DETERMINATION OF DIELECTRIC PROPERTY AND IONIC CONDUCTIVITY OF CdS/SO$_3$H-P(S-DVB) NANO COMPOSITES

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ABSTRACT

DETERMINATION OF DIELECTRIC PROPERTY AND IONIC CONDUCTIVITY OF CdS/SO3H-P(S-DVB) NANO COMPOSITES. Cadmium sulfide sulfonatedpoly (styrene-divinylbenzene) [CdS/SO$_3$H-P(S-DVB)] nano composites with different CdS contents were successfully synthesized by ion exchange and precipitation processes at SO$_3$H-P(S-DVB) matrix. The characterized, dielectric property and ionic conductivity of the nano composites were also examined. The polymer matrix and the chemical interaction between CdS nano particles with polymer were analyzed using Fourier Transform Infrared (FT-IR) spectroscopy. The CdS nano particles was confirmed from Diffuse Reflectance Ultraviolet - Visible (DR UV-Vis), X-Ray Diffractometer (XRD) and Atomic Absorption Spectroscopy (AAS) analysis results. Scanning Electron Microscope (SEM) techniques were used to observe the particle size of the nano composites, while a morphology of the nano composites was also investigated using Transmission Electron Microscope (TEM) techniques. The SEM and TEM studies showed that the CdS nano particles are attached on the surface of polymer matrix. Dielectric property and ionic conductivity of the nano composites have been studied using an Impedance Analyzer, respectively. Present study shows that the influence of CdS nano particles loading levels on the dielectric property and ionic conductivity of the nano composites. The dielectric constant and ionic conductivity of the CdS/SO$_3$H-P(S-DVB) nano composites decreased with increasing content of CdS nano particles as effect replacing of proton by CdS nano particles, respectively.

Keywords : Cadmium sulfide-sulfonatedpoly (styrene-divinylbenzene), Nano composites, Dielectric property, Ionic conductivity

ABSTRAK

PENENTUAN SIFAT DIELEKTRIK KONDUKTIVITAS ION NANO KOMPOSIT CdS/SO$_3$H-P(S-DVB). Nano komposit cadmium sulfidapoli (stirena divinilbenzen) tersulfonasi [CdS/SO$_3$H-P(S-DVB)] dengan kandungan CdS yang berbeda telah berhasil disintesis melalui tahapan penukaran ion dan pengendapan pada matriks SO$_3$H-P(S-DVB). Karakterisasi, sifat dielektrik dan konduktivitas ion nano komposit juga telah dilakukan. Matriks polimer dan interaksi kimia antara CdS dengan polimer telah dianalisis menggunakan spektroskopi *Fourier Transform Infra Red* (*FT-IR*). Nano partikel CdS telah dikonfirmasi keberadaannya dengan menggunakan analisis *Diffuse Reflectance Ultraviolet - Visible* (*DR UV-Vis*), *X-Ray Diffractometer* (*XRD*), *Atomic Absorption Spectroscopy* (*AAS*) dan *Scanning Electron Microscope* (*SEM*). Teknik *SEM* digunakan untuk mengamati ukuran partikel dari nano komposit, sedangkan morfologi dari nano komposit diamati secara *Transmission Electron Microscope* (*TEM*). Hasil pengamatan menggunakan *SEM* dan *TEM* menunjukkan bahwa nano partikel CdS terbentuk dipermukaan partikel-partikel SO$_3$H-P(S-DVB). Sifat dielektrik dan konduktivitas ion masing-masing telah dianalisis menggunakan Impendansi Analiser. Hasil penelitian menunjukkan adanya efek penambahan nano partikel CdS pada sifat dielektrik dan konduktivitas ion nano komposit. Tetapan dielektrik dan konduktivitas ion nano komposit CdS/SO$_3$H-P(S-DVB) menurun dengan naiknya kandungan nano partikel CdS sebagai akibat penggantian proton pada polimer oleh nano partikel CdS.

Kata kunci : Cadmium sulfide-sulfonatedpoly (styrene-divinylbenzene), Nano composites, Dielectric property, Ionic conductivity

INTRODUCTION

Studies and syntheses of polymer nano composites, including polymer/ceramic nano composites, polymer/inorganic nano composites and polymer/metal nano composites with high dielectric constant have been actively explored. The utilized polymer nano composites for electronic application have many advantages such as light weight, shape-flexibility, cost effectiveness, and good process ability of the material [1-5]. The properties of polymer nano composites are appealing for two reasons. First of all, they possess large interfacial exchange coupling through a dipolar interface layer and leading to enhancement in polarization and polarizability in polymer matrix near the interface. As a result, enhanced dielectric constant can be expected in the polymer matrix near the interfaces. Secondly, the nanoscale particles also make it possible to reduce the thickness of polymer matrix film to nano range, and thus increase its already high breakdown strength even further by avoiding avalanche effect [1,6,7].

