Preparation of Water-based ITO Sol Solution and 4-Vinylpyridine/styrene-ITO Colloidal Nanocomposites

(수계 ITO 나노졸 용액의 제조와 4-Vinylpyridine/styrene-ITO 콜로이드 나노컴파지트의 제조에 관한 연구)

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Abstract

Indium tin oxide (ITO) nanoparticles with In/Sn = 9 : 1 (at.%) were prepared by chemical coprecipitation method in an aqueous solution. The coprecipitate prepared at room temperature showed the crystal structure of indium oxide in X-ray diffraction when it was annealed at the temperature above 300 °C under air atmosphere. Reduction process was accomplished to improve the electrical property of ITO powder and the powder changed from yellow to dark green. However these green ITO powder with particle sizes in the range of 15 - 25 nm were not well dispersed such as other nano-sized particles because of high value of free surface energy. Dispersing agents such as polyvinylpyrrolidone and commercial agents were used to improve dispersibility of the water-based ITO sol solution and a comparative study on dispersibility of each sol solution was carried out. The dispersibility of water-based ITO sol solution was the best when polyvinylpyrrolidone was used as a dispersing agent. Near IR-radiation reflective film was prepared by spin coating method using ITO sol solution. 4-Vinylpyridine/styrene-ITO colloidal nanocomposites were prepared by using the well-dispersed ITO sol solution. The preparation of nanocomposites was carried out with different kinds of surfactants in aqueous media at 70 °C. The influence of the surfactants employed in preparing 4-vinylpyridine/styrene-ITO colloidal nanocomposites was studied.

1. Introduction

In recent years, considerable effort has been devoted to nano-sized materials in the studies of their fundamental mechanism, such as the size effect and the quantum effect, and in applications of these materials. Indium tin oxide, one of transparent conducting oxides, has attracted a great deal of attention due to its remarkable properties and technological application. Indium tin oxide (ITO) film has high visible transmittance, high infrared reflectance, good electrical conductivity, excellent substrate adherence and hardness.[1-5] Those properties have made ITO films applied as transparent electrodes for use in LCD (liquid crystal display), PDP (plasma display panel), coating material for use in CRT, transparent conducting thin films, IR-radiation reflective films, low-emissive windows and solar cells.[6-10] While several preparation methods such as sputtering, spray pyrolysis and dip coating methods have been employed for making thin films of ITO, researches on ITO nanoparticles and its dispersibility in an aqueous solution are still quite sparse.[11-15] It is important to have sol solution with good dispersibility because the quality of dispersion affects technical application. In the previous researches on ITO nanoparticles, metal alkoxides were used as raw materials for preparing ITO nanoparticles, but it was very difficult to obtain indium and tin alkoxide because of preparation problems, unavailability or expensive cost. Therefore, we prepared ITO nanoparticles using inorganic metal salts as raw materials. Metal salts are cheaper than metal alkoxides and are very easy to handle.[16] In this work, ITO nanoparticles were easily prepared by chemical coprecipitation method but the particles were not well dispersed in an aqueous solution as other nano-sized particles. The dispersibility of ITO particles in an aqueous solution was improved by adding dispersing agents such as polyvinylpyrrolidone. The well-dispersed ITO sol solution was used to prepare near IR-radiation reflective film. Near IR-radiation reflective film was prepared by spin coating of the ITO sol solution and reflectance in the near IR-radiation was characterized.

In the past few years nanocomposites materials have become one of the most extensively studied materials all over the world as they have shown to possess several applications such as effective quantum electronic devices, toners in photocopying, drug delivery and sensors.[17] Nanocomposites formed by combining polymers and inorganic nanoparticles, have been great interest to researchers. Of the many possible polymer-inorganic nanocomposites, the polymer-silica nanocomposites have received lots of attention. In the 1970s worker at DuPont described the synthesis of uniform spherical polymer-silica composites with average diamerters ranging from 500 nm up to 20 ㎛ in the patent literature.[18] In 1992 Armes et al. reported the synthesis of colloidally stable polyaniline-silica nanocomposite particles by polymerizing aniline in the presence of an ultrafine aqueous silica sol.[14] More recently, this kinds of works have been extended to include various polymer such as polypyrrole, polymethyl methacrylate and polyvinylpyridine. Despite of lots of works on nanocomposites, there are few reports on other polymer-metal oxide nanocomposites.[19] In this work, 4-vinylpyridine/ styrene-ITO colloidal nanocomposites were prepared by using the well-dispersed ITO sol solution. These copolymer-ITO nanocomposites will have great application potentials.

2. Experimentals

2-1. Materials

Indium nitrate pentahydrate ($In(NO_3)_3 \cdot 5H_2O$, Aldrich 99.9%) and tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Aldrich 98%) as inorganic reactants and ammonium chloride (Aldrich 99.99%) and ammonium hydroxide (Aldrich 99.99+%) as precipitation agents were used to prepare ITO nanoparticles. EFKA 4330 (EFKA), NP 1050 (Dongnam Chemical Iindustries), BYK 190 (BYK Chemie), polyacrylic acid-ammonium salt (Aldrich) and polyvinylpyrrolidone (Aldrich, Mw10,000) as dispersing agent were used to prepare ITO sol solution. Distilled water was used as dispersing solvent. Hydrochloric acid (HCl, Aldrich) and ammonia solution (NH_3, Junsei) were used to adjust pH of the solution. Styrene (Aldrich) and 4-vinylpyridine (Aldrich) as monomers, and sodium dodecyl sulfate (Aldrich) and cetyltrimethylammonium bromide (Aldrich) as surfactants were used to prepare polymer colloidal nanocomposite. Ammonium persulfate (Aldrich) was used as a initiator. In all experiments the resistivity of distilled water was 18 ㏁.

2-2. Methods

2-2-1. Preparation of ITO nanoparticles by coprecipitation method

$In(NO_3)_3 \cdot 5H_2O$ (2.6 g, 6.7 mmol) and $SnCl_4 \cdot 5H_2O$ (0.26 g, 0.74 mmol) were dissolved in 40 ^oC distilled water (10 mL) and the solution was stirred for 30 min. NH_4Cl (0.068 g, 1.3 mmol) was added to the mixture solution and the solution was heated at 40 ^oC for 10 min. A 10 wt.% NH_4OH solution was added to the mixture to be until pH 7 at room temperature. A 10 wt.% NH_4OH solution was used as a precipitation agent. After white slurry was formed, it was washed with 50 °C distilled water 4 - 5 times to remove impurities. The washed precipitates were filtered and dried at 70 °C for 24 hrs. The dried powder was sintered at 200 °C, 300 °C. 500 °C and 700 °C for 3 hrs under air atmosphere. This primary annealing was carried out to crystallize particles and remove impurities. Yellow ITO powder was obtained by this primary annealing. The secondary annealing under hydrogen atmosphere was accomplished at 250 °C for 10, 30 and 50 min to improve the electrical properties of powder by increasing oxygen vacancy and concentration of carrier. This reduction process affected the color of ITO powders. Finally dark green ITO powder was obtained.[20]

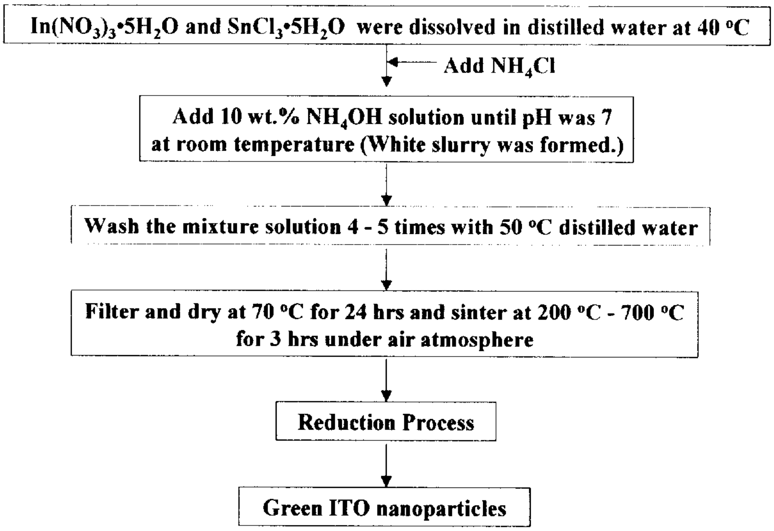


Figure 1. Schematic drawing of preparation of ITO nanoparticles by coprecipitation method

2-2-2. Preparation of water-based ITO sol solution

Water-based ITO sol solution was easily prepared by adding ITO nanopartilces to an aqueous solution containing different kinds of dispersing agents. As dispersing agents, EFKA 4330, NP 1050, BYK 190, polyacrylic acid-ammonium salt (PAA) and polyvinylpyrrolidone (PVP) were used. The constant amount of ITO powder (0.4 g) was added to an aqueous solution (5.0 mL) that included different amount of dispersing agents (0.004 g, 0.08 g, 0.24 g, 0.4 g, 0.8 g). The pH of the aqueous solution containing dispersing agents was adjusted with 0.1 M ammonium solution and 0.1 M hydrochloride acid solution. Ultrasonication was applied to these ITO sol solutions for 10 min. After the ultrasonication, ball mill (Shimadzu Vibrating Mill) was applied to the ITO sol solution for 10 min. Zirconium bead with 0.8 mm diameter was used as ball mill. The water-based ITO sol solutions with different pH (pH 3 - pH 10) were prepared.

2-2-3. Preparation of near IR-radiation reflective films

Near IR-radiation reflective films were prepared with the water-based ITO sol solution on slide glass by spin coating. The slide glass was stored in KOH (5 g) dissolved isopropyl alcohol solution (100 mL) for 3 hrs to have a hydrophilic surface and dried for 2 hrs at 50 °C before spin coating. ITO sol solution (0.03 mL) was spread on slide glass and rotation with 300 rpm was applied for ITO sol coating on the slide glass. The coated slide glass was dried for 3 hrs at 70 °C.

