MetaMateria Materials for Coatings

MetaMateria is an innovative developer of nano-enabled materials and manufacturing methods that can be used to enhance performance and functionality. The focus is on the practical application of nanomaterials for components, devices and engineered systems.

Several core technologies are utilized for the preparation of coatings, infiltration of porous materials, or modification of existing coating formulations. These include:

Engineered nanoparticles & and dispersions
Nanostructured inorganic or metallic coatings
Polymer-modified hybrid materials
Approaches for depositing nanoparticles onto porous surfaces

Given below is a description of the core technologies and examples of how these have been applied, mostly to address specific customer needs.

A wide range of inorganic and metallic nanostructured coatings have been made by using colloids (dispersions of nanoparticles). Coatings are used to protect or change a surface property of another material. It may be desirable to increase scratch resistance, make the surface self-cleaning or electrically conductive, while maintaining transparency or some other property. Many applications exist in the energy and environmental markets, as well as for other commercial products.

Colloids of Dispersed Nanoparticles

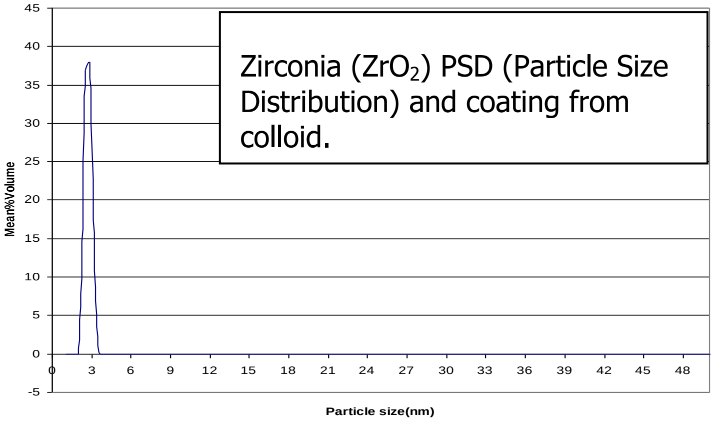
MetaMateria uses solution based techniques for the synthesis of nanoparticles of ceramic oxides and metals. In order to minimize agglomeration, efforts are placed on maintaining liquid dispersions of the nanoparticles, often done during or shortly after synthesis. These liquids appear clear because visible light is not scattered by nanoparticles or agglomerates below 25 nm. Shown at the right is a clear colloid of CGO (Gd doped Ceria).

Depending upon the composition and the solvent, suitable surface active reagents are added for passivation and development of dispersions. These transparent "clear colloids" are excellent additions to monomers or for deposition as thin films or for infiltration of a porous material.

Oxide and metal films may need further thermal processing for densification and to remove impurities associated with nanoparticle surfaces (organics and hydrates). Typical thermal treatments are between 150°C and 600°C, sometimes in a controlled atmosphere. Exact temperatures depend on the composition and requirements for materials being treated.

Many nanomaterials compositions can be prepared as colloids.

Nanoparticles will often have a very uniform particle size, as illustrated below.



Zirconia (ZrO_2) PSD (Particle Size Distribution) and coating from colloid.

YBCO & YSZ Colloids

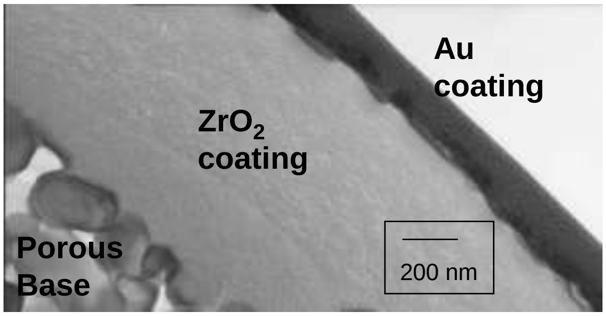
Examples of clear colloids, along with typical solids loading and approximate particle size are given below. Many other materials not listed have been prepared. Particle size can be varied. These colloids were prepared for specific applications. New applications to meet the specific interests of potential customers usually can be prepared.

