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Preparation and Characterization of Inorganic-Organic Nanocomposite Coatings

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1. Introduction

In recent years, more and more researchers are devoted themselves to studying nanocomposite hybrid materials. Since, the combination of different components in the nanosize range can yield new materials that may combine the advantages of each component and nanomaterials. Inorganic – organic hybrids nanocomposite materials is an example of this kind of materials, which have become a creative alternative with unusual features of the materials in industry. In fact, the art of combining dissimilar components to yield improved materials is not new. It goes way back to ancient construction materials like Adobe (Gomez-Romero et al., 2001). He used to build houses and buildings by a mixture made from the clay (inorganic) and straw (organic), where the straw was provided the mechanical properties for clay. However, the modern concept of hybrid materials goes way beyond the concept of a mixture between their components, actually falls between the concept of a mixture and a compound. A compound is formed by carrying out a chemical reaction between their components, where the properties of each part are eliminated to form a new material with different properties. In a mixture, a physical interaction between the components is involved. Whereas, the hybrid concept falls into a category where the interphase between their components is increased compared to a mixture, and their interactions will be at the molecular level (Judeinstein et al., 1996; Yacaman et al., 1996).

The main idea in development of the *hybrid materials was to take advantage of the best properties of each component that forms a hybrid, trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect; that results in the development of new materials with new properties.*

The first interest in the development of hybrid materials was mainly based on the design of hybrid polymers with special emphasis on structural hybrid materials. A variety of silicates, polysiloxanes etc. modified with organic groups or networks for improvement of mechanical properties, were the first type of hybrid materials investigated.

The expectations for hybrid materials go further than mechanical strength, such as thermal and chemical stability. Magnetic hybrids (tricarboxylic substituted radical and Cu ions), Electronic hybrids used in electronics (transistors, diodes), and Functional Hybrids.

Considering that, the main characteristics of functional hybrid materials bind to the chemical activity of their components, exploring their optical and electrical properties, luminescence, ionic conductivity, and selectivity, as well as chemical or biochemical activity, give a way to the materials that can be applied for: sensors, selective membranes, all sorts of electrochemical devices, from actuators to batteries or electrochemical supercapacitors, supported catalysts or photoelectrochemical energy conversion cells, etc. So, highly sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings, making them attractive for industrial applications in high speed machining (Veprek, et al., 1995, 2001), tooling optical applications and magnetic storage devices because of their special mechanical, electronic, magnetic and optical properties due to size effect (Andrievski et al., 2001; Cantor et al., 2001); Mazaleyrat, et al., 2000; Provenzano et al., 1995).

Taking into account the great diversity of extended and molecular inorganic species, small organic molecules and available polymers for the design of the hybrid materials, it is clear that the variety of combinations is tremendously enormous. The wide range of possible hybrids would include innovative combinations, starting from inorganic clusters, fullerenes or metal nanoparticles dispersed in organic polymers to organic and organometallic molecules, biomolecules or enzymes dispersed in inorganic sol-gel polymers, or macrocycles or polyethylene oxide chains intercalated into silicate minerals.

In general, the inorganic-organic hybrid materials can be classified by using several criteria's based on their field of application or on their chemical nature. If we consider classification on the chemical bonding as a base, it would result more useful to distinguish common characteristics and would help us understanding related behaviors and properties. In this case, classification of inorganic-inorganic materials, based on the chemical bonding nature between organic-inorganic interphase will be consisted of two major groups: Class I, where organic and inorganic components are embedded and only weak bounds (ionic bonds, hydrogen bonds or Van der Waals interactions) give the cohesion to the whole structure; and in Class II, where two components are linked together through strong chemical bonds (covalent, ionic-covalent or coordination bonds). In this work we will consider a very simple and logic classification based on the morphological combinations of the inorganic-organic hybrid components as follow (Bier, et al., 2002):

- Class 1. Inorganic matrix systems: where organic materials were embedded in an inorganic polymer. Synthesis of nanohydroxyapatite composite based on combining HA matrix and organic polymers, especially those showing the proper bioactivity, can be considered as an example of this category.
- Class 2. Organic matrix systems: where inorganic materials are embedded in an organic polymer. Some of the oldest and well-known organic-inorganic hybrids of this category are used in the paint industry by dispersion of the inorganic pigments into organic binders.
- Class 3. Interpenetrated networks systems: where inorganic and organic polymeric networks are independently formed without mutual chemical bonds. The incorporation of inorganic macro-molecular networks into organic polymer structures is an example of this category.

- Class 4. Truly hybrids systems: where inorganic and organic polymeric systems with mutual chemical bonds are formed. These true hybrids have been specifically explored successfully for the development of new binders for use in high technology coatings.
- Class 5. Inorganic core/shell matrix systems: where, the potential and ability of the core/shell nanoparticles to obtain structures with combinations of the properties that neither individual material possesses is in consideration. The incorporation of inorganic core-shell ZnO-SiO₂ networks into organic polymer structures is an example of this category.

In this context, referring to the above cited category of the Inorganic-organic hybrid materials, some of the inorganic-organic hybrid nanocomposites materials which we have studied during the near past years will be explained

2. Class 1. Inorganic matrix systems

2.1 Synthesis of hydroxyapatite nanocomposites

The first group of inorganic-organic hybrids nanocomposites studied in our laboratory was in situ biomimetic synthesis of hydroxyapatite (nHAp) nanocomposite in simulated body fluid (SBF) at room temperature [17-19]. The synthesized hydroxyapatites with bone-bonding properties were widely used in hard tissue replacement due to their biocompatibility and osteoconductive properties. But the brittleness of HAp materials limits their use. One of the proposed methods to solve the problem was combination of HAp matrix (inorganic) with different organic polymers, such as collagen, wheat starch, gelatin and starch-gelatin mixture (organic). These natural biopolymers which are biodegradable, biocompatible, water soluble and inexpensive in comparison to the other biodegradable polymers, can be considered as a good candidate to impart *suitable biological and mechanical properties to the synthesized nanocomposites*. The effect of biopolymer template and its influence on the final morphology of nHAp has been revealed in this work via formation of rod like nHAp with about 6-12 nm width and 45-85 nm length (Fig. 1-2), in similarity with bone like material in human body. The shape of HAp crystals in a natural bone is needle-like or rod-like in 40-60 nm length, 10-20 nm width, and 1-3 nm thickness (Kikuchi et al., 2001; Mollazadeh, et al., 2007; Ramakrishna et al., 2001; Toworfe et al., 2006). The morphology and behavior of in vitro cultured BMSCs on n-HAp/starch nanocomposite was investigated under phase-contrast microscope and MTT assays evaluation. Fig. 2a-c presents phase-contrast micrographs of the cell attachment on HAp/0.5 g and nHAp/0.8 g starch biocomposite after culturing for 1, 3 and 7 days. At first day, recognition of elongated fusiform of BMSCs was too hard. After 3 days, a few BMSCs cells were present and after 7 days, a large amount of the proliferated cells, forming cell colony, were fully attached to the biocomposite. This observation, obviously showed that, n-HAp/ starch composite has no negative effect on the cell morphology, viability and proliferation. In MTT assays, starch and n-HAp /3.1 g starch composite were used to culture BMSCs for 1, 3 and 7 days, therewith a culture without biocomposite or biopolymer was used as blank control group. From the data in Fig. 3, the cell number was increased with the culture time on all tested groups. At the first and third day, there were no significant differences between absorbance values of the samples. While, after 7 days, the cells on biocomposite and control group were proliferated rapidly. As it can be find from this data, BMSCs cultured on biocomposite have much more proliferation compared to the gelatin in all the periods of time. The result shows that the presence of n-HAp in the composite has obvious effect on the proliferation of BMSCs.