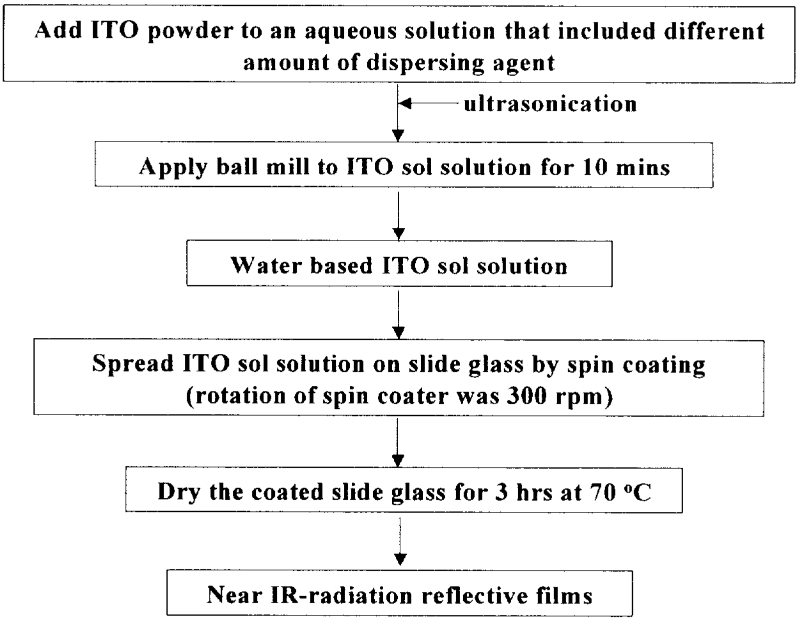


Figure 2. Schematic drawing of preparation of water-based ITO sol solution and near IR-radiation reflective films

2-2-4. Preparation of copolymer/ITO colloidal nanocomposites

1) Preparation of 4-vinylpyridine/styrene-ITO nanocomposite by using surfactant-free method

The 4-vinylpyridine/styrene-ITO colloidal nanocomposite were prepared by using surfactant-free method. The styrene (5 mL) and 4-vinylpyrine (1 mL) were added to 100 mL of an aqueous solution at approximately pH 10 containing either bare ITO nanoparticles or the water-based ITO sol solution in a two-necked round bottom flask with magnetic stirring. The mixture was purged with nitrogen and an aqueous solution of ammonium persulfate ($(NH_4)_2S_2O_8$) initiator (1 wt% based on monomer) was added to the mixture with magnetic stirring. The polymerization was performed for 24 hrs at 70 ^oC under nitrogen atmosphere.

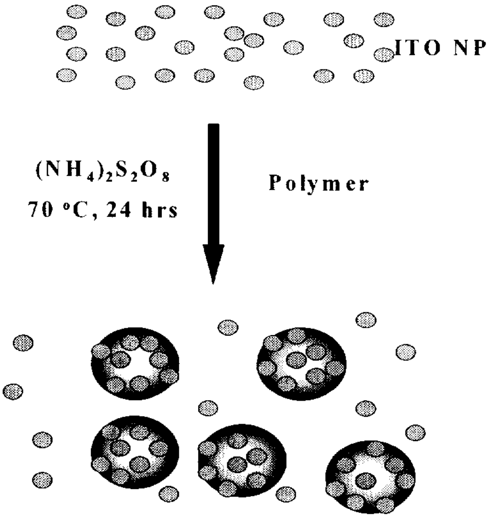


Figure 3. Schematic drawing of preparation of 4-vinylpyridine/styrene-ITO nanocomposite by using surfactant-free method

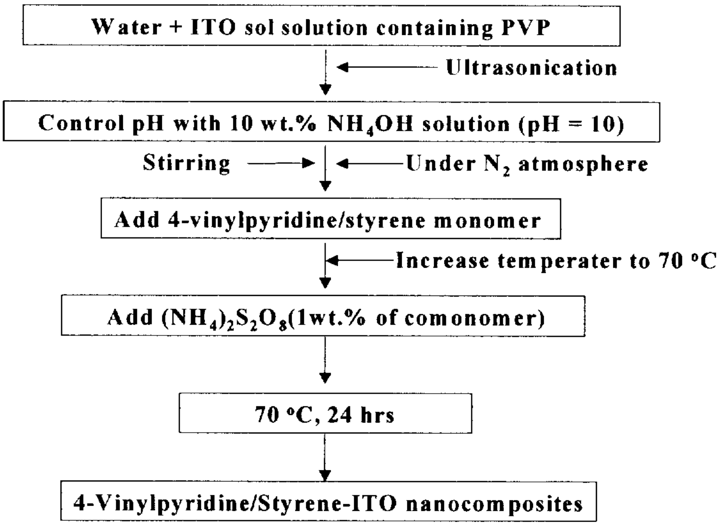


Figure 4. Schematic drawing of preparation of 4-vinylpyridine/styrene-ITO nanocomposite by using surfactant-free method

2) Preparation of 4-vinylpyridine/styrene-ITO nanocomposite by using surfactants

For the preparation of the copolymer-ITO colloidal nanocomposites, an oil phase consisting of styrene (2.6 mL), 4-vinylpyridine (0.51 mL) and hexadecane (0.16 mL) was mixed with the aqueous surfactant solution containing 0.03 g of surfactant as listed below. As surfactants, the anionic sodium dodecyl sulfate (SDS) and the cationic cetyltrimethylammonium bromide (CTMA-Br) were used. The role of hexadecane is to prevent the formation of rigid aggregates and improve the stability of the emulsion.[21-22] A 0.1 M ammonia solution or 0.1 M hydrochloride acid solution was added to the mixture to adjust pH of the solution. The distilled water used for preparing the aqueous surfactant solution was purged with nitrogen for 30 min before it was used for the aqueous surfactant solution. The mixtures were stirred for 1 hr under nitrogen atmosphere. The stated amount of either the water-based ITO sol solution or bare ITO nanoparticles were added to the mixture. The water-based ITO sol solution with pH 5 contains 8% ITO powder and 1.6% polyvinylpyrrolidone. The polymerization was started by increasing the temperature to 70 °C and then an aqueous solution of ammonium persulfate ($(NH_4)_2S_2O_8$) initiator (1 wt% based on monomer) was added. The reaction was carried out for 1 hr.

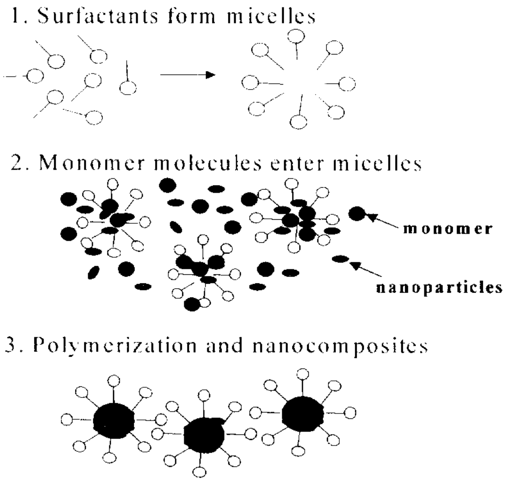


Figure 5. Schematic drawing of preparation of 4-vinylpyridine/styrene-ITO colloidal nanocomposite by using surfactants

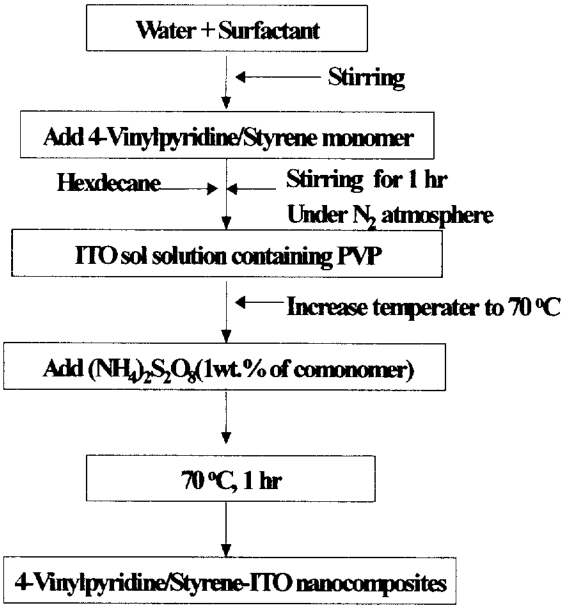


Figure 6. Schematic drawing of preparation of 4-vinylpyridine/styrene-ITO colloidal nanocomposite by using surfactants

2-3. Analysis

The crystal structure, morphology and chemical composition of the products were characterized with X-ray powder diffraction (XRD, Philips, X'Pert-MPD system), transmission electron microscope (TEM, Jeol Model JEM-2010), scanning electron microscope (SEM, Hitachi Model S-2400) and energy dispersive X- ray spectrometer (EDS, Hitachi Model, H-7500), respectively. Diffractional scanning calorimeter (DSC, Pyrisl Model Perkin Elmer.) was used to know the phase transition. Dispersibility of the water-based ITO sol solution was characterized with Zeta potential analyzer measurement (Brookhaven Instrument, USA). Near IR-radiation reflectance of ITO film was characterized with Near IR-spectrometer (Perkin Elmer, Spectrum GX).

3. Background

3-1. Nanoscience

The prefix "nano" originates from the Greek word for dwarf, and thus refers to something small. As a prefix for a unit of time or length, it means one billionth of that unit. Thus, a nanometer (nm) is 10^{-9} meter. The dot over this letter "i" is approximately one million nanometers in diameter. The fundamental building blocks of nature, atoms and molecules, have dimensions in the nanometer domain (i.e., the nanoscale). Many water molecules can easily occupy a sphere 1 nm in diameter. The DNA double helix is approximately 2 nm wide. The way molecules, for example, assemble into larger, superamolecular entities on the nanoscale determines important material properties (e.g., electrical, optical, and mechanical properties). Of course, it has long been recognized that nature performs this assembly very well in the creation of the sophisticated molecular machinery that supports our life on earth. In short, by controlling structure on the scale of ~ 1 - 100 nm, one can, in principle, ultimately design new materials with specific properties. Scientists have long imagined the possibility of manipulating individual atoms and molecules. Over the past 20 years, a variety of tools have been developed, the so-called scanning probe microscopes, that indeed make it possible not just to "see" individual atoms and molecules on the surfaces of materials (i.e., create images) but to move atoms and molecules on the nanoscale as well. Thus, we have a new paradigm by which science can be conducted. Competitive programs with this new perspective should, by definition be interdisciplinary, involving physics, chemistry, biology, medicine, and materials science, among other fields. Nanoscience is the study of phenomena on the scale of ~ 1 - 100 nm. Nanotechnology is the ability to create and control objects on this same scale with the goal of preparing novel materials that have specific properties and, thus, functions. Although current nanotechnology research is primarily exploratory, and it may take years to realize many of the goals envisioned, the prospect for significant applications is high.

3-2. Optical and electronic properties of indium tin oxide (ITO)

Indium tin oxide (ITO) is an n-type degenerate semiconductor and ITO thin films are widely used as infrared reflectors and transparent electrodes. The optical properties of ITO are a direct consequence of the position of the plasma frequency and the magnitude of the electronic scattering time as defined in the Drude free-electron model. ITO has an optical band gap of 3.6 eV with a plasma frequency in the near IR spectral region.[23]

The plasma frequency for ITO occurs in the near IR region, thus causing this material to be reflective in the mid IR region and transparent in the visible region. Therefore, the position of the plasma frequency is critical in determining the optical properties of the material. As a result of these properties, ITO is transparent in the visible and reflective in the infrared spectral regions. These properties allow ITO thin films to be used in a wide range of optical and electronic applications such as heat shielding materials and electrochemical sensors.[24]

ITO is also conductive which makes it an ideal material for a variety of applications. For instance, ITO thin films are used as panel displays, heat shields and electrodes. The electronic and optical properties of ITO are strongly dependent on the preparation and annealing procedures used in the production of thin films. For instance, the plasma frequency of ITO has been shown to be a function of sheet resistance.[24]

Unlike silicon, ITO is a degenerate semiconductor whose charge carrier density depends on high doping levels of Sn atoms. These calculations showed that small differences in the tin doping level alter the charge carrier concentration which strongly affect the electronic (conductivity) and optical (plasma frequency) properties of ITO. It is well-known that oxygen deficiencies contribute to the charge carrier density and the conductivity of conducting metal oxides.