Name	**Concentration (wt%)**	**Solvent**	**Size**
OXIDES			
TiO_2	**5**	**IPA**	**6 nm**
CeO_2	**10**	**Water**	**3 nm**
Al_2O_3	**5**	**Water**	**9 nm**
ZrO_2	**8**	**Water**	**3 nm**
ZrO_2	**10**	**Butyl acetate**	**6 nm**
Al_2O_3-ZrO_2	**10**	**Water**	**9 nm**
CGO (Ce-Gd-O)	**20**	**Water**	**8 nm**
YSZ (Y-Zr-O)	**20**	**Water**	**7 nm**
SSZ (Sc-Zr-O)	**20**	**Water**	**2 nm**
Y_2O_3	**15**	**Water**	**5 nm**
LSM (La-Sr-Mn-O)	**25**	**1,4 Butanediol**	**25 nm**
LSM	**10**	**Decanol**	**NA**
YBCO (Y-Ba-Cu-O)	**20**	**1,4 Butanediol**	**NA**
$LiCoO_2$	**10**	**1,4 Butanediol**	**20 nm**
YBCO	**16**	**Decanol**	**NA**
METALS			
Ag	**0.5**	**Methanol**	**7 nm**
Cu	**0.6**	**Propyleneglycol**	**3 nm**
Ni	**0.5**	**Propyleneglycol**	**8 nm**
Sn	**0.5**	**Methanol**	**5 nm**

Coatings from Colloids

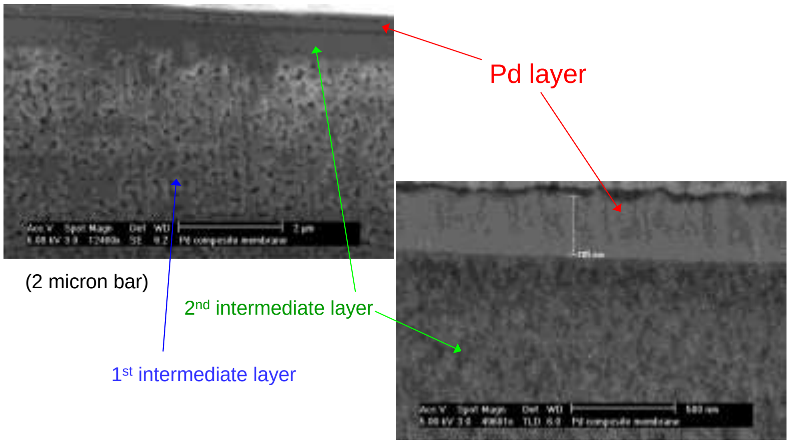
The key to success in developing high quality coatings builds on the MetaMateria core strength of preparing well-dispersed nanoparticles. The quality of any coatings depends on three factors; homogeneity and dispersion of the colloidal suspension, surface roughness and quality of the surface to be coated, and cleanliness of both the surface and deposition environment. The figure below shows that agglomerated nanoparticles result in low-quality, cracked coatings, whereas dispersed particles provide coherent coatings.

Utilizing its coating techniques, MetaMateria is able to produce ultra-thin nanoparticle coatings which bridge seemingly impossible distances, such as illustrated below for a dense zirconia coating (heated to 600 C), a fuel cell coating on alumina and a palladium membrane for hydrogen purification deposited on a series of more porous coatings.



Porous alumina substrate with nanostructured coating

Pd Membrane Cross-Section (285 nm thick)



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Hybrid Nanocomposite Coatings

In recent years, new methodologies to prepare materials containing organic and inorganic materials as single phase were developed that produce new systems called hybrids, ceramers, or Nanocomposites (NCs). They often exhibit properties completely different from the base polymeric materials, even those with micron size inorganic particles. The unexpected behaviors in scratch resistance, tensile strength, abrasion resistance, thermal stability and transparency are observed due to the enormous interfacial adhesion region characteristic of nanoparticles. Properties are strongly influenced by the nature of the interface; hence a high interface allows unusual properties.

