process. They are often contaminated with many metallic impurities, which are known traps for electronic applications. They also exist in aggregate forms with 20 to 30% rutile impurities that are hard to disperse for transparent coating applications. Although high anatase content can be achieved using sulfate process, it is hard to remove sulfate groups during sintering of sulfate process derived TiO_2. The sulfate groups move to surface of the nanoparticles during sintering and interfere with dyeing process resulting in low performing DSSC.

Tuning Pore Size and Pore Volume of Titanium Dioxide Coatings

The performance of Dye Sensitized Solar Cells depend on the surface area of mesoporous TiO_2 film, surface states on TiO_2 nanoparticles, dye coverage on the TiO_2 surface and impregnation of electrolyte or solid state hole conducting materials inside the nanoporous film.

Reducing the size of nanoparticles will increase the surface area, while reducing the pore size and pore volumes of the nanoporous film. Both dye sensitization and pore-filling of electrolyte or hole conductor inside the nanoporous films are adversely influenced by lower pore size and pore size distributions causing low performance and device instability.

Chou and his coworkers have carried out systematic study on the effect of TiO_2 particle size on the performance of Dye Sensitized Solar Cells. The solar conversion efficiency more than tripled by increasing the size of TiO_2 nanoparticles from 10 nm to about 22 nm.[2] This effect is even greater for bulkier sensitizing molecules and highly viscous electrolyte or organic and inorganic hole conducting materials.

Poor filling of organic or inorganic hole conducting materials in dye sensitized TiO_2 film is well documented in the literature.[3] Collaborative work carried out with École polytechnique fédérale de Lausanne (EPFL) demonstrated direct correlation between hole-conductor filling, device performance and stability. Table 2 shows the effect of TiO_2 particle size on the relative performance of Solid State Dye Sensitized Solar Cells made by filling with organic hole-conductor molecule-spiro-MeO-TAD and polymeric hole-conductor, poly (3-hexylthiophene).

Table 1: Effect of TiO_2 particle size on photovoltaic performance of Solid State DSSC tested under AM 1.5 conditions

Particle Size (nm)	Voc (V)	Jsc (mA/cm^2)	Fill Factor	Overall Conversion Efficiency	Hole Conductor
20	0.798	5.63	0.314	1.41 %	Spiro-MeO-TAD
30	0.799	5.74	0.589	2.71 %	Spiro-MeO-TAD
20	0.713	3.155	0.428	0.968 %	Poly(3-hexylthiophene)
60	0.802	3.901	0.504	1.575 %	Poly(3-hexylthiophene)

The lifetime of Solid State DSSC under continuous one sun irradiation conditions is greatly enhanced from less than 100 hours to over 1000 hours by increasing the TiO_2 size from 20 nm to 30 nm. (Supporting document is available upon request) Large pore sizes (25 to 40 nm pore diameter) are needed for efficient cobalt electrolyte based cells as well as Perovskite based Solar Cells.

What is special about G24 Power Colloids?

G24 Power produces high purity titanium oxide nanoparticles based on sol-gel synthesis, in desired particle size with narrow size distribution. We have capacity to manufacture >100 kg/week using industrial grade titanium autoclaves to avoid iron contamination.

Our colloids are very pure with TiO_2 content of >99.8% based on trace metal analysis and contain $\leq$10ppm of Fe, Na and K. Our coating fluids are prepared from hydrothermal process derived nanoparticles using proprietary polymeric binder in water and could be used to coat on any substrates employing spin, slot, blade coatings, gravure, microgravure or screen printing techniques with near zero volatile organic compounds (Zero VOC). This process produces transparent coatings on desired substrates.

The sol-gel derived TiO_2 particles are generally hydrated, partially crystallized anatase which forms uniform film before calcination (sintering). During calcination the nanoparticles partly coalesce forming nice necking sites with highly crystalline domains needed for good electron transport to achieve high performance in solar cells.