3-3. Chemical reaction of indium tin oxide (ITO)

3-3-1. Preparation of indium tin hydroxide

Indium nitrate and tin chloride react with ammonium hydroxide to produce indium tin hydroxide particles by following mechanism.

$$In(NO_3)_3 + 3NH_4OH \longrightarrow In(OH)_3\downarrow + 3NH_4^+ + 3NO_3^-$$

$$SnCl_4 + 4NH_4OH \longrightarrow Sn(OH)_4\downarrow + 4NH_4^+ + 4Cl^-$$

Since indium salt and tin salt are present in the same aqueous phase, doping reaction takes place between indium hydroxide and tin hydroxide proportional to their compositions and indium tin hydroxide particles are precipitated as they are formed.

$$In(OH)_3{:}Sn(OH)_4\downarrow + 7NH_4 + 3NO_3^- + 4Cl^-$$

3-3-2. Calcination steps

In synthetic methods, the calcination step was indispensable for the following reasons:(1) The residual water and the residual organic compound such as the surfactant and solvent, had to be removed by evaporation in air in order to yield phase-pure oxide product. (2) The usually amorphous precipitate should be transformed to crystalline oxide at a high temperature. It is possible that sometimes the removal of impurities is incomplete at a low calcination temperature, while at a related high calcination temperature, the size of the particles obviously increases and agglomeration sometimes occurs, a phase transition takes place as well.[25]

1) Primary calcination

This primary calcination was carried out to yield oxide particles and remove impurities. Indium hydroxide particles doped with tin hydroxide are converted into indium tin oxide particles by calcination above 300 °C under air atmosphere.

$$In_{18}Sn_2(OH)_{2(31-X)} \longrightarrow In_{18}Sn_2O_{31-X} + (31-X)H_2O$$

2) Reduction process

Reduction process was carried out to improve the electrical properties of powder by increasing oxygen vacancy and concentration of carrier.

This secondary calcination under hydrogen atmosphere was accomplished at 250 °C and it produced oxygen vacancy. This reduction process affects the color of ITO powders. Yellow ITO powder was converted to dark green ITO powder.

$$In_{18}Sn_2O_{31-X} + yH_2 \longrightarrow In_{18}Sn_2O_{31-(x+y)} + yH_2O$$

3-4. Water based dispersion stability

One of the most important properties of water dispersions is their stability. It determines the system ability to keep its original properties during a long period. Dispersions are characterized by sedimentation and aggregation stabilities. Sedimentation stability is the system ability to maintain a uniform distribution of particles in the whole system volume. It depends on the intensity of the thermal motion of the molecules. The terrestrial gravitation field and the dispersion medium viscosity have an influence on that motion. Colloidal systems. especially liozolic ones, have particles with small sizes and a high sedimentation stability. Systems with large particles, e.g. suspensions or emulsions. are qualified as sedimentation unstable systems. The aggregation stability of colloidal systems is of great practical and theoretical importance. It means the particles do not form aggregates and keep their original size. Aggregation stability is determined by the surface or surface layer properties at the boundary of dispersed phase and medium. It is defined by the free surface energy or by the forces acting among the molecules within adsorbed films. Two methods describing the aggregation stability of dispersions are known: a thermodynamic one and another according to kinetics rules.[21] The thermodynamic method considers the heterogeneity and the dispersibility of the system as the reasons of aggregation. Instability is related to a high value of free surface energy. The decrease of surface energy means a more stable state for the system. It can be obtained by reduction of the particle area (flocculation and coagulation) or as a result of a decrease of the surface tension (e.g. adsorption of stabilizer at the interface). This provides stability to the particles and is a necessary condition for colloidal systems to exist. At present, considering the stability of dispersions from the thermodynamic point of view is a very debatable subject. There is no clear relationship between the stability of a dispersion and properties like surface tension. Indeed, the decrease of interfacial tension is not always related to an increase of the aggregation stability of the dispersion.[26] From the kinetics point of view, aggregation stability of colloidal systems is conditioned by the state of the films adsorbed on the surface of the particles and by the forces interacting among them. A colloidal system is static and the interactions of particle pairs cannot characterize the properties of the whole system. In that case, it is required to consider the coagulation phenomenon. Let us consider the nature of the forces acting between the particles. In principle, they can be divided into attractive and repelling forces. The particle attraction is conditioned by the van der Waals forces and three basic kinds of interactions are involved: orientation, induction and dispersion. The most universal ones are the dispersive forces. In the case of colloidal systems, they are especially important since their role is decisive in the coagulation of the particles. In the presence of adsorbed films, repulsive forces are acting simultaneously with attractions among colloidal particles. They have different character depending on the stabilizer type and properties. The surface-active agents of ionic character form an electrical double layer on the particle surface and when particles come close to each other they are repelled by electrostatic forces. The electrostatic repulsion forces and molecular attraction forces vary with distance in a different way. Therefore, there is a potential barrier in the interaction energy curve of two particles which determines the probability of an irreversible flocculation of the particles. First of all, the value of the potential barrier depends on the properties of the electrical double layer. The origin of the electrical double layer can be of two types: the ionization of molecules in a superficial layer of the solid particles or the adsorption at the surface of the solid particles of ions present in the dispersion medium. As the double layer is thicker, the repelling interaction of the particles is more intense and the probability of aggregation is smaller. Adsorbed films of surfactants can also be a source of entropic repulsion between particles due to the thermal motion of the molecular segments forming these films. This is especially the case with macromolecular compounds. Thus, the solvate-adsorptive films formed on the particle surface can be a mechanical-structural barrier impeding the particles to come too close to each other and protecting against aggregation. Formation of the electrical double layer is related to the adsorption of charges (e.g. ions) from the dispersion medium on the particles. As a result, a potential drop in the interphase appears. Ions move from the solution to the particle surface or from the particle surface to the solution depending on the ratio of their chemical potential. In both cases, the particle surface gets an overcharge which is compensated by the counter-ions and an electrical double layer appears at the surface. The first method is called the adsorption one and the second is called the dissociative one. An electric field, whose intensity is characterized by the potential, acts in the electrical double layer. The potential directly on the particle surface is called the thermodynamic potential. In the first part of the electrical double layer, ions are at a distance determined by their sizes. The second part of the electrical double layer is formed by the interaction of external forces (e.g. electrostatic forces). It is close to the surface of contact but does not always correspond to the distance of maximum proximity.

3-5. Properties of infrared radiation

Infrared radiation, electromagnetic radiation having a wavelength in the range from c.75 × 10^{-6} cm to c.100,000 × 10^{-6} cm. Infrared radiation thus occupy that part of the electromagnetic spectrum with a frequency less than that of visible light and greater than that of most radio waves, although there is some overlap. The name infrared means “below the red”, beyond the red, or lower-frequency (longer wavelength), end of the visible spectrum. "Near infrared" light is closest in wavelength to visible light and "far infrared" is closer to the microwave region of the electromagnetic spectrum. Infrared radiation is thermal, or heat radiation. In other words, we experience this type of infrared radiation every day in the form of heat.

The heat that we feel from sunlight, a fire, a radiator or a warm sidewalk is infrared. It was first discovered in 1800 by Sir William Herschel, who was attempting to determine the part of the visible spectrum with the minimum associated heat in connection with astronomical observations he was making. In 1847, A. H. L. Fizeau and J. B. L. Foucault showed that infrared radiation has the same properties as visible light, being reflected, refracted, and capable of forming an interference pattern. Infrared radiation is typically produced by objects whose temperature is above 10 K.

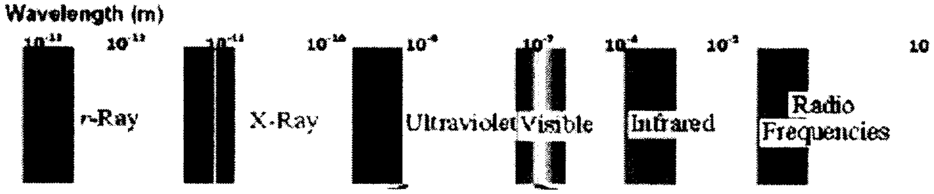


Figure 7. Classification electromagnetic radiation

3-6. Emulsion polymerization

What follows is a description of a typical emulsion polymerization. A typical conventional emulsion polymerization recipe will consist of water, surfactant, monomer and initiator. Water serves as both a transport and heat transfer medium. An surfactant is a hydrocarbon chain with one end being hydrophobic and the other, hydrophilic. If the concentration of surfactant is high enough, the hydrophobic ends of several surfactants (usually about 50 to 100) form aggregates known as micelles. The surfactant serves as a stabilizer for polymer particles and monomer droplets. That is, the hydrophobic ends will attach to the particles while the hydrophilic ends will remain in the water phase. The charges on these surfactants form what is known as an electrical double layer which prevents the particles from coagulating. In other words, the serves to keep the particles suspended in the water. The micelles can also be the location of particle nucleation. Monomer is present in the reaction in the form of large droplets. These droplets act as a reservoir of monomer. The monomer in the droplets diffuses through the water phase and into the micelles due to thermodynamic reasons. Initiator is added to the reaction mixture and dissociates into two radicals in the presence of heat. The initiator radicals are extremely reactive and readily react with any monomer in the water phase. The monomer in the water phase continues to add to the radical until the chain grows long enough such that its solubility in water is exceeded. The oligomeric radical chain (multiple monomeric units) is now hydrophobic enough to enter a polymer particle or enter a micelle to nucleate a new particle. This is known as micellar nucleation. Another form of nucleation, homogeneous nucleation, can occur but is not included in our animation. Thus, the conventional emulsion polymerization will occur in three stages. The first stage involves the nucleation (birth) of polymer particles. This can occur by either micellar or homogeneous nucleation (the latter mode is not included in our animation). The second stage involves the growth of the particles until the monomer droplets disappear. The third and final stage begins with the disappearance of the monomer droplets and continues until the end of the reaction.

Nowadays, we know at least three different groups of emulsion polymerization techniques, namely the macro-, mini- and microemulsion polymerization.[22] Macroemulsion polymerization was conventional emulsion, which is described above. In the macroemulsion polymerization one starts from large monomer droplets and surfactant micelles in the water phase. During the polymerization, the monomer diffuses through the water phase and particles with a diameter of usually larger than 500 nm are formed. Due to the increase of the interfacial area, the surface tension of a lates increases with polymerization. In miniemulsion polymerization, relatively stable oil droplets with interfacial tensions larger than zero and droplet sizes within a size range of 50 nm to 500 nm are prepared by shearing a system containing oil, water, surfactant and a water insoluble hydrophobe. Theses minidroplets can be polymerized to polymer latex particles, ideally in a 1:1 copying process. The identity of the monomer droplets before and the particles after the polymerization was recently shown by a combination of SANS, surface tension measurements and conductometry. The diffusion of monomer through the water phase is suppressed by addition of a hydrophobe to the monomer phase. Due to a constant low coverage of the droplets and particles with surfactant, the surface tension remains constantly high. Depending on the choice of the surfactants, particles with an anionic, cationic or nonioinc surface can be polymerized.