Size-dependent phenomena of nanoscale particles to dramatically improved performance represents a major driving force for polymer NCs. Many crystalline materials (e.g. 3D nano metal oxides, 2D layered clays, and 1D carbon nanotubes) are used for reinforcement of polymer networks. Different inorganic oxide nanoparticles, such as SiO_2, Al_2O_3, CeO_2, ZrO_2 or TiO_2 are employed in a host of NCs of polymers, such as acrylates, epoxies or styrenes.

The key factors for development of enhanced performance of NCs are to obtain a uniform distribution of nanoparticles within the polymer matrix, large active surface to promote a strong interface between the matrix and nanoparticles, and strong adhesion strength on the substrates. Despite considerable efforts, attempts to improve scratch resistance are often accompanied by deterioration in other properties, such as impact strength, hydrophobicity or substrate adhesion properties.

Traditionally, most work is done using exfoliated nanoclay additions or carbon nanotubes or nanoparticles (2–100 nm); however, dispersion of these high surface area materials in the polymer is a significant problem. Yet nano-sized metal oxide fillers represent an attractive alternative to conventional fillers because of their nanometer size and their large active surface. In almost all of these composite polymer classes, however, several issues exist which limit application of these materials. These include:

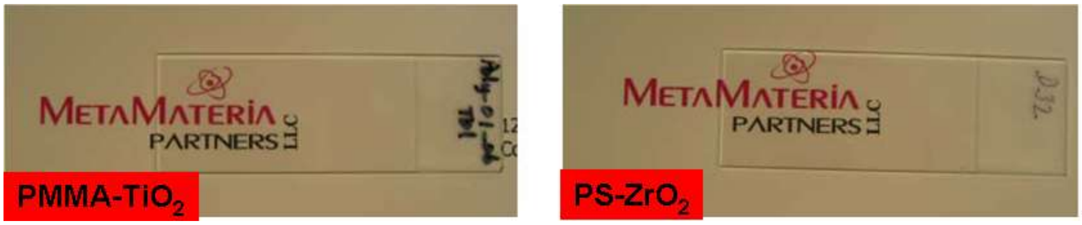
a) Composites are made by physical blending of nano fillers with the polymer, which require exceptional mixing approaches to obtain uniform compositions
b) Poor or no chemical bonding interactions between polymer chains and the fillers
c) Aggregation of nanomaterials leading to inhomogeneous distribution of fillers.

MetaMateria methods for preparing nanoparticle dispersions (colloids) helps overcome these limitations. The approach used offers significant economic potential as it is an inherently a cost effective approach and early results are promising in that they indicate significant, encouraging changes in composite properties. This approach also addresses a key problem associated with improving the chemical bonding interactions of polymer matrix with the filler oxides by allowing design of a more synergistic relationship between the filler and the elastomer, thus providing uniform distribution of nanomaterials within the polymer matrix. Improving filler-polymer interactions also significantly improved mechanical properties of the nanocomposite, which is expected. Also, the approach can use simple polymerization procedures and standard workout conditions.

Exploratory work by MetaMateria demonstrated the viability of this concept by establishing high-hardness and transparent hybrid nanocomposite coatings of acrylate or styrene polymers containing 2% TiO_2 or ZrO_2 nanofillers. Chemical or UV radiation induced condensation of these network polymers results in optically clear coatings as thick as 100 microns with extremely low lateral shrinkage. It is expected that by selectively defining polymerization variables, the syntheses of the nanocomposite can be optimized such that metal oxide nanofiller-acrylic polymers are produced with desirable properties such as high scratch hardness, low optical loss and low lateral shrinkage.

Hybrid Coating Test Results

Shown below are two transparent 100 micron thick coatings. On the left is an acrylate (PMMA) containing 2%TiO_2 (titania) and on the right polystyrene (PS) containing 2% ZrO_2 (zirconia). The Hardness values and Young's modulus are shown in the table. The PMMA harness increased over seven times with the addition of 2 wt% TiO_2, which is much harder than stainless steel and equivalent to many glasses.