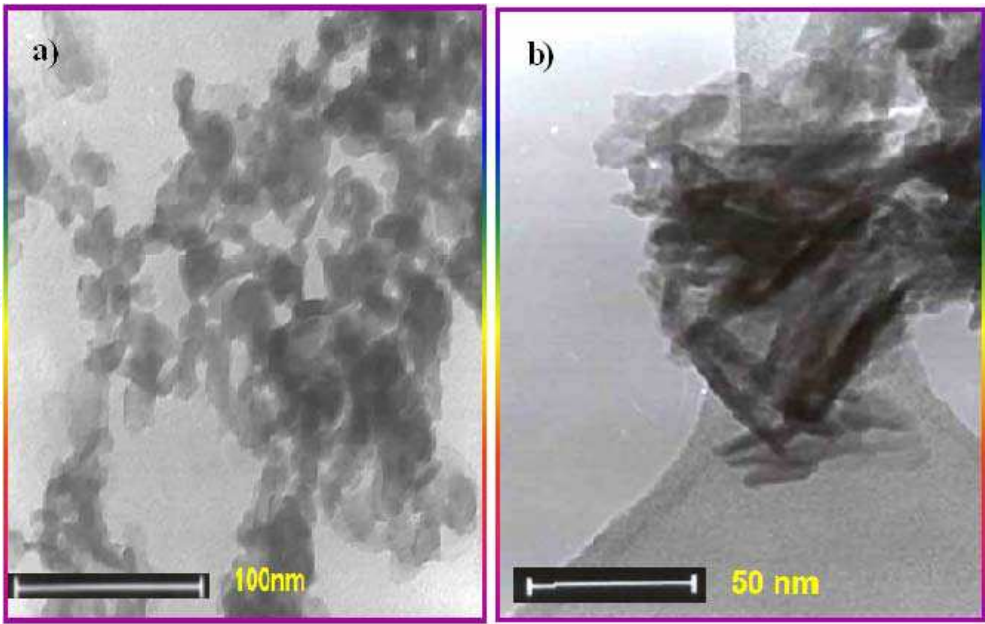


Fig. 1. TEM image of HAp nanoparticles synthesized in absence (a) and presence of 0.8 g starch (b).

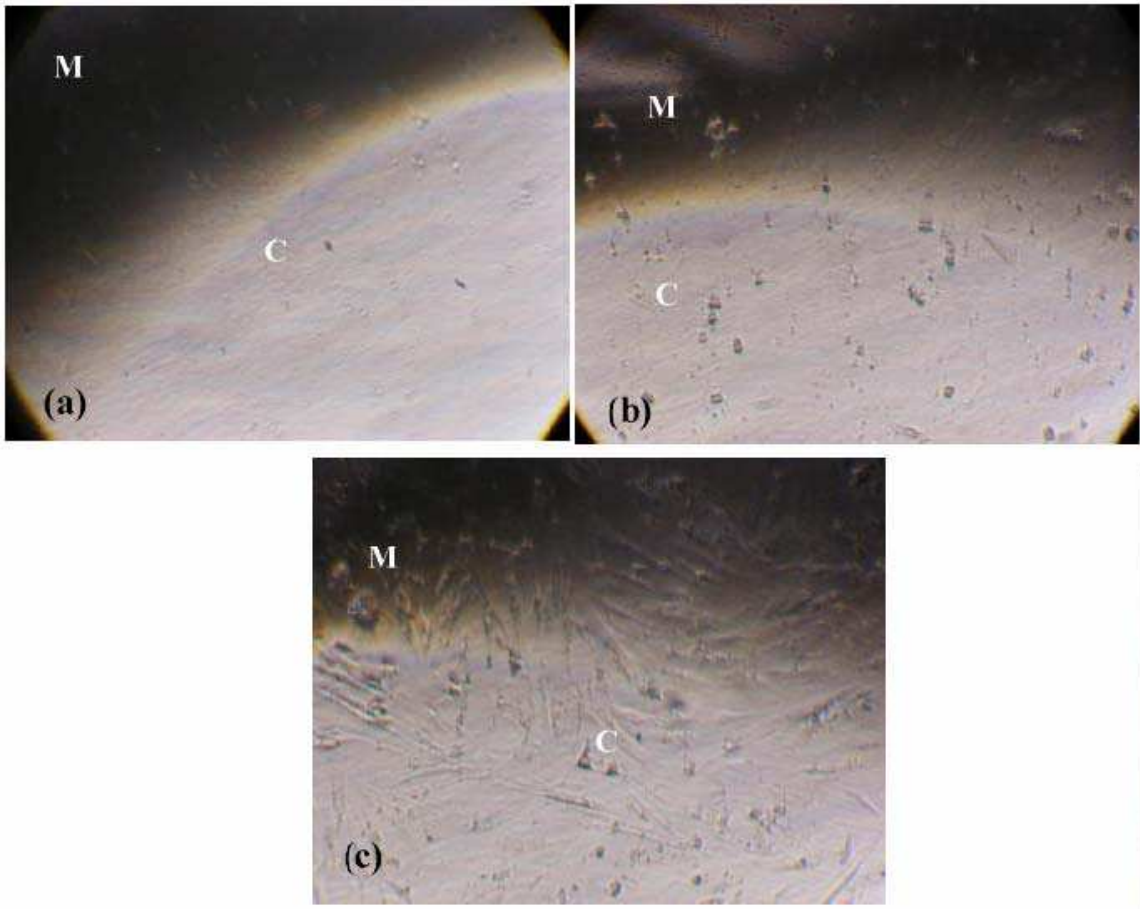


Fig. 2(a-c) presents phase-contrast micrographs of the cell attachment on the nHAp /0.8 g starch biocomposite after culturing for 1, 3 and 7 days.

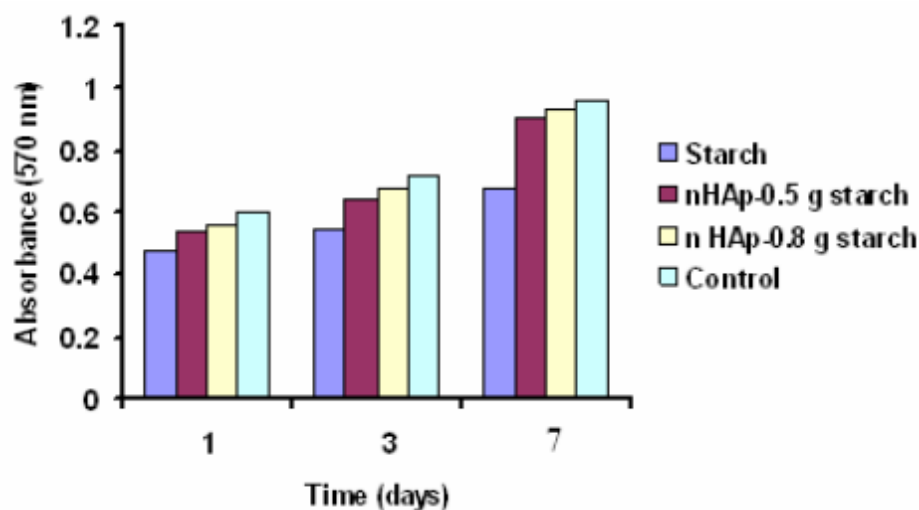


Fig. 3. MTT assays for proliferation of BMSCs combined with gelatin, nHAp/0.5 g and nHAp/0.8 g starch cultured for 1, 3 and 7 days, compared with the control under the same culture condition.