Many researchers have developed methods for synthesis of high dielectric properties polymer nano composites. The first approach process for enhancing the dielectric constant of a polymer nano composites is to disperse a high dielectric constant insulating ceramic (ferroelectric materials), namely nanoceramic using barium titanate (BaTiO$_3$) [8,9], lead titanate (PbTiO$_3$), lead zirconatetitanate (PZT) [10], strontium titanate (SrTiO$_3$) [11] into pure polymers. The second approach to obtain high dielectric constant polymer nano composites was achieved by dispersing conductive fillers into pure polymers. The common conductive materials used to produce the polymer nano composites are carbon nano fibers, metals such as silver (Ag) nanoparticles [12], aluminium (Al) and nanoparticle aluminium [13], cadmium oxide (CdO), zink sulfide (ZnS)[14], polymers such as polyaniline (PANI) [15], and organic acids such as sulfamic acid [16] and copper pthalocyanine. The third approach to increase dielectric properties of pure polymer was to utilize an inorganic and organic materials such as, titanium oxide (TiO$_2$) [17,18], aluminium oxide (Al$_2$O$_3$) [19], zinc oxide (ZnO$_2$) [20] and also other polymers such as poly(trimethyleneterephtalate) (PTT) [21]. The results showed that the dielectric constant of the polymer nano composites increases compare than pure polymer.

The used of CdS nanoparticles as nanofiller have received great attention because of their unique electrical and optical properties. The selected approach of synthesis methods and the intrinsic of chemical properties of selected polymers will be produced on nanoscaleCdS by encapsulated within polymer or attached on polymer matrices. The combination of CdS nanoparticles and pure polymer have developed a CdS/polymer nano composites with a high dielectric constant and improved physicochemical properties.

In this present study, we synthesized and characterizedof CdS/SO$_3$H-P(S-DVB) nano composites. The effect of influence of CdS nanoparticleon dielectric propertyand ionic conductivity of the nano composites was discussed in detail.The materials were synthesized bysulfonation and ion exchange-precipitation method. The as-synthesized CdS/SO$_3$H-P(S-DVB) nano composites were characterized using X-Ray Diffraction (XRD), Fourier Transformation Infrared (FT-IR), Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM), UV- Visible Diffuse Reflectance (UV-Vis DR) spectroscopy, AC Impedance Analyzer and Thermal Conductivity Analyzer.

METHODS EXPERIMENTAL

Chemicals

Styrene 99.00 % (Sigma), divinyl benzene 99.00 % (Sigma) , sodium dodecyl sulphate 98.00 % (Sigma), 2-propanol p.a.(Merck), 2,2'-azobisisobutyronitrile 98.00 % (Himedia), ethanol p.a. (Merck), methanol p.a. (Merck), H$_2$SO$_4$/SO$_3$p.a. (Merck), Cd(NO$_3$)$_2$99.00 % (Merck), Na$_2$S 99.00 % (Merck), NaOH p.a. (Merck), NaClp.a (Merck)

Preparation of P(S-DVB), SO$_3$H-P(S-DVB) and CdS/SO$_3$H-P(S-DVB)

Pure poly(styrene-divinylbenzene) [P(S-DVB)] was synthesized by *in-situ* polymerization at 70- 80 ºC in miniemulsion system. Meanwhile the miniemulsion system was prepared using sodium dodecyl sulfate (SDS) as surfactant, 2-propanol as co-stabilizer, water and styrene-divinylbenzene as oil-phase. The preparation involved stirring a mixture of 2.5 mL of 2-propanol, 1.80 gram of styrene, 0.60 gram of divinylbenzene and 2,2'-azobisisobutyronitrile (AIBN) for 1 h. After stirring for 1 h, the mixture was added to 20 mL 0.1 M of SDS in water and then ultrasonication was carried out for 15 minute followed by more stirring for 1 hour. Then *in-situ* polymerization was done at 70-80 ºC for 6 hours. The polymer was filtered and then washed with water, ethanol and methanol, to remove surfactant and monomer residues, before drying for 4 h at 100 ºC.