G24 Power has a proprietary technology to create a bimodal particle size distribution to improve light harvesting in near infrared (NIR) region without compromising surface properties. These colloids are nicely distributed in the coating fluid with secondary particle sizes of over 150 nm and with primary particles of 18 – 30 nm chemically connected to the secondary particles. This coating fluid is again made as environmentally benign aqueous paste that could be coated on any substrates. G24 Power is also capable of producing organic solvent based colloidal pastes to address some client's screen printing and other coating needs.

One of the prime concerns of nanoparticles is ecotoxicity especially for materials that are photocatalytic such as TiO_2. At particle size lower than 80 nm under dark as well as under UV illuminations, the nanoparticles are known to cause damage to cellular lipids, carbohydrates, proteins and DNA[4] leading to inflammation and oxidative stress response. Since our bimodal nanoparticles are much bigger in size with integrated nanoparticles in 18 to 30 nm range, they provide high surface area without any health hazards known with particles less than 80 nm.

G24 Power's aqueous TiO_2 coating fluids come with many variations depending on the need for larger surface area and pore diameter/volumes. Most of these pastes can be coated using single coating step, sintered and dyed without employing generally used post $TiCl_4$ treatment process to achieve high solar conversion efficiencies. Table-2 shows photovoltaic and surface properties of films made from our aqueous colloids and compared with competitor's screen printable pastes made with either hydrothermal derived TiO_2 nanoparticles or Degussa's chloride process based P25 nanoparticles. All the cells were made on FTO-coated glass substrates under identical conditions using control dye and electrolytes generally used in the DSSC art. Here 12+4 suggests 12 micron thick nanoporous film and 4 micron thick light scattering film made of larger TiO_2 particles which is used to improve light harvesting in near infrared region; J_{sc} is short circuit current density and V_{oc} is open circuit voltage. All devices made from our aqueous colloidal pastes exhibit higher current density and efficiency compared to devices that were made with competitors TiO_2 pastes.

Table 2: Photovoltaic performance of DSSC made with various TiO_2 colloids and their surface characteristics

TiO_2 colloids	*Film thickness (microns)*	*Jsc (mA/cm^2)*	*Voc (V)*	*Post $TiCl_4$ treatment*	*Dye Loading*	*Surface area (m^2/g)*	*Pore diameter (nm)*	*Porosity (%)*	*Solvent Medium*
18TA	12+4	13.92	0.67	No	-	83.93	11.62	50.90	Water
18TB	12+4	14.63	0.67	No	-	84.07	23.55	62.28	Water
18TA	12+4	16.24	0.65	Yes	67.73	-	-	-	Water
18TB	12+4	15.76	0.66	Yes	48.89	-	-	-	Water
22TA	12+4	13.51	0.66	No	-	71.05	11.78	49.28	Water
22TB	12+4	11.79	0.67	No	-	73.89	21.55	61.22	Water
22TA	12+4	15.25	0.65	Yes	62.02	-	-	-	Water
22TB	12+4	15.04	0.65	Yes	40.30	-	-	-	Water
Competitor hydro-thermal based screen printable paste	12+4	9.48	0.69	No	-	77.94	28.70	69.09	α-terpineol
Competitor hydro-thermal TiO_2 paste	12+4	13.60	0.67	Yes	43.36	-	-	-	α-terpineol
Competitor P25 based screen printable[5]	12+4	-	-	-	-	-	-	-	α-terpineol
18OA (single layer)	16	13.52	0.65	No	61.14	63.08	16.90	50.81	Water
18OB (single layer)	16	16.33	0.67	Yes	47.69	66.71	30.10	59.02	Water
22OA (single layer)	16	15.52	0.66	No	58.11	55.32	22.32	49.28	Water
22OB (single layer)	16	14.41	0.67	Yes	44.48	52.63	35.39	55.97	Water
Competitor hydro-thermal TiO_2 paste	14+4	13.77	0.67	Yes	43.36	-	-	-	α-terpineol