3. Class 2. Organic matrix systems

3.1 Preparation and characterization of Ag/PVA nanorods by chemical reduction method

As an example for second category of inorganic-organic hybrid nanocomposites, silver nanorods was prepared in our laboratory with the average length of 280 nm and diameters of around 25 nm via a simple reduction process in the presence of polyvinyl alcohol (PVA, Mw=72,000) as solvent and protecting agent (Sadjadi et al., 2008). In this process, DMF has been served both as reductant and solvent. In the real reaction, two processes may be occurred simultaneously. At first, Ag nanoparticles are formed through homogenous nucleation and grow into multiply twinned particles (MTPs) with their surfaces bounded by the lowest energy {111} faces and then, *silver nanoparticles forming at the surface of the protecting agent or coming from the outer solution phase through Brownian motion aggregate into a 1D arrangement like a bunch of pearls, and grow into nanorods through Ostwald ripening.*

X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission-electron microscopy (TEM) and UV-Vis spectroscopy techniques were used to characterize the prepared samples. It was found out that both temperature and reaction time are important factors in determining morphology and aspect ratios of nanorods. The TEM images of asprepared Ag nanorods by the controlled-concentration and temperature are shown in Fig. 4(a,b), revealing the as prepared individual Ag nanorods and their constituent nanospheres. Fig. 4(c) exhibits the cross section of the multiply fivefold twinned fcc Ag prepared crystallite. High concentrated distribution of Ag/PVA nanorods is observable on the SEM images (Fig. 5). The UV-visible spectrum of as prepared Ag/PVA nanorods showed a broad absorption band at λ_{max} 458 nm. This characteristic peak was due to the oscillation of conduction band electrons of Ag known as the surface plasmon resonance (Cepak et al., 1998; Foss et al., 1994), (Link et al., 1999; Itakura et al., 1995; Jana et al., 2001). The position of plasmon absorption band (Khanna et al., 2005) was dependent of particle size, aspect ratio and diameter of nanorods and the broad nature of the absorption band in this case is indicative of the presence of both nanospheres and nanorods as reported in citrate reduction method (Zhou et al., 2006).

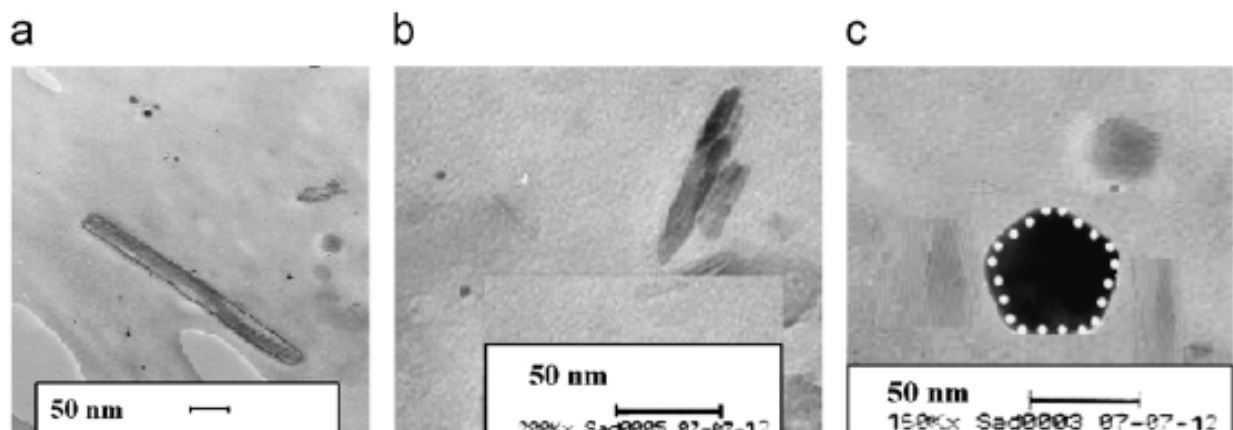


Fig. 4. Transmission electron microscopy (TEM) images of (a, b) individual nanosphere and nanorod crystals (c) cross section of Ag nanorods embedded in PVA.

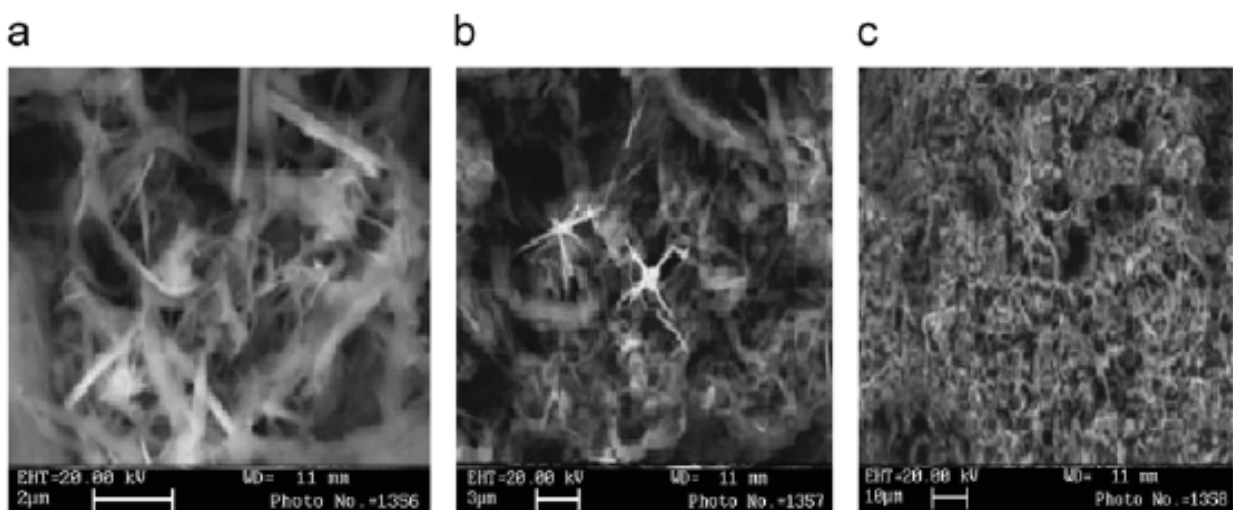


Fig. 5. (a, b, c) SEM image showing high concentrated distribution of Ag/PVA nanorods.

4. Class 3. Interpenetrated network (IPN) system

4.1 Preparation of silicon based polymeric coatings

The sol gel process is used to produce silicon-based polymeric structures as interpenetrating networks in organic binder systems. Conditions for eligibility to participate in an interpenetrated nanocomposite are as follows: the two polymers have to be synthesized in the presence of each other, the two monomers should have the similar reaction kinetics, and the resulting materials should not to be phase separated. Interpenetrated polymer network (IPN) synthesized in this work was composed of an organic phase (GY250 = diglycidyl ether of bisphenol), an aromatic amine like HY850 and an inorganic silica phase formed by sol-gel process from TEOS and was coated on the aluminum alloy (AA) substrate by dip coating method (Rahimi et al., 2005; Sadjadi et al., 2009). The hybrid network obtained in this manner has an excellent optical transparency and was characterized using different spectroscopic and microscopic techniques. A significant feature in formation of this hybrid network to enhance compatibility with hybrid materials is formation of covalent bonding between organic polymers and inorganic compounds (Matejka et al., 2000). All modification

of the structures of the molecular species and the new bonds formed or destroyed during the sol-gel process were studied by using FTIR spectroscopy. The results showed formation of the Si-O-C bonds during the reaction and opening the epoxy ring (the peak of epoxy group disappeared). The SEM micrographs (Fig. 6) showed well dispersed of small particles with the average particle size diameter of 20-70 nm. The Si mapping image of hybrid inorganic-organic coating on the aluminum substrate after curing showed uniform distribution of Si nanoparticles (Fig. 7).