Optical transparency of the PMMA-TiO_2 and PS-ZrO_2 composite coatings (100 micron thick)

	PMMA	TiO_2-PMMA	PS	ZrO_2-PS
Young's Modulus (GPa)	**2.4-3.3**	**65**	**2.3-4.0**	**40.0**
Hardness (GPa)	**1.0**	**6.7**	**0.3-0.6**	**1.8**
Load Penetration Depth (nm)	**1800**	**1030**	**1700**	**1100**

The hardness and modulus values of pure polymers and the hybid composites are shown. Hardness increases with the addition of nanoparticles and also Young's modulus values. The load penetration depth curve indicates that the titania fillers have an impact in hardening the composite film with values close to those of Corning glass. These results are a consequence of the reinforcement produced by the nano-oxide filler component in the organic–inorganic hybrid matrix.

Figures I and II show hardness, modulus and load-penetration curves of polyacrylate-TiO_2 and polystyrene-ZrO_2 composite coatings, respectively.

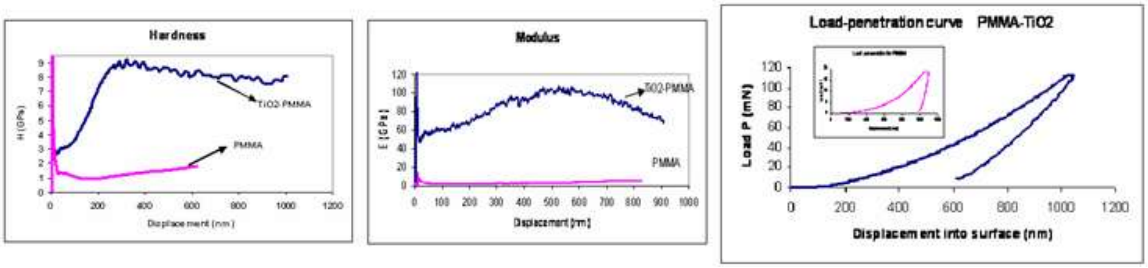


Figure I. Hardness, modulus and load-penetration curves of polyacrylate-TiO_2 composites

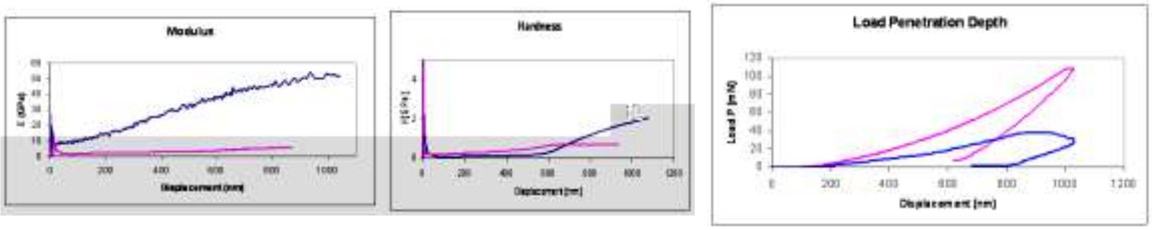
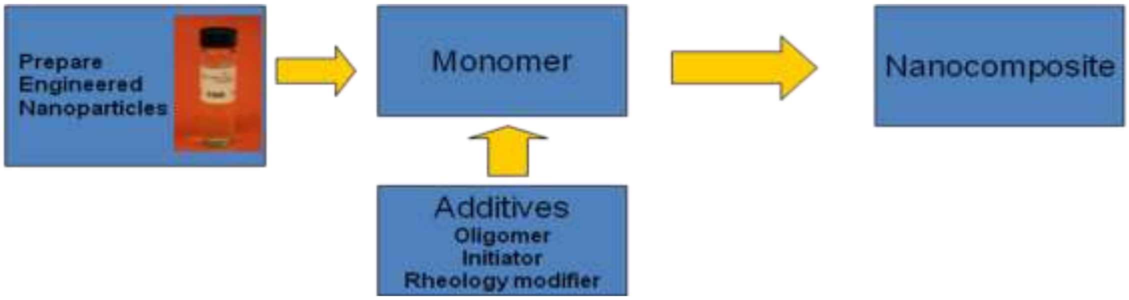
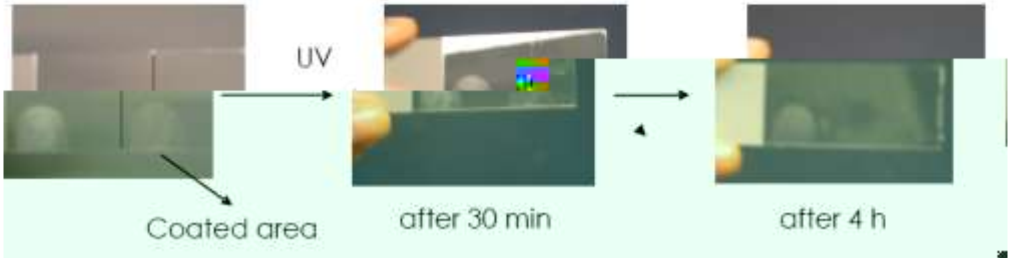