The third type of emulsions are the microemulsions. They are thermodynamically stable with an interfacial tension at the oil/water interface close to zero. The high amount of surfactant which is required for the preparation leads to complete coverage of the particles and therefore the surface tension of the microemulsion reaches the minimum value. During the polymerization, the particle size increases and results in latexes of 5 to 50 nm in coexistence with empty micelles.

4. Results and Discussion

4-1. Characterization of ITO nanoparticles

4-1-1. The phase transition of ITO nanoparticles

Figure 8 shows the DSC spectrum of the particles prepared by chemical coprecipitation method. Indium-tin hydroxide particles were converted to ITO by releasing water molecules from them as temperature was increased. The spectrum started to change from 250 ^{0}C and the peak was shown at 274.5 ^{0}C. It indicates that indium-tin hydroxide begins to change to ITO at 250 ^{0}C and indium-tin hydroxide completely changes to ITO at 274.5 ^{0}C.

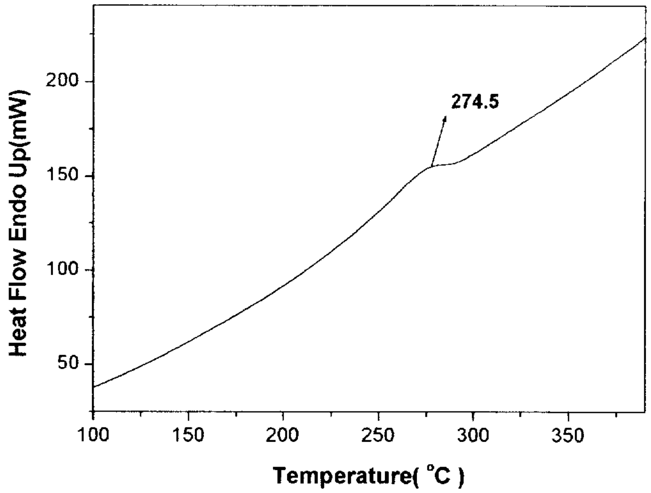


Figure 8. DSC spectrum of indium-tin hydroxide nanoparticles

4-1-2. The chemical structure and composition of ITO nanoparticles

The chemical structure and composition of ITO nanoparticles were characterized with XRD and EDS. XRD technique can be used for determination of the chemical structure of crystalline materials and identification of any crystalline material. Using XRD, a diffraction pattern is produced for each crystalline sample. This diffraction pattern is unique for each and every crystalline material, like a finger-print.

Figure 9 shows the XRD spectra of particles. Indium oxide crystal peaks were not observed in the XRD spectra of particles prepared at a room temperature and annealed at 200 ^{o}C. Indium oxide crystal peaks were shown in the XRD spectra of particles prepared at the temperature above 300 ^{o}C. The crystalline peaks in the XRD data of particles annealed at 300 ^{o}C, 500 ^{o}C and 700 ^{o}C well matched with the diffraction data of cubic indium oxide from the JCPDS card No 74-1990. The number (222), (400), (440) and (622) in the XRD spectrum correspond to the (hkl) values of the genuine indium oxide crystal. It shows that the particles annealed below 300 ^{o}C appear as indium hydroxide and the particles annealed above 300 ^{o}C appear as indium oxide.

The chemical composition of particles was analyzed with EDS. Elemental analysis is achieved by collecting the X-rays generated when the incident electron beam interacts with the atoms of the sample. Each element in the sample produces X-rays with characteristic energies whose peak intensities are related to the amount of the elements present. The energies of these X-ray photons are converted into electrical signals in a Si (Li) detector and are processed to produce an intensity spectrum in counts per second.

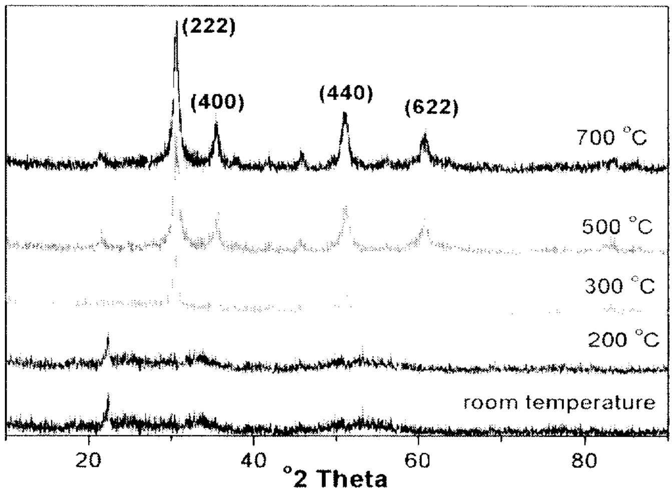


Figure 9. XRD spectra of ITO nanoparticles annealed under air atmosphere

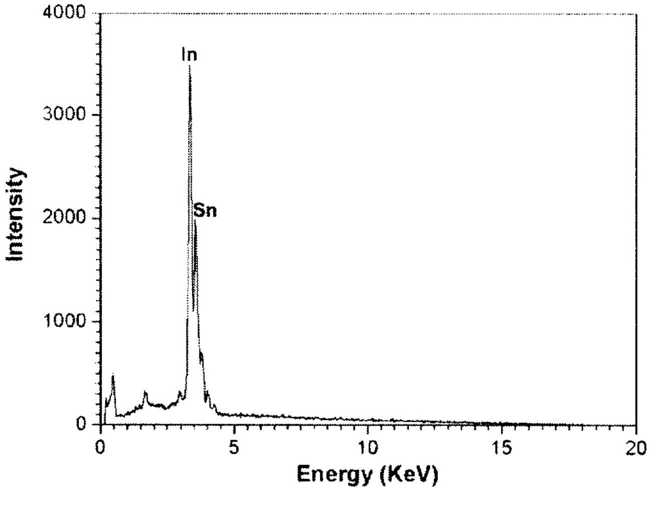


Figure 10. EDS spectrum of ITO nanoparticles annealed at 700 °C under air atmosphere

Figure 10 shows the EDS spectrum of ITO nanoparticles annealed at 700 ^{o}C. It was observed that In L_{a1} (3.2 KeV) peak and Sn L_{a1} (3.4 KeV) peak appeared. It indicates the presence of indium and tin elements in the products. It was found that the atomic ratio of indium to tin was 9 : 1. At this ratio, generally ITO nanoparticles have the highest conductivity.[12] XRD and EDS data showed that ITO nanoparticles with In : Sn = 9 : 1 (at. molar%) were well prepared.

4-1-3. The morphology of ITO nanoparticles

The morphology and size of ITO nanoparticles were characterized with transmission electron microscopy (TEM). Material for TEM must be specially prepared to obtain the thicknesses which allow electrons to transmit through the sample, much like light is transmitted through materials in conventional optical microscopy. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEM can reveal the finest details of internal structure in some cases as small as individual atoms. Samples were prepared by evaporation of the colloidal solution onto a 400 mesh Cu grid.

Figure 11 shows the TEM image of indium-tin hydroxide nanoparticles. The indium-tin hydroxide in this TEM image has a amorphous shape.

Figure 12 (a) and (b) show the TEM images of ITO nanoparticles annealed at 300 ^{o}C and 700 ^{o}C. By Figure 12 (a), ITO nanoparticles didn't have a typical shape and were much aggregated. As annealing temperature increased, the shape of particles was spherical. By Figure 12 (b), the shape of ITO nanoparticles was almost spherical and the diameter of particles was about 15 - 25 nm. However ITO particles were not well dispersed.

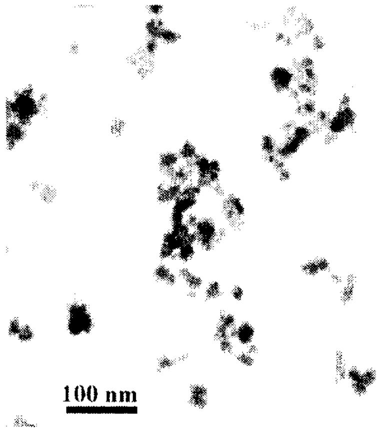
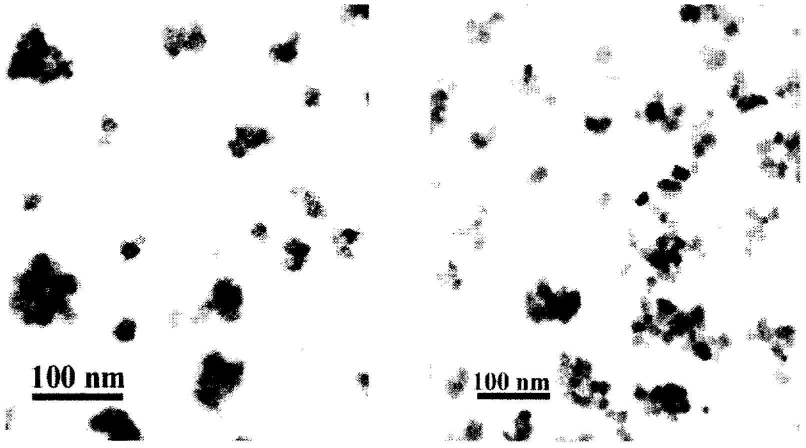


Figure 11. TEM image of indium-tin hydroxide nanoparticles



(a) (b)

Figure 12. TEM images of ITO nanoparticles: annealed at 300 °C (a) and annealed at 700 °C (b) under air atmosphere

4-1-4. Reduction process

Reduction process was carried out to improve the electrical properties of powder by increasing oxygen vacancy and concentration of carrier. This reduction process was accomplished at 250 °C and it produced oxygen vacancy. Figure 13 shows XRD spectra of ITO nanoparticles annealed at 700 °C under air atmosphere and then annealed at 250 °C under hydrogen atmosphere according to different annealing time (10 min., 30 min. and 50 min.). The crystalline peaks in the XRD data are well matched with the diffraction data of cubic indium oxide from the JCPDS card No 74-1990. The intensity is not much different according to annealing time.

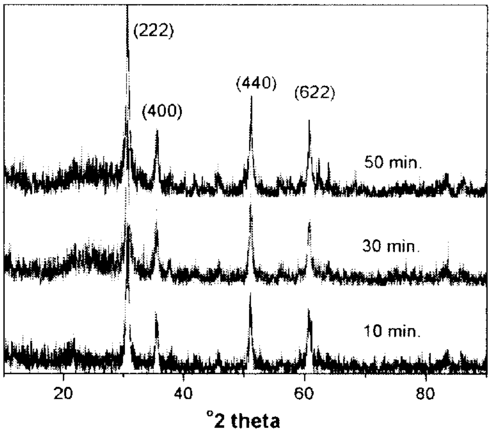


Figure 13. XRD spectra of ITO nanoparticles annealed at 700 °C under air atmosphere and then annealed at 250 °C under hydrogen atmosphere according to annealing time.