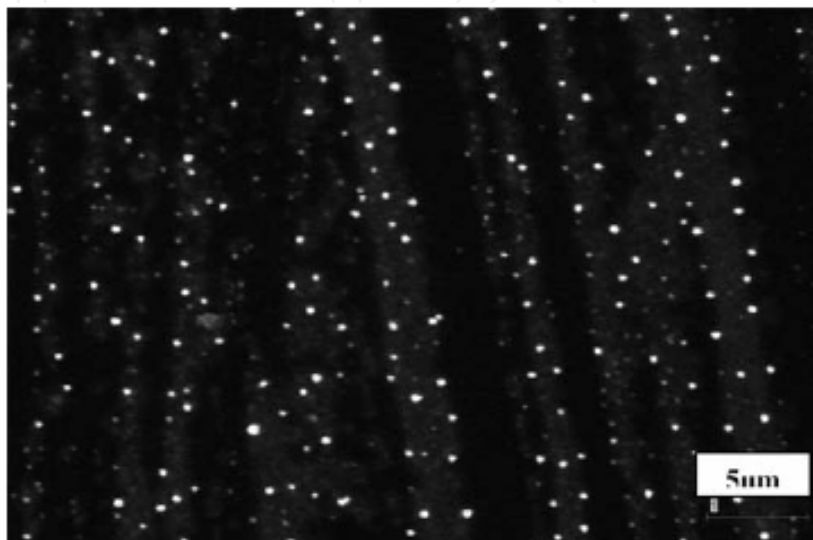


Fig. 6. The SEM image of inorganic-organic hybrid polymer on aluminium substrate after curing

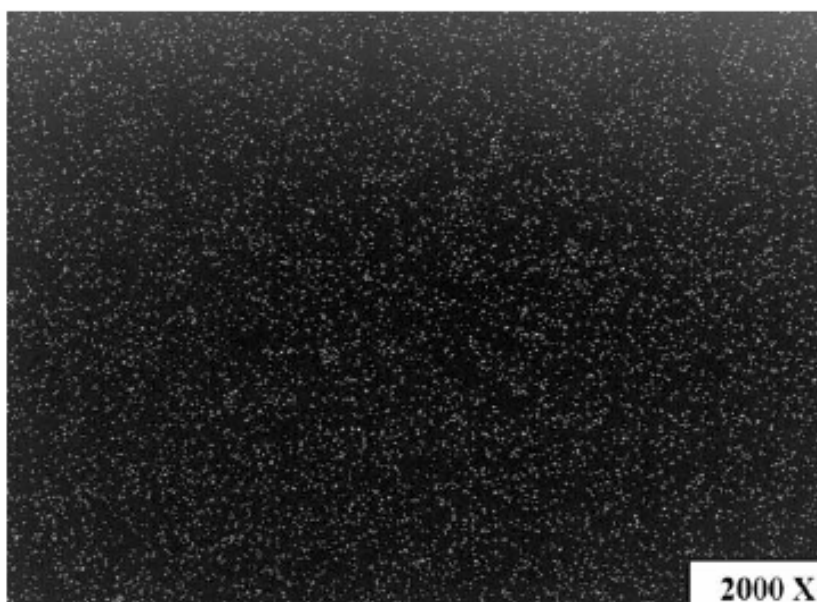


Fig. 7. Si mapping image of inorganic-organic hybrid on aluminium substrate after curing

4.2 Preparation of metallophthalocyanines on γ alumina support

Example of this category of inorganic-organic hybrid nanocomposite which we have prepared in our laboratory was metallophthalocyanines supported on γ -alumina as an effective

heterogeneous catalyst for oxidation of alcohols such as cyclohexanol, benzyl alcohol and hexanol (Lorber et al., 1996; Sadjadi et al., 2010; Sugimoto et al., 1985). Metallophthalocyanine (MPc) complexes have been used as alternative catalyst, because they have a similar structure to porphyrins and are cheaper, more stable to degradation *with higher catalytic performance*. Its incorporation with the solid supports for synthesis of heterogeneous catalysts is highly desirable (Geraskin et al., 2008; Sharma et al., 2003). The catalysts were prepared by dispersing MPc complexes (M= Fe, Mn and Co) into the already prepared γ -alumina. Formation of independent catalyst components have been confirmed and characterized by using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and UV-vis spectroscopy. Investigation on improvement of the catalytic activity of the prepared catalyst (MPc (Me= Fe, Mn and Co) complexes/ γ -alumina) in comparison with MPc (Me= Fe, Mn and Co) complexes is underway in our laboratory.

5. Truly hybrids systems

5.1 Preparation of hydrophilic nanocomposite coating

Research on *functional hybrid materials* has become one of the most rapidly developing fields of materials chemistry. In its most basic sense, a hybrid material is obtained by combining at least two components, commonly inorganic and organic, at the nanometer scale. Methods to synthesize inorganic-organic hybrid materials are often based on soft chemistry approaches, such as sol-gel processes, intercalation, exchange, or grafting. Considering the variety of combinations of components (and properties), inorganic-organic hybrids represent an intriguing class of materials with a large spectrum of applications. In this section we will focus on the synthesis of functional inorganic-organic hybrid materials, on the elucidation of structure-property relationships, as well as on the organization of hybrid building blocks. In this purpose, based on epoxy resin and titanate as precursor, we have prepared hydrophilic inorganic-organic nanocomposite coating films on the glass substrate. *Transparent hydrophilic nanocomposite films* based on TiO_2 on glass substrates have high potentiality for practical applications such as mirrors, window glasses, windshields of automobiles, and so on. Hydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets, thus making the surface anti-fog and easy to wash. Their further characteristics were good mechanical properties (scratch and abrasion resistance) [53-59] and stability against wet climate conditions and UV radiation (Watanabe et al., 1996). This kind of hydrophilic coatings can be used in preventing dewdrops forming inside the windowpanes and greenhouses, for the purpose of protecting vegetables from rotting by dewdrops.

The films on the glass substrates were prepared by dip-coating process from a sol containing alcoholic tetrabutyl titanate which after the curing treatment, the gel forms a stable thin homogeneous nanocomposite coating. The films obtained were transparent to the visible light and their surface hydrophilicity values were increased by increasing TiO_2 nanoparticles content. Characterization of the nanocomposite coating films, performed by TEM showed that the particle size of the superposed TiO_2 nanoparticles in nanocomposite films were estimated about 2–4 nanometer (Fig. 8). Atomic Force Microscopy (AFM) observation showed uniformity and three-dimensional surface profile of TiO_2 nanospheres in the nanocomposite films (Fig. 9). The contact angle test without coating and after coating (Fig. 10), gave a good evidence for hydrophilicity of the prepared nanocomposite coatings and the strong interaction between organic and inorganic phase with the formation of titania domains in the nanoscale range. Applied humidity resistance test showed the high stability of nanocomposite coating in humidity exposure.

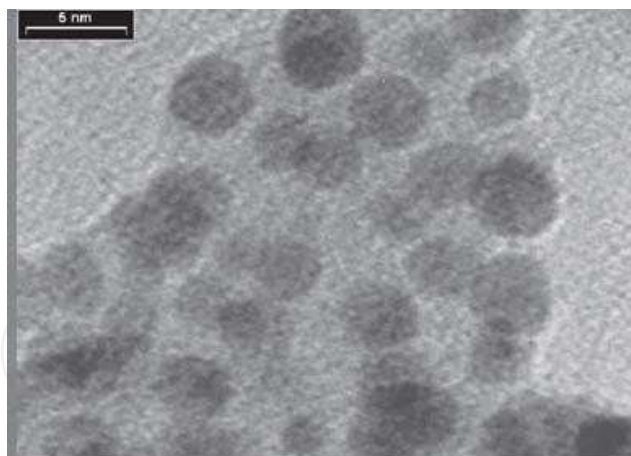


Fig. 8. TEM image of transparent hydrophilic inorganic-organic hybrid TiO_2 / epoxy resin hybrid coating film on glass substrate.