Figure II. Hardness, modulus and load-penetration curves of polystyrene-ZrO_2

The general approach taken for preparation of these materials is illustrated below.



MetaMateria also developed polymer nanocomposite materials containing effective photocatalysts for self-cleaning optically clear coatings. The approach deals with modifying the nano titania in order to improve absorbance of light and increase the photocatalytic effect. Preliminary experiments show that the polyacrylate composite coatings made of modified nano titania photocatalyst fillers exhibit superior photo degradation properties than conventional catalyst, as shown by degradation of finger prints under UV light.



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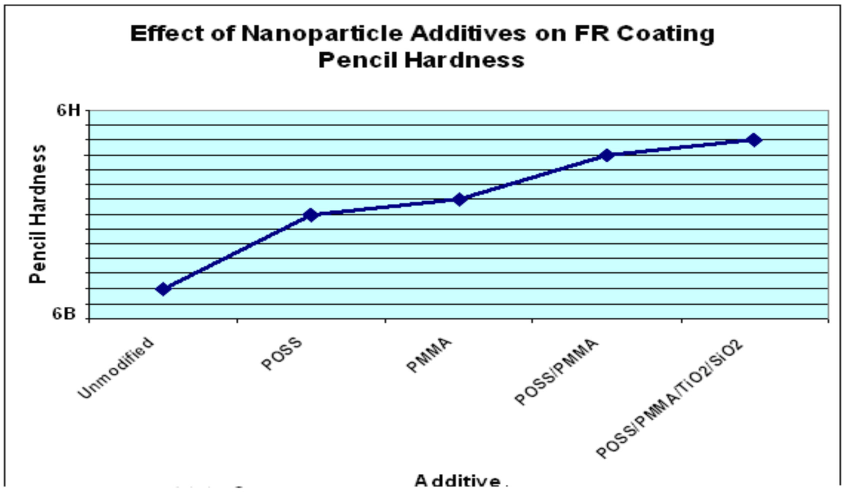
Foul Resistant Silicone Coatings with Improved Hardness

Another recent application of exploratory research was to improve the abrasion resistance of silicone materials used underwater for fouling resistance applications. The focus was to establish how the hardness of silicones can be improved by the incorporation of nanoparticles/some cross-linkers, which include: functionalized nanoparticles (TiO_2 and SiO_2), functional polyhedralsilsesquioxane (POSS) modified silicones, and a mehtylmethacrylate(MMA)/methacrylocypropyltrimethoxysilane (MEMO) copolymer.

The approach involves repairing interface adhesion characteristics between the cross-linkers and the silicone elastomer, while improving surface chemistry. Modified inorganic nanparticles/cross-linkers compatible to silicone polymers produce chemically bonded interfaces between organic-inorganic phases under controlled curing conditions. Terminal OH groups such as silanol on POSS, OH on SiO_2 or TiO_2 are expected to crosslink to silicones *via* –Si-O-Si-O- bonding and POSS-tetrapolymers are used to reinforce the silicone network. Silica in PMMA-MEMO crosslink silicones as relatively harder acrylates is expected to improve the fracture toughness of silicones. These properties resulted in homogeneous dispersion, increased surface energy, and enhanced mechanical strength of nanocomposite.