Figure 14 shows EDS spectrum of ITO nanoparticles after reduction process. In $L_{\alpha 1}$ (3.2 KeV) peak and Sn $L_{\alpha 1}$ (3.4 KeV) peak were observed and the atomic ratio of indium to tin was 9 : 1.

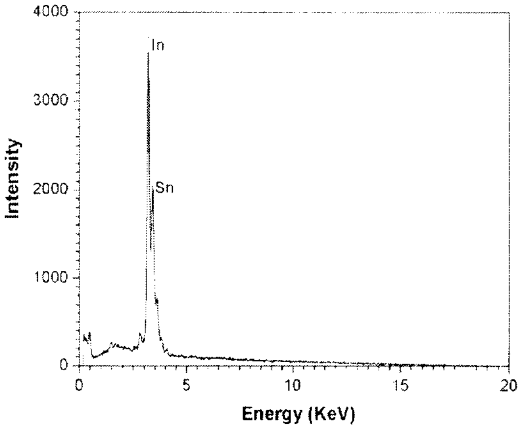


Figure 14. EDS spectrum of ITO nanoparticles annealed at 700 °C under air atmosphere and then annealing at 250 °C for 50 min under hydrogen atmosphere.

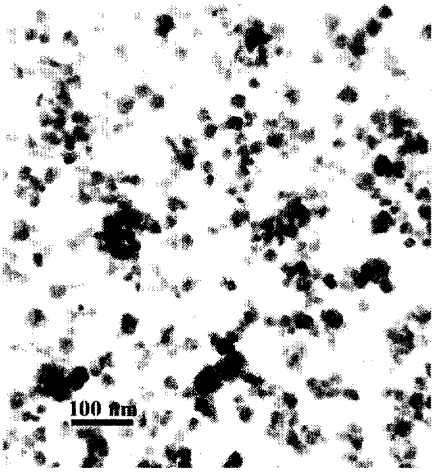


Figure 15. TEM images of ITO nanoparticles annealed at 700 °C under air atmosphere and then annealed at 250 °C for 50 min under hydrogen atmosphere

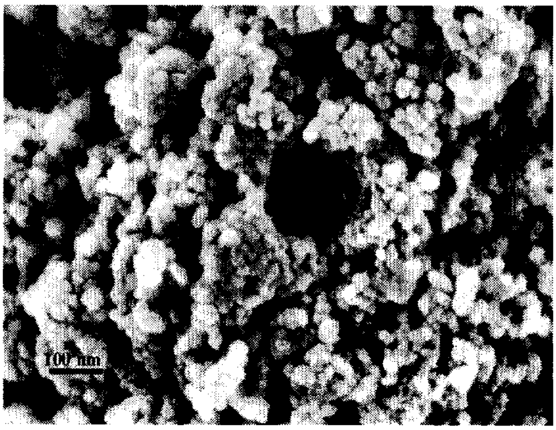


Figure 16. FE-SEM image of ITO nanoparticle annealed at 700 °C under air atmosphere and then annealed at 250 °C for 50 min under hydrogen atmosphere

Figure 15 shows TEM image of ITO nanoparticles after reduction process. Figure 16 shows field-emission scanning electron microscopy (FE-SEM) image of ITO nanoparticles after reduction process. A FE-SEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer (= billion of a millimeter). In the both Figures, the shape and diameter of particles is almost the same as that of ITO nanoparticles in Figure 12 (b). The ITO nanoparticles in these images were not well dispersed as other nano-sized particles. However it is imperative to have well dispersed ITO nanoparticles in an aqueous sol solution for application such as near IR-radiation reflective film.

4-2. Dispersibility of water-based ITO sol solution

4-2-1. Zeta potential

The dispersibility of ITO nanoaprticles at different weight percent of dispersing agents and at different pH of the sol solution was investigated by measuring the zeta potential of the water-based ITO sol solution. Figure 18 shows the zeta potential vs. the weight ratio of dispersing agents : ITO. Polyvinylpyrrolidone (PVP), polyacrlic acid (PAA), EFKA 4330, BYK 190 and NP 1050 were used as dispersing agent for preparing the water-based ITO sol solution. When PVP, NP 1050 and EFKA 4330 were used as dispersing agents, the absolute value of zeta potential was 38 mV, 39 mV and 36 mV, respectively. In case of using PAA and BYK 190 as dispersing agents, the absolute value of zeta potential was 21 mV and 12 mV. In general the higher the absolute value of zeta potential is, the stronger repulsive force is and the better dispersibility of sol solution is.[27] Figure 17 shows that dispersion of the solution is good enough when the absolute value of zeta potential is over 30 mV.[28] The absolute value of zeta potential was higher than 30 mV when PVP, NP 1050 and EFKA 4330 were used. Of the three dispersing agents, the absolute value of zeta potential of PVP and NP 1050 was the highest and the weight ratios of PVP : ITO and NP 1050 : ITO were 0.2 : 1 and 1 : 1 at the points, respectively. The absolute value of zeta potential was lower than 30 mV in case PAA and BYK 190 were used as dispersing agents. Therefore the water-based ITO sol solutions include PVP and NP 1050 as dispersing agents have the best dispersibility. In general, the dispersion of ceramic powder in solution can be improved when the absolute value of the zeta potential is increased after an addition of dispersing agent.[26-27] Figure 19 shows the zeta potential vs. pH of sol solutions. These ITO sol solutions had different value of pH with the same amount of dispersing agents. In case of PVP, the ITO sol solution with the weight ratio of PVP : ITO =

0.2 : 1 was used. In case of NP 1050, the weight ratio of NP 1050 : ITO of the sol solution was 1 : 1. In both cases, the water based ITO sol solution had the best dispersibility when the value of pH was 3 - 5.

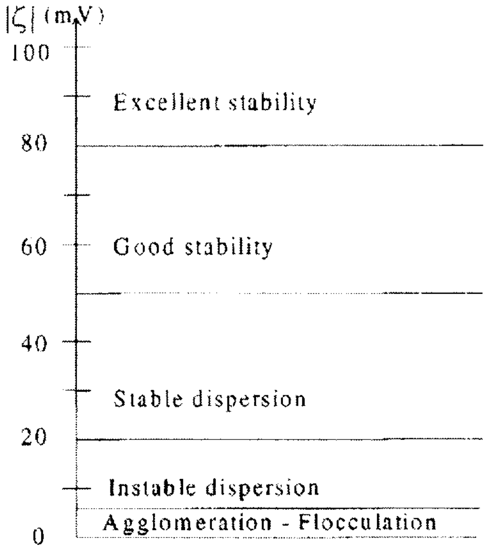


Figure 17. Slurry stability versus zeta potential.

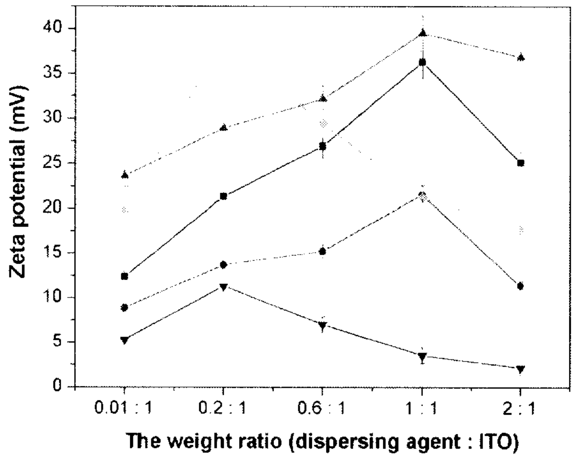


Figure 18. Zeta potential versus the weight ratio of DA : ITO nanoparticles according to dispersing agents (DA):

◆ : polyvinylpyrrolidone, ▲ : NP 1050, ■ : EFKA 4330,
● : BYK 190 and ▼ : polyacrylic acid

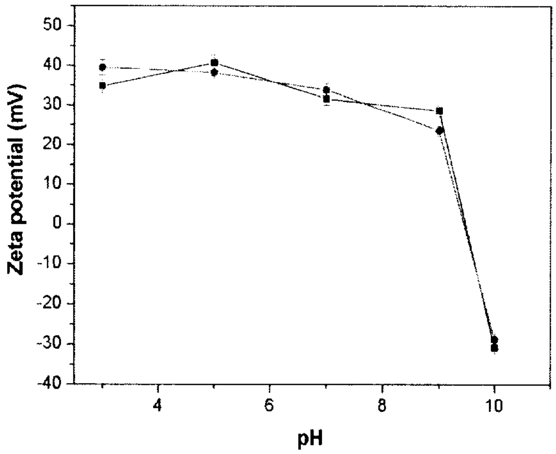


Figure 19. Zeta potential versus pH of the water based ITO sol solution:

● : polyvinylpyrrolidone, ■ : NP 1050

4-2-2. Change of turbidity

Dispersibility of the water-based ITO sol solution was characterized with the change of turbidity. Turbidity is the cloudiness of water and dispersibility of the water based ITO sol solution is known by measuring initial slopes of turbidity versus time.[29] The better the dispersibility of the water-based ITO sol solution is, the smaller the change of turbidity is and therefore the gentler the initial slope is.[29] In this study the change of turbidity of the water-based ITO sol solution was investigated according to various kinds of dispersing agents and amount of dispersing agent.

Figure 20 shows initial slopes of turbidity versus time of water-based ITO sol solution containing various kinds of dispersing agents and Table 1 shows initial slopes of water-based ITO sol solution containing different kinds of dispersing agents. From Figure 20 and Table 1, when NP 1050 and PVP were used as dispersing agents the absolute value of initial slopes is 0.51 and 0.6, respectively. The value is smaller than that of EFKA 4330, BYK 190 and PAA. It indicates that the change of turbidity is small and therefore the water based ITO sol solutions containing NP 1050 and PVP have good dispersibility. This result corresponds with the result from zeta potential analysis. Figure 21 and Figure 22 show initial slopes of turbidity versus time according to different amount of NP 1050 and PVP. Table 2 shows initial slopes of turbidity versus time according to different amount of NP 1050 and PVP. In case of NP 1050, when the weight ratio of NP 1050 to ITO was 1 : 1 the initial slope was the smallest and the dispersibility was the best. In case of PVP, when the weight ratio of PVP to ITO was 0.2 : 1 the initial slope was the smallest and the dispersibility was the best.