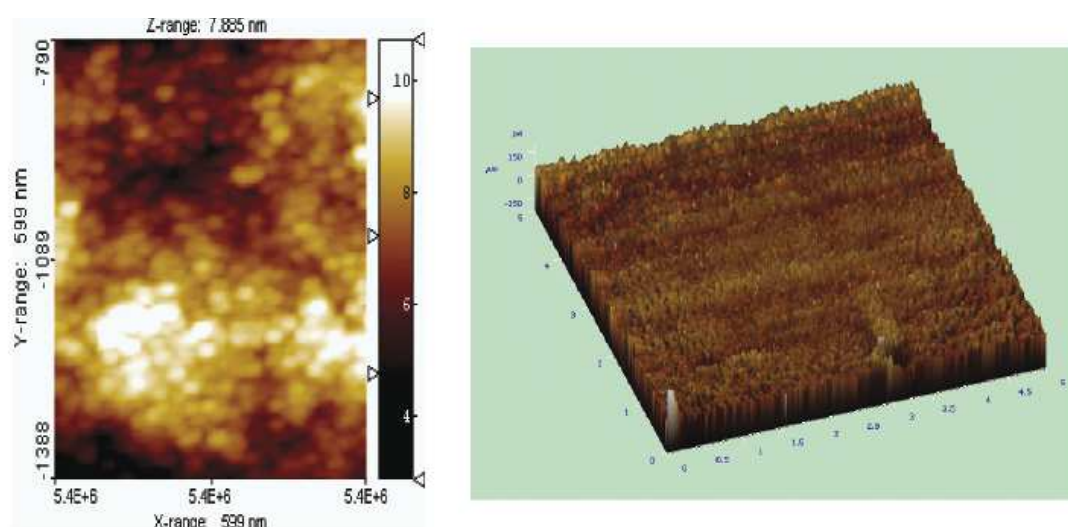


Fig. 9. AFM micrograph showed uniformity and a three-dimensional surface profile of TiO_2 nanospheres in the nanocomposite film.

6. Class 5. Inorganic core-shell matrix systems

In this category of the inorganic-organic hybrid coating, the ability and potential of the core/shell nanoparticles to obtain structures with combinations of properties that neither individual material possesses is in consideration. This category of core shell Inorganic – organic nanocomposite, due to the ease of manipulation of the nanoparticle morphologies, compositions and surface properties to earn the name of particle engineering, has attracted a lot of attention. It basically involves tailoring the surface properties of particles with a shell of controlled composition. The shell can alter the charge, functionality, and reactivity of the surface, or improve the stability and dispersive ability of the core. Furthermore, magnetic, optical, or catalytic functions can be imparted to the colloidal particles by the shell material. Spherical gold nanoparticles which have a Surface Plasmon Resonance at a wavelength of about 520 nm and a spherical silica core with a gold shell offering a very highly tunable Plasmon wavelength depending on the thickness of the shell and the core diameter is an example for this category of core shell nanocomposite.



Fig. 10. Transparent hydrophilic TiO_2 nanocomposite coating based on epoxy resin on glass substrate

6.1 Preparation of ZnO-SiO_2 /Epoxy nanocomposites by sol-gel method

As a first example of this category of core-shell inorganic-organic hybrid materials, ZnO-SiO_2 /Epoxy nanocomposites was synthesized in our laboratory by sol-gel process (YU et al., 2001). In this purpose, inorganic core shells of ZnO-SiO_2 were firstly prepared and embedded then in the organic polymeric networks. The morphology of the coating surface was elucidated by SEM and a mapping technique to investigate the dispersion of inorganic phase in the hybrid matrix. Figures 11 and 12 represent SEM photographs of pure glass without coating and inorganic core-shell ZnO/SiO_2 /epoxy hybrid nanocomposites coating. This image shows that the ZnO/SiO_2 particles were uniformly dispersed throughout the polymer matrix in nanometer sizes as well as good miscibility between organic and inorganic phases.

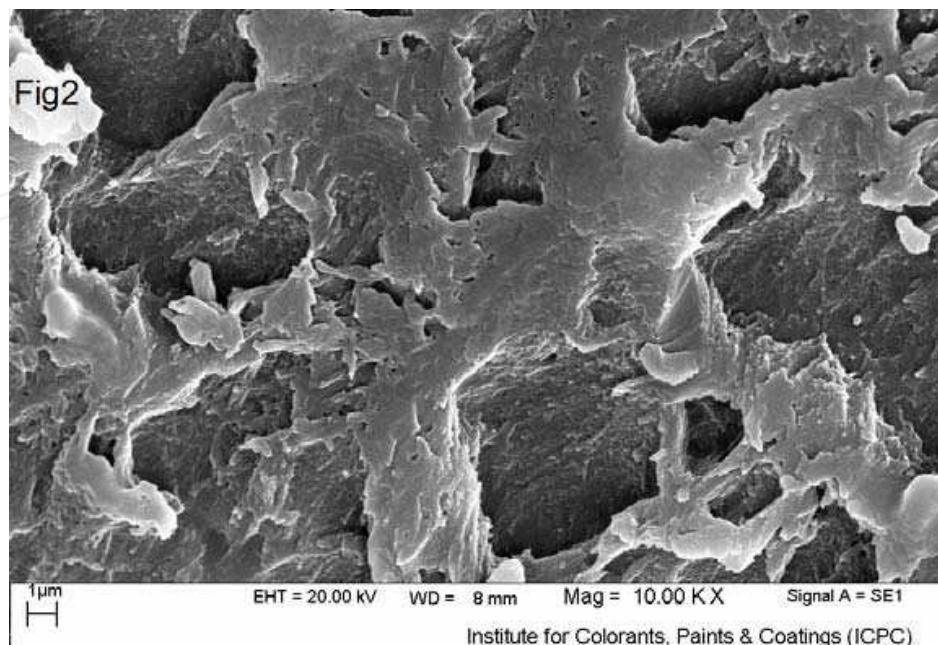


Fig. 11. SEM image of the surface of epoxy/polyethylene

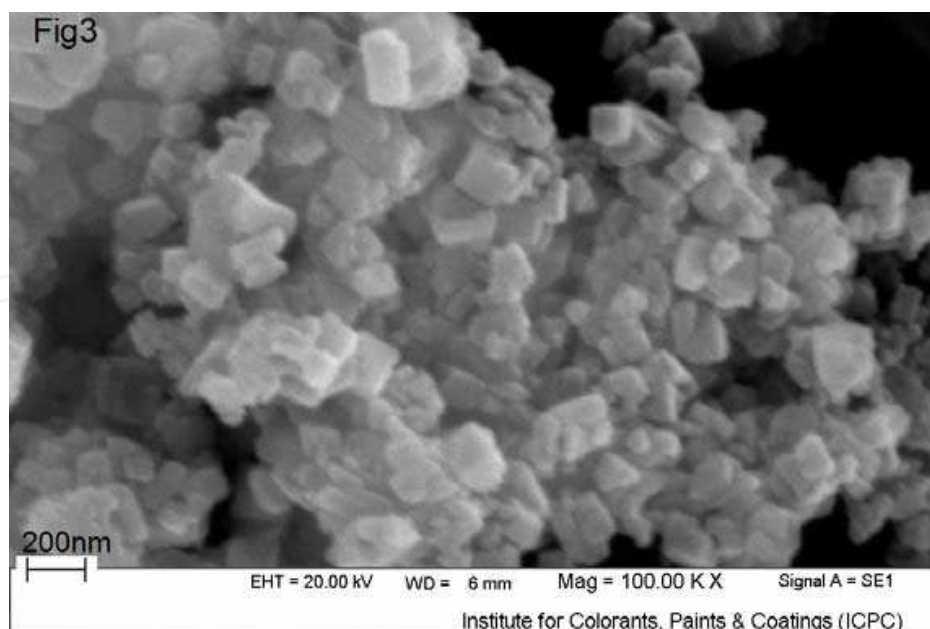


Fig. 12. SEM image of the surface of Gy250/HY850/ GPTMS/ZnO-SiO₂ nanocomposite film