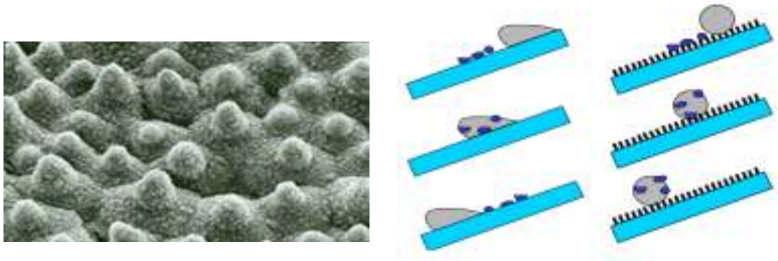


6B → 5B → 4B → 3B → 2B → B → HB → F → H → 2H → 3H → 4H → 5H → 6H

Superhydrophobicity or Ultrahydrophobicity

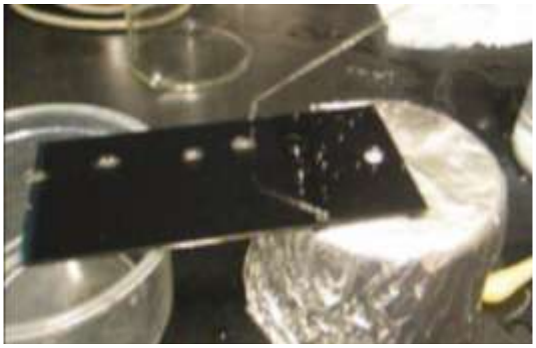
Hydrophobicity of surfaces is generally achieved by coating surfaces with plastic or wax-like materials to prevent the ingress of water. During the past decade, the hydrophobicity of many biological surfaces has attracted considerable interest. In particular, the lotus flower leaf (*Nelumbo nicifera L*), which exhibit ultrahydrophobicity has been widely investigated. The lotus flower leaf surface is macroscopically smooth but shows a microscopic roughness on different length scales down to the submicrometer scale.

Illustrated below is the microstructure of lotus leaf (a). Water repellency occurs mainly by epicuticular wax crystalloids that cover the surface in a regular microrelief of about 1-5 µm in height. Not only are the lotus leaves ultrahydrophobic but they are self-cleaning, since water droplets rolling across a lotus leaf carry away contaminants and clean the surface. This "self cleaning" effect is achieved only due to the surface roughness in the lotus leaf, whose rough surface decreases the wetability of the lotus leaf and the contact angle for the dirt is reduced. Both (b) and (c) depict a summarizing diagram that emphasizes the correlation between surface roughness and self cleaning. On a smooth surface contaminants are only moved by the water droplets. Contrary to this, on a rough surface they stick to the droplet rolling off the leaf, thus being washed out. The principles of a lotus leaf can also be applied to physical artificial surfaces to generate ultrahydrophobicity or superhydrophobicity.



(a) (b) (c)

(a) Microstructure of a lotus (*Nelumbo nicifera L*) shows epicutilar wax crystalloids. Schematic representation of "self cleaning" effect for (b) smooth surface and (c) rough surface



A surface with both receding and advanced water contact angles above 150° is considered to be ultrahydrophobic. The common way for enhancing the hydrophobicity is lowering the surface energy. However, even materials with low surface energy (6.7 mJ/ m^2 with regularly aligned closest hexagonal packed - CF_3 groups) gives a water contact angle of only around 120°. Surfaces with water contact angles of more than 150° are developed only by introducing proper roughness or material surfaces having low surface energy. Experiments using a nanocomposite coating shows that surfaces with superhydrophobic properties are feasible. The picture shows the flow of water droplets on a superhydrophobic polymer hybrid formed using functionalized TiO_2 nanoparticles.

To discuss applications for this technology, contact

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