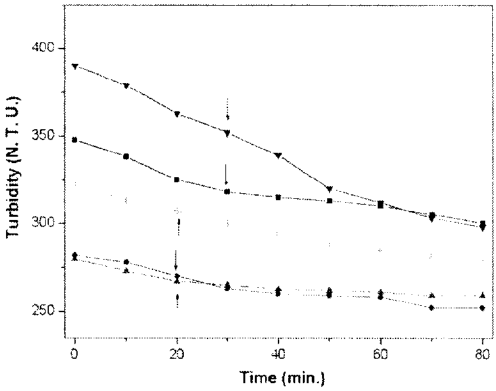


Figure 20. Initial slopes of turbidity versus time of water based ITO sol solution containing different kinds of dispersing agents:

▼ - polyacrylic acid, ■ - BYK 190, ◆ - EFKA 4330,
● - NP 1050, ▲ - polyvinylpyrrolidone

Dispersing agent	EFKA 4330	BYK 190	NP 1050	PVP	PAA
Initial slope	-0.8	-1.03	-0.51	-0.6	-1.26

Table 1. Initial slopes of water based ITO sol solution containing different kinds of dispersing agents

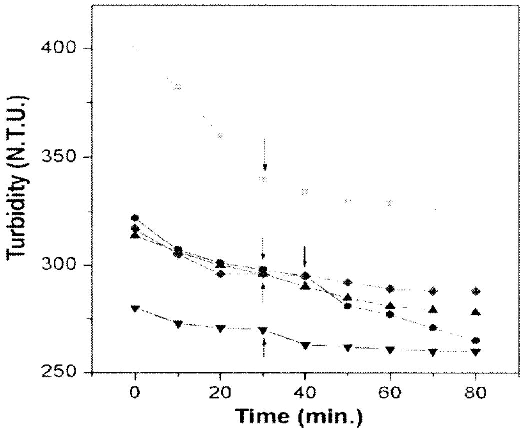


Figure 21. Initial slopes of turbidity versus time according to different amount of dispersing agent in case of NP 1050:
■ NP 1050 : ITO (0.01 : 1), ● NP 1050 : ITO (0.2 : 1),
◆ NP 1050 : ITO (2 : 1), ▲ NP 1050 : ITO (0.6 : 1), ▼ NP 1050 : ITO (1 : 1)

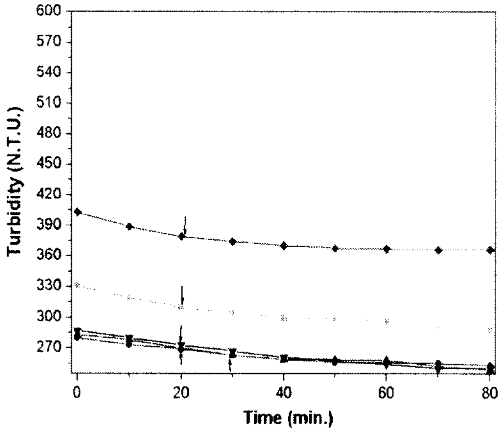


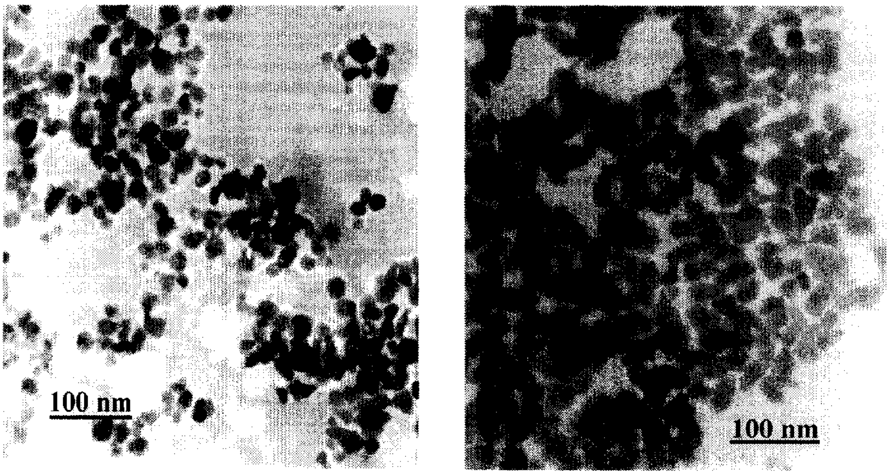
Figure 22. Initial slopes of turbidity versus time according to different amount of dispersing agent in case of PVP:
◆ PVP : ITO (2 : 1), ■ PVP : ITO (0.01 : 1), ▼ PVP : ITO (1 : 1),
▲ PVP : ITO (0.6 : 1), ● PVP : ITO (0.2 : 1)

DA:ITO (wt.%) Dispersing agents (DA)	0.01 : 1	0.2 : 1	0.6 : 1	1 : 1	2 : 1
NP 1050	−2.02	−0.63	−0.6	−0.32	−0.53
PVP	−1.05	−0.55	−0.65	−0.7	−1.2

Table 2. Initial slopes of turbidity versus time according to different amount of NP 1050 and PVP

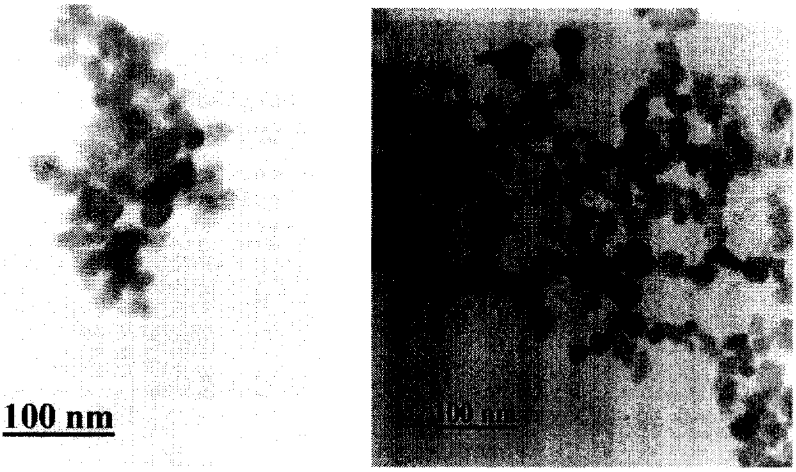
4-2-3. Transmission electron microscopy (TEM)

The dispersibility of the ITO sol solution was also confirmed by TEM images. Figure 23 (a) and (b) show TEM images of the water-based ITO sol solution including EFKA 4330 and BYK 190 as dispersing agents. Figure 24 (a) and (b) show TEM images of the water- based ITO sol solution including PAA and NP 1050 as dispersing agents. Figure 25 (a) is the TEM image of the water-based ITO sol solution including PVP and Figure 25 (b) is the HR-TEM image of that. By Figure 23 (b) and Figure 24 (a), much aggregation of the particles was observed when BYK 190 and PAA were used as dispersing agent. On the other hand the dispersibility of the water based ITO sol solution was quite good when EFKA 4330, PVP and NP 1050 were used as dispersing agents. This results from zeta potential analysis and turbidity analysis. Especially PVP is a good diapersing agents of the ITO sol solution. Figure 25 (a) and Figure 15 showed the diameter of particles was determined as about 15 - 33 nm. Dispersibility of ITO nanoparticles was better in Figure 25 (a) than that in Figure 15 and the aggregation of ITO nanoparticles was seen in Figure 15. Those mean dispersion of nanoparticles related to the role of the dispersing agent. A few reports introduce the preparation of ITO powder by emulsion technique or coprecipitation method.[2-3] However ITO nanoparticles prepared by both methods were not well dispersed despite use of surfactant and the size of those was much large as about 45 - 75 nm.[4-5] In this work, PVP was used to improve dispersibility of ITO nanoparticles in an aqueous solution. The image in upper side of Figure 25 (a) was enlarged image of ITO particle. It was observed that PVP was continuously coated on the particle surface in the images of Figure 25 (a). TEM image was measured after staining of the sample with uranyl acetate (2%) to observe organic polymer such as PVP. According to TEM image, it was known that the addition of dispersing agent such as PVP gave good dispersibility of particles by coating on the particle surface. Figure 25 (b) shows high-resolution TEM (HR-TEM) image of ITO nanoparticles. In Figure 25 (b), indium oxide lattice spacing of 2.92 Å was consistent with the lattice spacing of (222) plane in the XRD spectrum of indium oxide crystal. The existence of lattice planes on the HR-TEM image means the crystalline of indium oxide. From both Figure 25 (a) and (b), it was known that the particle was indium tin oxide particle and PVP was coated on the surface of ITO particles. The thickness of PVP coated on the surface was estimated as about 6 - 7 nm. In general, polymer coating on the surface of particles makes steric repulsive force by positive surface charge increase and results in an improved dispersibility of particles.[24-25] PVP coating on the surface of ITO particles improved the dispersibility of ITO particles in an aqueous solution.



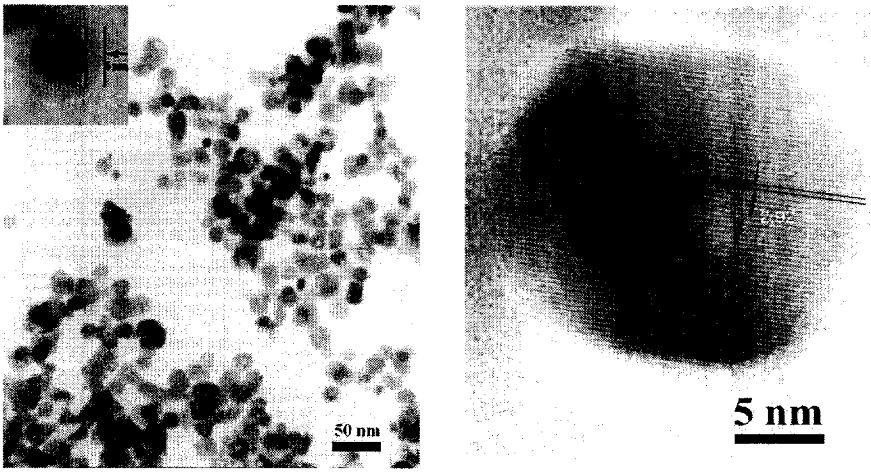
(a) (b)

Figure 23. TEM images of the water-based ITO sol solution include EFKA 4330 (a) and BYK 190 (b) as dispersing agent



(a) (b)

Figure 24. TEM images of the water-based ITO sol solution include polyacrylic acid (a) and NP 1050 (b) as dispersing agent