6.2 Preparation and characterization of transparent SiO₂-Ag/PVP nanocomposit

As a second example of the core-shell inorganic systems, transparent SiO₂-Ag/PVP nanocomposite mirror films were prepared by sol gel method and characterized (Sadjadi et al., 2009). The results showed that, silica modified PVP is a remarkably powerful capping agent for preparation of 1D arrangement of Ag nanoparticles and this kind of prepared inorganic/organic nanocomposite can now be developed towards optical and medicinal based applications (Elechiguerra et al., 2005; Sondi et al., 2008; Suvorova et al., 2005; Zheng et al., 2001). The broad nature of the UV -Visible absorption band at $\lambda_{\text{Max}} = 410 \text{ nm}$ due to the oscillation of conduction band electrons of Ag indicated the presence of both embedded sphere and assembled nanospheres in SiO₂ modified PVP (Cepak et al., 1998; Jana et al., 2001; Link et al., 1999). Transparency dependent on the Ag nanoparticle size was about 96% in the infra-red region (Fig. 12, 13). The FTIR results indicated that the steric effect in the reaction between silver and PVP will be important when the particles size grow up upon curing of the sol and the main reaction between silver nanoparticles embedded in silica modified PVP may occur between O atoms of silica modified PVP and Ag nanoparticles. The XRD data confirmed that the Ag nanoparticles are crystalline with fcc structures having a preferred crystallographic orientation along the (220) direction. The grain size of the silver nanospheres estimated from the XRD peak width (and using Scherrer's formula), was about 8.4 nm. TEM observations from the side section of the prepared sample illustrated individual Ag nanosphere (Fig. 14) as well as self assembled nanosphere in a twinned wire like shapes with an average length of 200-250 nm and diameters of around 20-25 nm. TEM observations from side section of nanowires suggest that the transformation of Ag nanospheres to Ag nanowires is achieved by the oriented self assembling of the several spherical particles followed by their fusion. Resulting Ag nanowires have a twinned fcc structure, and they appear in an cubic assemblage in fourfold twinning. SEM image of as prepared SiO₂-Ag/PVP nanocomposites illustrating homogenous mechanical mixture of the polymer and nanoparticles is given in Fig. 16.

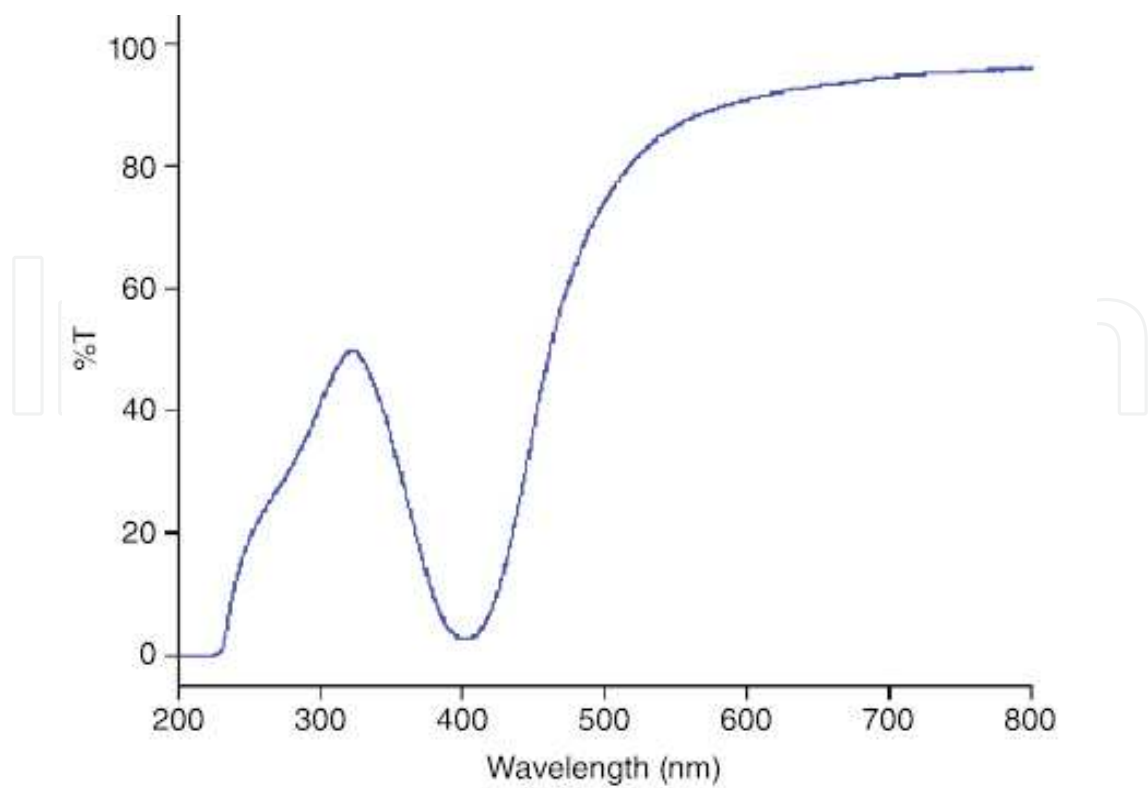


Fig. 13. Transmittance spectrum of the as prepared core shell inorganic hybrid $\text{SiO}_2\text{-Ag/PVP}$

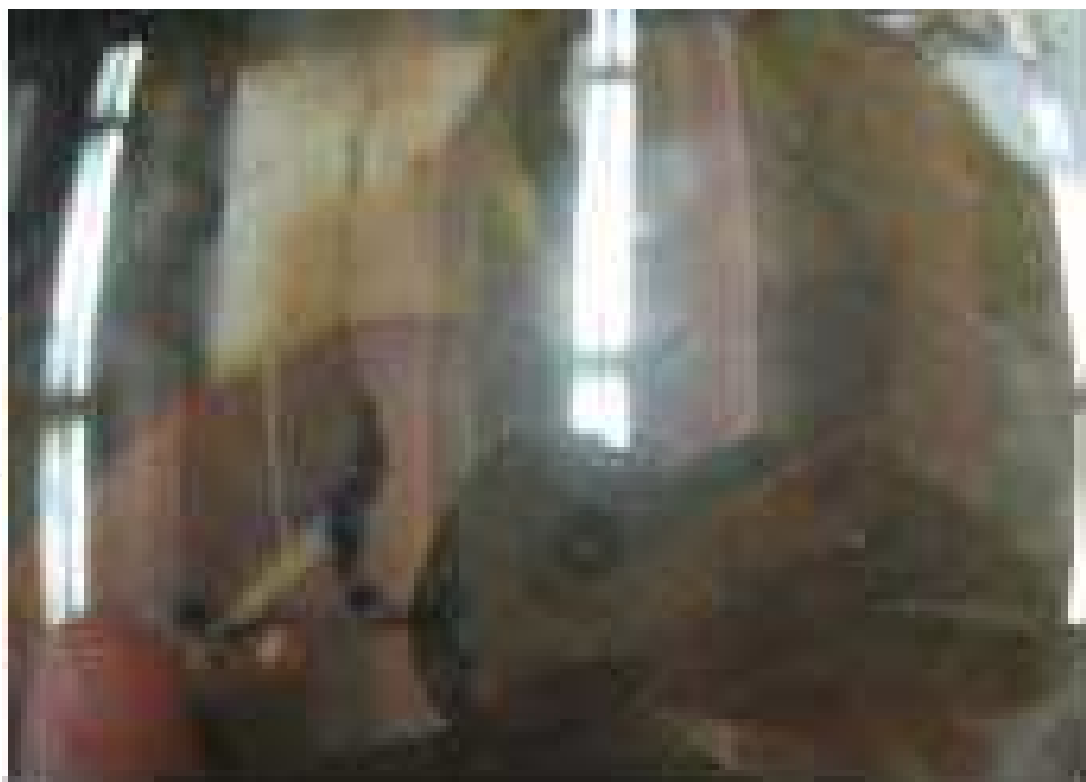


Fig. 14. Transparent mirror coating of as prepared core shell inorganic hybrid $\text{SiO}_2\text{-Ag/PVP}$ nanocomposite films.