The improved performance of Dye Sensitized Solar Cells made using G24 Power's aqueous colloidal pastes have also been confirmed at Prof. Graetzel's Laboratory at EFPL. Table 3 shows the photovoltaic characteristics of Dye Sensitized Solar Cells fabricated using three of our aqueous colloids and competitor's best organic solvent based colloidal paste. Our single coatable TiO_2 based solar cells exhibit highest performance based on the data shown in the Table 3. There is no need to deposit a second layer of light scattering TiO_2 or other dielectric scattering particle layers for making high performance solar cells. The second layer normally form very weak bonding to the first nanoporous film, often causing delamination and other mechanical issues during sintering process. One can avoid these issues and improve their product yields using G24 Power's single coating process based TiO_2 pastes.

Table 3: Relative performance of DSSCs made using G24P colloids compared to competitor- built and tested at EPFL

TiO_2 colloids	Film thickness (microns)	Jsc (mA/cm^2)	Voc (V)	Fill factor	Solar Conversion Efficiency (%)	Post $TiCl_4$ treatment	Dye/Electrolyte
18OB (single layer)	12	14.7	0.759	0.76	8.50	Yes	C101/Z960
18TA (transparent + scattering layers)	9+6	16.0	0.710	0.74	8.50	Yes	C101/Z960
22OB (single layer)	12	14.9	0.750	0.74	8.34	Yes	C101/Z960
Competitor- hydrothermal screen printable paste (transparent + scattering)	8+4	15.0	0.697	0.76	8.00	Yes	C101/Z960

Key Benefits of G24 Power Colloids

- High purity colloids with less than 10ppm of Fe, K and Na, with crystal purity of 96-98% anatase.
- All G24 Power pastes are based on aqueous TiO_2 colloids and form near zero volatile organic compounds during coating and sintering processes.
- G24 Power aqueous colloid based dye sensitized solar cells exhibit higher performance than some other brands of TiO_2, confirmed by École Polytechnique Fédérale de Lausanne.
- Organic solvent based screen printable pastes are produced upon request.
- XXXA class of G24 Power colloids can be coated, sintered and used to make photoelectrodes without the need for any post $TiCl_4$ treatment ($TiCl_4$ treatment is not a viable option for most industrial production of DSSC)
- High performance can be achieved using G24 Power's opaque XXOA/XXOB class colloids using single coating step. This avoids need for making mechanically weak second light scattering layer which often delaminates during sintering and dyeing processes.
- $TiCl_4$ treatment is recommended for XXXB class colloid based coatings, which offers better pore size adjustment needed for emerging Perovskite type solar cells. A pore diameter of as large as 35 nm is achieved using 22OB colloidal paste.
- XXTB/XXTA class materials are good candidates for transparent window applications and Building Integrated Photovoltaic (BIPV) Dye Sensitized Solar Cells.

G24 Power has developed many versions of aqueous and organic solvent based TiO_2 pastes with pore diameters ranging from 12 nm to 35 nm with variable light scattering, porosity and surface area characteristics. G24 Power offers hydrothermal derived anatase TiO_2 colloids with narrow particle size fractions in the range from 18 to 30 nm to suit various applications in Dye Sensitized and Perovskite Solar Cells, requiring precise performance tuning. Particles sizes less than 10 nm are also available for Cosmetic, Photocatalytic, and Piezoelectric Capacitor Applications.

References

1. *Pira International Market Report.*
2. *T. P. Chou, et al, "Titania Particle Size Effect on the overall Performance of DSSC", J. Phys. Chem. C, 111, 6296 (2007).*
3. *I. Ding, J. M-Kyriazi, N. Cevey-Ha, K. G. Chittibabu, S. Zakeerudein, M. Graetzel, M. McGehee, Organic Electronics, 11, 2017 (2010).*
4. *Kelly et al, "Oxidative stress in toxicology: Established mammalian and emerging piscine model systems", Environ. Health Perspect. 106, 375–384 (1998).*
5. *The coatings made using Aldrich grade Screen printable paste based on P25 cracks during sintering process and we were not able to make decently performing cells.*