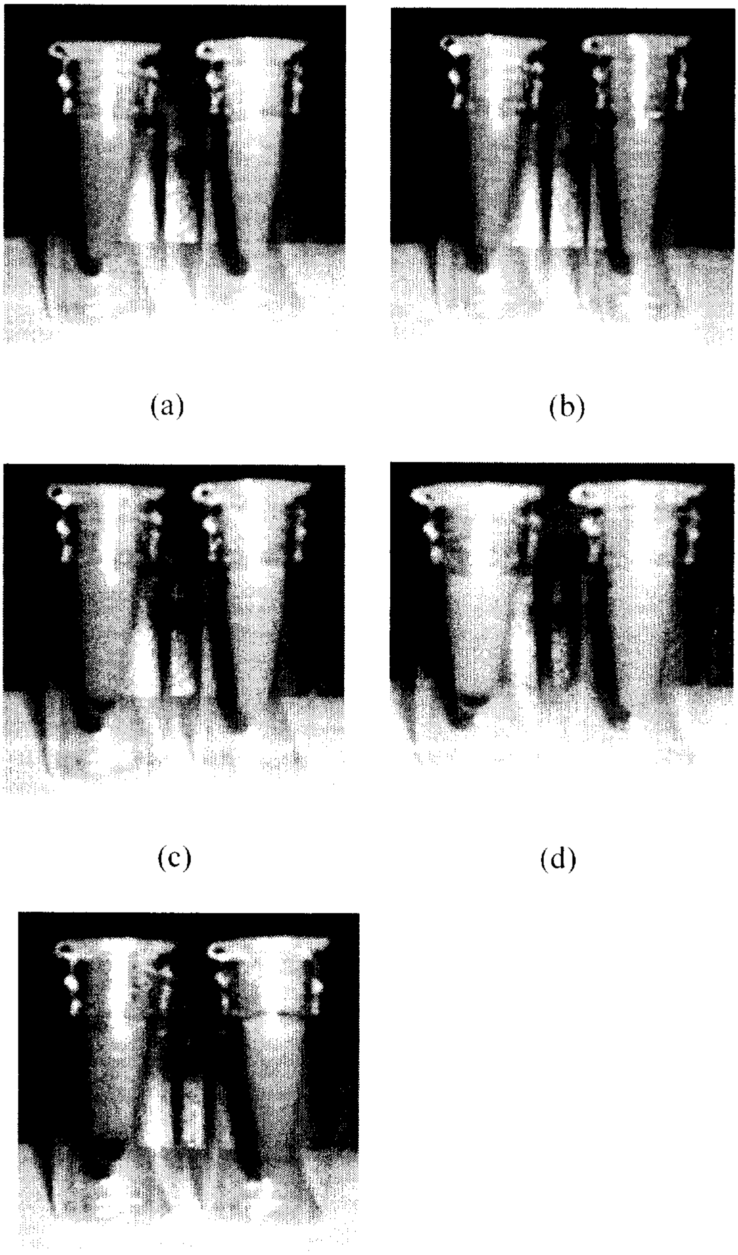


(a) (b)

Figure 25. TEM image of the water-based ITO sol solution include polyvinylpyrrolidone (a) and HR-TEM image of it (b)

4-2-4. Stability of the water-based ITO sol solution

The duration of the stability of the water-based ITO sol solution was investigated by following Figure 26. The Figure 26 shows sedimentation of ITO powder in an aqueous solution as time goes. In the Figure 26, left side one is the ITO sol solution without a diapersing agent and right side one is the water-based ITO sol solution with PVP as a dispersing agent. The every condition was the same in the both cases except for using a dispersing agent. There was a certain difference between two ITO sol solutions in sedimentation rate. The sedimentation was observed in left side one after 5 hrs and there was a certain difference after 15 days while any sedimentation was not observed in right side one. According to this result, the duration of the stability of the water based ITO sol solution was over 20 days.



(a) (b)

(c) (d)

(f)

Figure 26. Stability of the water based ITO sol solution:
right after starting (a), after 10 min (b), after 5 hrs (c), after 7 days (d) and 15 days (e)

4-3. Near IR-radiation reflective film

Figure 27 shows near IR-radiation (NIR) transmission spectra of slide glass and ITO film. Curve A shows NIR transmission spectrum of slide glass and curve B shows NIR transmission spectrum of ITO film prepared with the water-based ITO sol solution. According to curve A spectrum, slide glass had NIR transmission more than 90% in the range from 850 nm to 3500 nm and it means that slide glass cannot reflect NIR-radiation. From curve B spectrum, NIR reflectance of ITO film was over 90% in the range above 1500 nm. Therefore, ITO film had good NIR-radiation reflectance. In the previous work, NIR reflectance of ITO film was only 60% at 1500 nm. The NIR-radiation reflective film prepared in this study has better NIR reflectance.

Figure 28 shows the cross-sectional view of ITO film. The cross-sectional view was characterized with SEM. According to the SEM image in Figure 28, the thickness of the film was determined as 390 nm.

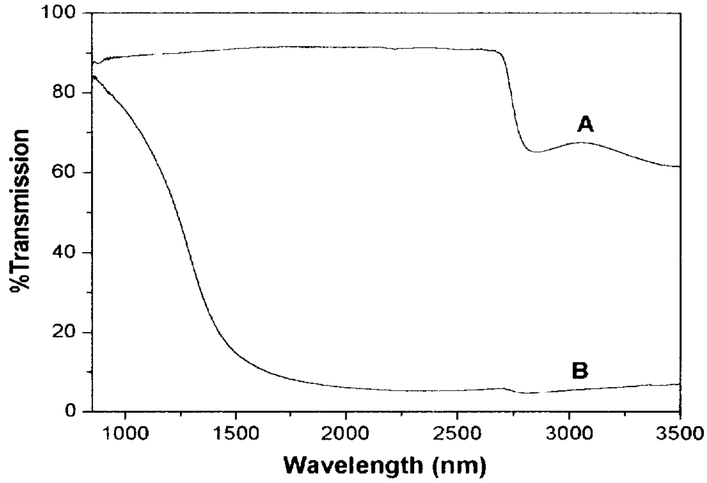


Figure 27. Near IR-radiation transmission spectrum of ITO film: slide glass A, ITO film B

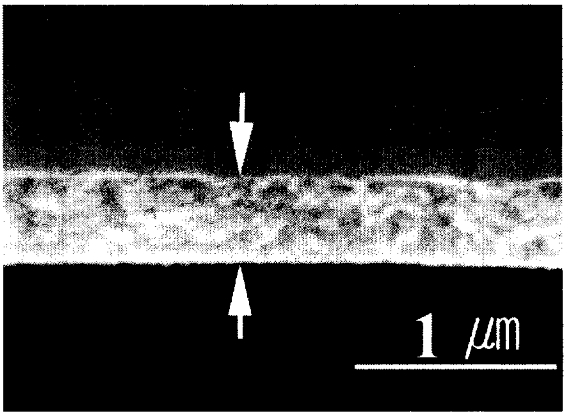


Figure 28. SEM image of ITO film

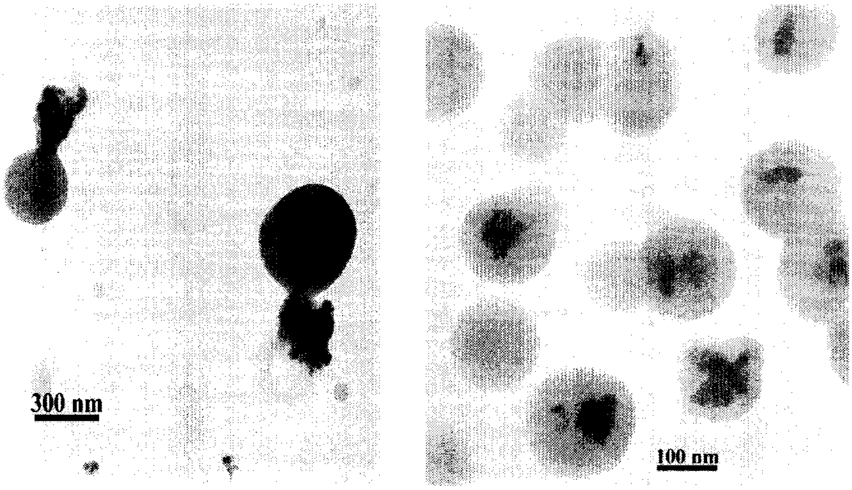
4-4. 4-Vinylpyridine/styrene-ITO colloidal nanocomposite

4-4-1. 4-Vinylpyridine/styrene-ITO colloidal nanocomposite by using surfactant-free method

The aim of this work was to prepare stable 4-vinylpyridine/styrene-ITO colloidal nanocomposite by a "surfactant free" route.[18,30] Copolymer of 4-vinylpyridine/styrene was used for preparing this nanocomposite because it was difficult to form polymer-ITO nanocomposites with only styrene. 4-Vinylpyridine was selected for two reasons. First, since the surface of well dispersed ITO sol solution is acidic, it seems that using a basic monomer would lead to acid-base interaction. Second, the ideal vinyl monomer is water soluble but poly(4-vinylpyridine) is water-insoluble in neutral and basic media. This is necessary in order to coat and bind the ITO nanoparticles together and form stable colloidal nanocomposite.[30]

A set of two nanocomposite preparations were carried out in order to examine the effect of PVP coated on the surface of ITO nanoparticles on the preparation of 4-vinylpyridine/styrene-ITO colloidal nanocomposite. Of the two nanocomposite preparations, one was carried out with bare ITO nanoparticles and the other was carried out with the water-based ITO sol solution containing PVP for preparing 4-vinylpyridine/styrene-ITO colloidal nanocomposite. Each of the two cases produced stable colloidal dispersion but 4-vinylpyridine/styrene-ITO nanocomposites were formed only in case of using the water-based ITO sol solution. TEM was used to investigate the morphology of the nanocomposite and confirmation of the formation of that.

Figure 29 (a) shows TEM image of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by using bare ITO nanoparticles. In Figure 29 (a), ITO nanoparticles could not enter the polymer of 4-vinylpyridine/styrene and therefore 4-vinylpyridine/styrene-ITO nanocomposites was not formed. Figure 29 (b) shows TEM image of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by using the water-based ITO sol solution. In this Figure, the formation of 4-vinylpyridine/styrene-ITO colloidal nanocomposites was observed and the diameter of those was 130 - 160 nm. 4-Vinylpyridine/styrene contained ITO nanoparticles within the polymer but only some parts of copolymer had ITO nanoparticles and the ITO nanoparticles in the polymer were much aggregated.



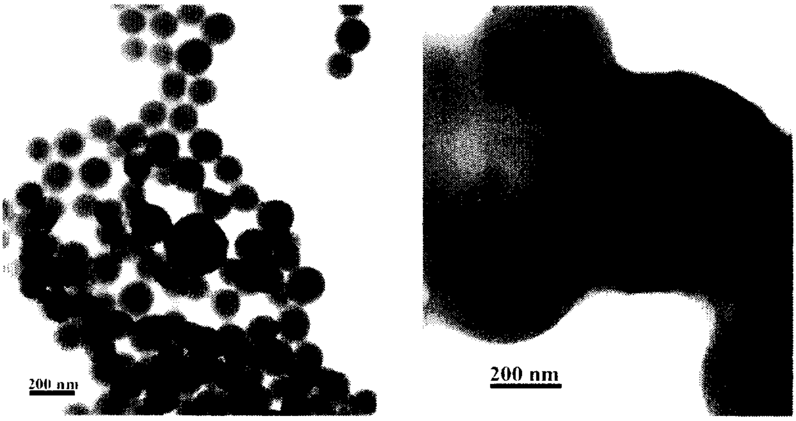
(a) (b)

Figure 29. TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by using bare ITO nanoparticles (a) and the water-based ITO sol solution containing PVP (b)