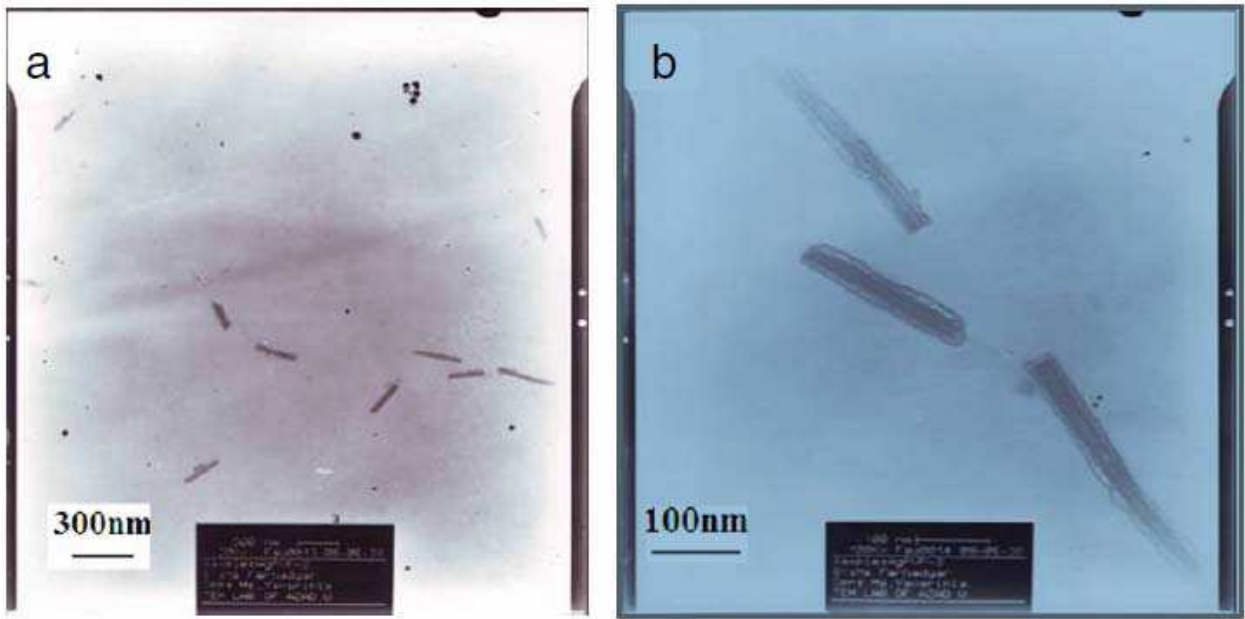


Fig. 15. TEM image of (a) Individual embedded Ag nanospheres assembled Ag nanosphere as a bunch of peals on the silica modified PVP, (b) side section of the Ag nanospheres crystallite assembly.

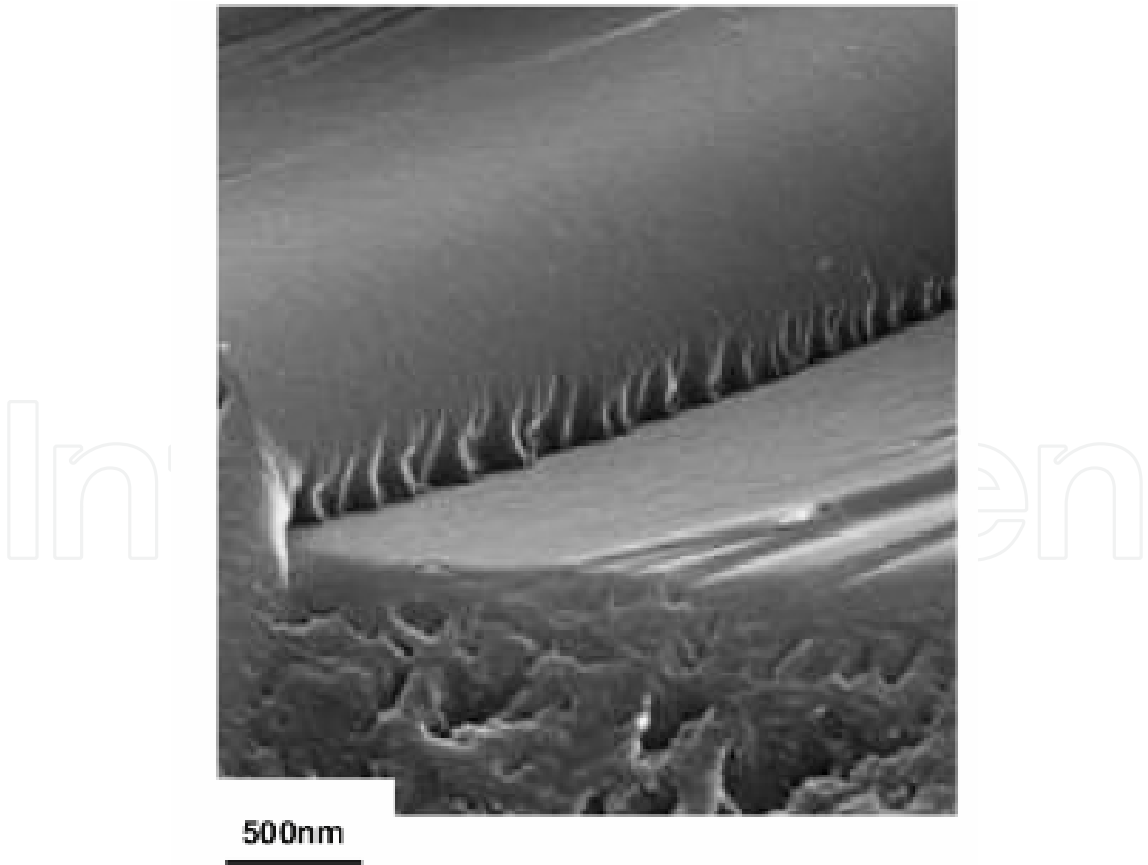


Fig. 16. SEM image of as prepared SiO₂-Ag/PVP nanocomposites illustrating homogenous mechanical mixture of the polymer and nanoparticles.

7. Summary

Class 1. Inorganic matrix systems:

- HAp nanocomposite synthesis can be performed at room temperature by a mimetic method using wheat starch as a template agent.
- Controlling the shape and size of HAp nanoparticles is possible by choosing appropriate template and wheat starch is a good example.
- The effect of wheat starch template and its influence on the final morphology of nHAp is revealed via formation of rod-like nHAp with about 6–12nm width and 45–85nm length. The crystal shape of
- Morphology of the synthesized HAp using starch as a template is similar to the inorganic phase of human natural bone.
- In vitro bioactivity of the synthesized nHAp at the presence of wheat starch biopolymer is confirmed by formation of a layer of carbonated apatite on the surface of synthesized HAp after soaking them in SBF solution.
- The presence of n-HAp in the composite has obvious effect on the proliferation of BMSCs.

Class 2. Organic matrix systems:

- Polyvinyl alcohol (PVA) is a remarkably powerful capping agent for Ag ions.
- Di methyl formamide (DMF) is an appropriate solvent and reductant agent for the preparation of silver nanoparticles.
- Controlling the shape and size of silver nanoparticles by choosing an appropriate capping agent and solvent at ambient temperature is possible.
- Recorded UV-visible spectra indicated well-defined absorption bands for Ag nanoparticles or nanorods due to the surface plasmon resonance phenomena.
- The XRD patterns confirmed that the Ag nanorod is crystalline with fcc structure having a preferred crystallographic orientation along {2 2 0} direction, and a straight, continuous, dense Ag nanorod has been obtained with a diameter of 25 nm.
- SEM and TEM observations along a series of relevant directions showed that the silver nanorods have an average length of 280 nm and diameters of around 25 nm.
- TEM observations from cross section of nanorods suggested that the transformation of Ag nanospheres to Ag nanorods is achieved by oriented attachment of the several spherical particles followed by their fusion.
- Resulting Ag nanorods have a twinned fcc structure, and they appear in a pentagonal shape with fivefold twinning. The fivefold axis, i.e. the growth direction, normally goes along the (110) zone axis direction of the fcc cubic structure

Class 3. Interpenetrated network system:

- In this category of organic-inorganic hybrid system, the organic phase was composed of GY250 (diglycidyl ether of bisphenol A) and HY850 (aromatic amine); and an inorganic silica structure was formed by sol-gel process.
- The organic-inorganic hybrid material (nanocomposite) was coated on the aluminum alloy (AA) substrate by dip coating method.
- Obtained hybrid network coatings possess excellent optical transparency.
- ²⁹Si NMR spectrometry elucidated the type of formed molecular species and their structure.

- The modification of the structures of all molecular species and the bonds formed or destroyed during the sol-gel process were endorsed by using the FTIR spectroscopy.
- Formation of Si-O-C bond during the reaction and opening the epoxy ring was confirmed by FTIR spectra.
- Thermal stability of the prepared coating samples was confirmed by using TGA.
- SEM micrographs show that the Small dispersed particles of 20-70 nm diameter have been showed by SEM micrographs.
- ***Preparation of metallophthalocyanines on γ -alumina support***
- Metallophthalocyanines encapsulated in γ -alumina nanoparticles were directly synthesized by addition of the metal salt, phthalonitrile, urea and ammonium heptamolybdate to the γ -alumina'
- Cobalt, iron and manganese phthalocyanines incorporated with γ -alumina pores proved to be active, efficient and reusable catalysts for oxidation of various alcohols with good conversion percentage and 100% selectivity.

Class 4. Truly hybrids systems

- ***Preparation of hydrophilic nanocomposite coating***
- Transparent hydrophilic organic-inorganic nanocomposite hybrid coating films based on epoxy resin were prepared using tetrabutyl titanate by a simple sol-gel method.
- Suitable conditions to obtain a complete conversion for preparation of the nanocomposite coatings, at a molecular level were established.
- The films were prepared on the glass substrates by dip-coating from a sol containing alcoholic tetrabutyl titanate which after the curing treatment, the gel forms a stable thin homogeneous nanocomposite coating.
- Obtained films were transparent to visible light and their surface hydrophilicity values were increased by increasing TiO₂ nanoparticles content in the water damp permeable self leveling flooring system.
- Characterization of the nanocomposite coatings performed by TEM showed that the size of the superposed TiO₂ nanoparticles in nanocomposite films were estimated about 2–4 nanometer.
- AFM observation showed uniformity and a three-dimensional surface profile of TiO₂ nanospheres in the nanocomposite film.
- The contact angle test without coating and after coating, gave a good reason for hydrophilicity of the nanocomposite coating and the strong interaction between organic and inorganic phase with the formation of titania domains in the nanoscale range.
- Applied humidity resistance test showed the high stability of nanocomposite coating in humidity exposure.

Class 5. Inorganic core-shell matrix systems:

- ***Preparation of ZnO-SiO₂/Epoxy nanocomposites by sol-gel method***
- Thin film inorganic-organic hybrid coatings was successfully produced by sol-gel method reacting of GLYMO/ZnO-SiO₂/EPOXY/aromatic (diglycidyl ether of bisphenol A) and HY850 (aromatic amine)/ PEG surfactance at room temperature.
- The optically transparent Prepared films were resistance to cracking, with excellent adhesion properties.

- The FTIR spectra confirmed formation Si-O-Si and Si-O-C, Zn-O-Si bonds and epoxy ring opening during the process.
 - The Si mapping image confirmed uniformly distribution of dispersed inorganic nanoparticles in hybrid nanocomposites, which results in the formation of transparent coatings.
 - Anti-fog coatings were prepared by incorporating PEG and surfactant to siliceous precursors.
 - Hydrophilic properties of the surfaces were verified by contact angle measurements.
 - Hydrophilic OH groups can be introduced in the hybrid system through chemical bonds, leading to an improvement of the wetting behavior without a change in the adhesion properties.
 - It was shown as the amount and molecular weight of the added PEG, and surfactant is increased there is an obvious increase in hydroxyl content and the higher the hydroxyl content, the lower contact angle for water of the hydrophilic nanocomposite coatings. SEM show the small dispersed particles which are aggregated in larger irregular aggregates of nano size.
- ***Preparation and characterization of transparent SiO₂-Ag/PVP nanocomposite:***
- A transparent mirror films of inorganic/organic hybrid of SiO₂-Ag/PVP has been prepared by sol gel method.
 - Silica modified PVP is a remarkably powerful capping agent for preparation of 1D inorganic-organic nanocomposite coating.
 - Inorganic-organic transparent mirror films can be developed towards optical and medicinal based applications.
 - The broad nature of the UV-Visible absorption band at $\lambda_{\text{Max}} = 410 \text{ nm}$ due to the oscillation of conduction band electrons indicated the presence of both embedded sphere and assembled nanospheres in SiO₂ modified PVP.
 - Transparency of the prepared mirror films was dependent of Ag nanoparticle size and was about 96% in the infra-red region.
 - FTIR results indicated importance of the steric effect in the reaction between silver and PVP when the particles size grow up upon curing of the sol.
 - The main reaction between silver nanoparticles embedded in silica modified PVP was occurred between O atoms of the silica modified PVP and Ag nanoparticles.
 - The XRD data confirmed that the Ag nanoparticles were crystalline with fcc structures having a preferred crystallographic orientation along (220) direction.
 - The grain size of the silver nanospheres estimated from the XRD peak width (and using Scherrer's formula), was about 8.4 nm.
 - TEM observations from of the side section of prepared samples illustrated individual Ag nanosphere as well as self assembled nanosphere in a twinned wire like shapes with an average length of 200-250 nm and diameters of around 20-25 nm.
 - TEM observations from side section of nanowires suggest that the transformation of Ag nanospheres to Ag nanowires is achieved by the oriented self assembling of the several spherical particles followed by their fusion.
 - Resulting Ag nanowires have a twinned fcc structure, and they appear in an cubic assemblage of fourfold twinning.
 - SEM image of as prepared SiO₂-Ag/PVP nanocomposites illustrated homogenous mechanical mixture of the polymer and nanoparticles .

8. Conclusion

In this work, a very simple and logic classification based on the morphological combinations of the inorganic –organic hybrid components were considered to study some limited examples of Inorganic-organic coating systems. We think that, it is still very soon to give some road maps to design and achieve a new inorganic –organic hybrid nanocomposite material with some proper properties.

9. Acknowledgements

The authors express their thanks to the Vice presidency of Science and research Branch, Islamic Azad University and Iranian Nanotechnology Initiative for their encouragement, permission and financial support.

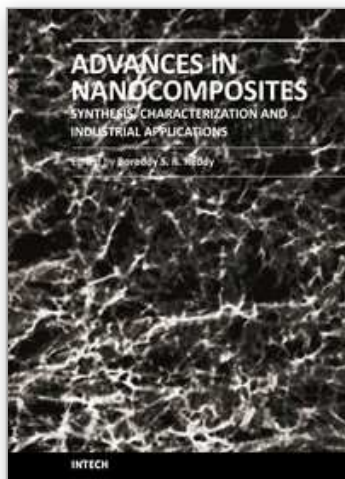
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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications

Edited by Dr. Boreddy Reddy

ISBN 978-953-307-165-7

Hard cover, 966 pages

Publisher InTech

Published online 19, April, 2011

Published in print edition April, 2011

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

How to reference

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Mirabdullah Seyed Sadjadi, Nazanin Farhadyar and K. Zare (2011). Preparation and Characterization of Inorganic-Organic Nanocomposite Coatings, *Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications*, Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-165-7, InTech, Available from: <http://www.intechopen.com/books/advances-in-nanocomposites-synthesis-characterization-and-industrial-applications/preparation-and-characterization-of-inorganic-organic-nanocomposite-coatings>

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