4-4-2. 4-Vinylpyridine/styrene-ITO colloidal nanocomposite by using surfactants

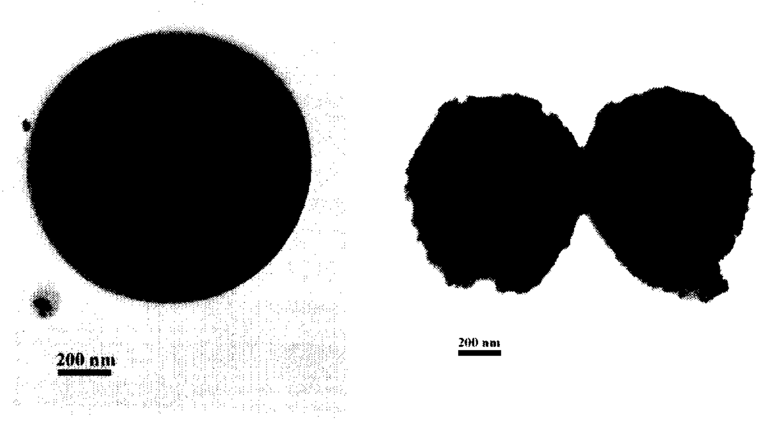
In this work 4-vinylpyridine/styrene-ITO colloidal nanocomposite was prepared by using surfactants. The efficiency of anionic and cationic surfactants and the effect of the amount of surfactant were investigated. 4-Vinylpyridine/styrene-ITO colloidal nanocomposites were prepared by using anionic and cationic surfactants. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTMA-Br) were used as anionic and cationic surfactants, respectively. Figure 30 (a) and (b) show TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by SDS at pH = 3 and pH = 10, respectively. Figure 31 (a) and (b) show TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by CTMA-Br at pH = 3 and pH = 10, respectively. When the SDS was used as the surfactant, there is only a few ITO nanoparticles on the surface of the 4-vinylpyridine/styrene particles at pH = 10. On the contrary, in case of CTMA-Br the formation of 4-vinylpyridine/styrene-ITO nanoparticles was observed at pH = 10. These result from interaction between surfactants and ITO nanoparticles. In case of SDS, repulsive force between anionic SDS and ITO nanoparticles prevents formation of nanocomposites.[31] However in case of CTMA-Br, charge coupling and induced dipole interaction between cationic CTMA-Br and ITO nanoparticles help ITO nanoparticles attach copolymer.[31]

At pH = 3, when the SDS was used as the surfactant, only copolymer of 4-vinylpyridine/styrene was formed rather than the desired 4-vinylpyridine/ styrene nanocomposites. In case of CTMA-Br, 4-vinylpyridine/styrene-ITO nanocomposites were formed in some part of sample but free ITO nanoparticles were observed. The reason why alkaline condition (pH = 10) is better for the formation of nanocomposites is related to use of 4-vinylpyridine. 4-vinylpyridine can provide a strong acid-base interaction with ITO nanoparticles at that alkaline condition and the acid-base interaction gives additional stability during emulsion polymerization.[31] According to this, it was known that it is necessary to find the adequate type of surfactant to prepare 4-vinylpyridine/styrene-ITO colloidal nanocomposites.



(a) (b)

Figure 30. TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by SDS at pH = 3 (a) and pH = 10 (b)



(a) (b)

Figure 31. TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared by CTMA-Br at pH = 3 (a) and pH = 10 (b)

Figure 32 shows TEM image of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared with CTMA-Br at pH = 10 by using bare ITO nanoparticles. When the bare ITO nanoparticles were used, 4-vinylpyridine /styrene contained a few ITO nanoparticles but free ITO nanoparticles were observed beside of nanocomposite. For the preparation of 4-vinylpyridine /styrene-ITO nanoparticles nanocomposites, it is necessary for inorganic nanoparticles such as ITO to have hydrophobic surface so that they can be dispersed into the hydrophobic monomer phase.[21] Therefore ITO nanoparticles were coated with a layer of PVP prior to dispersing ITO nanoparticles into the oil phase.

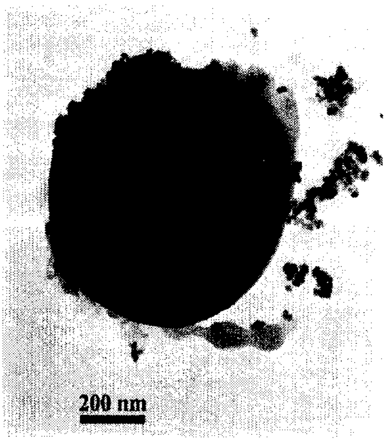
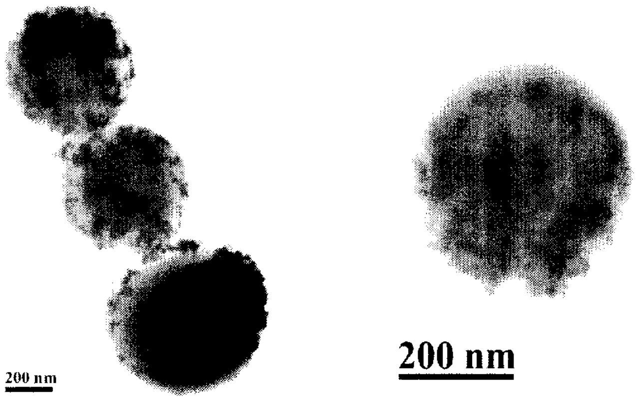


Figure 32. TEM image of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared with CTMA-Br at pH = 10 by using bare ITO particles

The size of these nanocomposites could be controlled by the amount of the surfactant.[31] Figure 33 (a) and (b) show TEM images of 4-vinylpyridine/ styrene-ITO colloidal dispersion prepared with CTMA-Br (0.06 g) and CTMA-Br (0.09 g) at pH = 10. All nanocomposites are spherical as shown in Figure 31 (b), Figure 33 (a) and (b). Especially encapsulation of ITO nanoparticles into 4-vinylpyridine-styrene was formed as shown in Figure 33 (a) and (b). The diameter of the nanocomposite in Figure 31 (b) is about 796 nm. The diameters of the nanocomposites in Figure 33 (a) and (b) are about 595 nm and 368 nm, respectively. The diameter of the nanocomposite was decreased as the amount of CTMA-Br was increased. This resulted from the diameter of monomer droplet which was formed in initial reaction. The concentration of CTMA-Br affects the diameter of monomer droplet.



(a) (b)

Figure 33. TEM images of 4-vinylpyridine/styrene-ITO colloidal dispersion prepared with CTMA-Br (0.06 g) (a) and CTMA-Br (0.09 g) (b) at pH = 10.

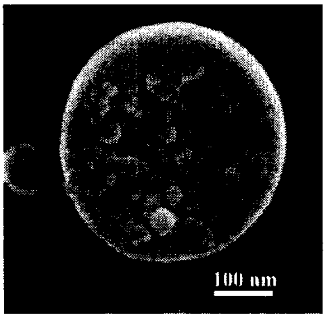


Figure 34. FE-SEM image of 4-vinylpyidine/styrene-ITO colloidal dispersion prepared with CTMA-Br (0.09 g) at pH = 10.

5. Conclusion

In this work, indium tin oxide (ITO) nanoparticles whose the atomic ratio of indium to tin was 9:1 were prepared by chemical coprecipitation method. The coprecipitate prepared at room temperature showed the crystal structure of indium hydroxide in X-ray diffraction and these indium hydroxide particles were converted to indium oxide particles after it was annealed at the temperature above 300 °C under air atmosphere. This primary annealing under air atmosphere was carried out to crystallize particles and remove impurities. The secondary annealing under hydrogen atmosphere was accomplished to improve the electrical properties of powder by increasing oxygen vacancy and concentration of carrier. This reduction process affects the color of ITO powders. ITO powder color under air atmosphere was yellow, but was changed from green to dark green and gray under hydrogen atmosphere as annealing temperature and time increased. The ITO nanopaeticles have a spherical shape and the size of particles is 15 - 25 nm. However the ITO particles were not well dispersed as other nano-sized particles. It is imperative to have well dispersed ITO nanoparticles in an aqueous sol solution for application such as near IR-radation reflective film. The water based ITO sol solution was easily prepared by adding ITO nanoparticles to an aqueous solution containing dispersing agents such as polyvinylpyrrolidone and NP 1050, etc. This ITO sol solution had good dispersibility with the absolute value of zeta potential of more than 30 mV. Near IR-radiation reflective film was prepared on glass substrate by spin coating using this ITO sol solution. NIR reflectance of the ITO film was over 90% in the range above 1500 nm.

Lastly 4-vinylpyridine/styrene-ITO colloidal nanocomposites were prepared by two kinds of emulsion polymerization. One is conventional emulsion polymerization method using surfactants. In this method application of surfactants throughout the process gives very different results. SDS, when applied under basic condition, assists the colloidal stability but does not really improve formation of nanocomposites. The cationic CTMA-Br leads to an improvement of the coupling of copolymer and ITO nanoparticles. The other is a facile route to colloidal nanocomposites by surfactant free emulsion polymerization. The resulting nanocomposites have relatively narrow size distribution, mean nanocomposite diameters of 130 - 160 nm. Depending on using bare ITO nanoparticles or ITO sol solution, the results were very different. The presence of the water based ITO sol solution is essential for the formation of colloidal nanocomposites.

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7. Korean Abstract

본 연구는 indium tin oxide (ITO) 나노졸 용액의 제조와 이를 이용한 적외선 차단 필름의 제조 및 고분자-ITO 나노복합물의 제조에 관한 것이다. 본 연구에서 ITO 나노 입자는 질산인듐과 염화주석을 수용액에서 반응시켜 콜로이드 입자로 석출한 후 air 분위기에서 1차 소성과 hydrogen 분위기에서 2차 소성 시켜 제조되었다. 1차 소성은 결정 생성 및 불순물 제거를 위해 행해졌고 2차 환원 소성은 격자 사이의 산소 결함을 증가시켜 carrier concentration의 증가를 위해 행해졌다. 2차 환원 소성의 결과 ITO 분말의 색은 노란색에서 진한 녹색으로 변하였다. 이렇게 공침법에 의해 얻어진 최종 ITO 나노입자는 15 - 25 nm 정도로 둥근 형태의 입자였다. 다른 나노 크기의 입자와 마찬가지로 본 연구에서 합성되어진 ITO 나노입자 역시 높은 표면 자유 에너지로 인하여 수용액에서의 분산성이 양호하지 않았다. 적외선 차단 필름의 제조 등 실제 ITO 나노입자의 응용에 있어서는 분산성의 문제가 중요하므로 본 연구에서는 ITO 나노입자의 분산성 향상을 위해 polyvinylpyrrolidone, NP 1050 및 EFKA 4330 등의 고분자 또는 상업용 분산제를 첨가하여 분산성이 우수한 수성 ITO 나노졸 용액을 제조하였으며 이를 이용하여 스핀코팅 방법으로 90% 이상의 적외선 차단력을 지닌 적외선 차단 필름을 제조하였다.

마지막으로 본 연구에서는 emulsion polymerization에 의해 기존의 surfactant를 사용하는 방법과 surfactant를 사용하지 않는 방법에 의해 4-vinylpyridine/styrene-ITO 콜로이드 나노복합물을 제조하였으며 surfactant의 종류에 따른 4-vinylpyridine/ styrene-ITO 콜로이드 나노복합물 형성의 영향에 대해 연구하였다. ITO 나노입자의 경우 cationic surfactant인 cetyltrimethylammonium bromide (CTMA-Br)를 사용할 경우 ITO 나노입자가 고분자에 encapsulation된 4-vinylpyridine /styrene-ITO 나노복합물을 제조할 수 있었다.