The next step is the sulfonation reaction of the polymer with H$_2$SO$_4$/SO$_3$. In the preparation of SO$_3$H-P(S-DVB), 10.0 mL H$_2$SO$_4$/SO$_3$was added slowly to 0.5 gram of P(S-DVB). The mixture was slowly stirred and maintained at 50 ºC for 1 h, followed by careful dilution of the mixture with water. The SO$_3$H-P(S-DVB) was filtered and then washed with water until neutral pH was obtained and finally dried at 100 ºC for 4 hours. The preparation of occluded cadmium ion on the surface of SO$_3$H-P(S-DVB) was achieved by ion exchange method. This preparation involved stirring a mixture of 0.5 gram SO$_3$H-P(S-DVB) with various mmol of cadmium ion in methanol solution for 24 hours.

The solution was filtered and then washed with water, ethanol, and methanol, to effectively remove excess cadmium ion and then dried for 4 hours at 100 ºC. The final step was the synthesis of CdS/SO$_3$H-P(S-DVB) nano composites by precipitation reaction of Cd^{2+}/SO$_3$H-P(S-DVB) with sulfide anion solution. About 0.5 gram of Cd^{2+}/SO$_3$H-P(S-DVB) was soaked in a solution of various mmolNa$_2$S. 9 H$_2$O in 50:50 H$_2$O: methanol and then was stirred for 24 hours. The CdS/SO$_3$H-P(S-DVB) nano composites was filtered and then was washed with water, ethanol and methanol, successively and dried at 100 ºC for 4 hours.

Determination of milliequivalents (meq) H$^+$ and degree of sulfonation of SO$_3$H-P(S-DVB) and CdS/SO$_3$H-P(S-DVB)

The sulfonate content (degree of sulfonation) of SO$_3$H-P(S-DVB) was determined by titration method. A 0.1 gram of SO$_3$H-P(S-DVB) was dissolved in mixture of 15 mL of toluene and 2 mL ethanol. The solution was titrated with standardized methanol solution of potassium hydroxide (KOH), using phenolphthalein as indicator. The ion exchange capacity of SO$_3$H-P(S-DVB) was determined (with unit of meq/gram of dry polymer of sulfonated polymer) by measuring concentration of hydrogen (H$^+$) that was exchanged with sodium cation when acid sulfonated polymer samples were equilibrated with sodium (Na$^+$) solution. 0.1 gram sample of acid polymer was placed into 100 mL of 0.2 mL NaCl solution and shaken sporadically for 24 hour, the amount of hydrogen ion released by the polymer was determined by titration with 0.01 M NaOH.

Characterization

The structure of CdS at the nano composites was characterized by XRD using a Bruker Advance D8 Difractometer with CuKα (λ = 1.5405 A) radiation as the diffracted monochromatic beam at 40 kV and 40 mA and was scanned in the 2θ range between 20º-70ºat ambient temperature. The cadmium (Cd) and sodium (Na) content of the CdS/SO$_3$H-P(S-DVB)nano composites samples were determined using Perkin Elmer AA400 Atomic Absorption Spectrometer equipped with flame atomizer and EDL lamp for Cd and Na. The particle size of CdS nanoparticles at the nanocompoites was determined by UV-Vis Diffuse Reflectance (UV-Vis DR) using Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer. In preparation of the samples for UV-Vis DR, the samples was finely grinded and placed in a sample vessel, before placing the sample vessel on a sample holder to be analyzed. The scanned wavelength ranges between 350-700 nm.The pure polymer, sulfonated polymer and CdS/SO$_3$H-P(S-DVB)nano composites were characterized by FT-IR spectroscopy using a Perkin Elmer Spectrum

One FT-IR Spectrometer at room temperature and the spectra were recorded in the region of 4,000-400 cm^{-1}.

Preparations of samples for FT-IR characterization were done using KBr pellet technique. FT-IR spectra were recorded at room temperature with 4 cm^{-1} resolution. Field Emission Scanning Electron Microscope (FESEM), Zeiss Supra 35VP VP Series model was used to determine the morphology and particles size of the nano composites. Samples were mounted on stubs using double-sided tape and then coated with gold using instrument model BIO-RAD Polaron Divison SEM Coating System machine at 10^{-1} mbar with 30 mA for 75 minutes. Gold coating is needed to prevent charge build-up on the sample surface, besides increasing secondary electron emission. Then, the stubs were put in field emission scanning electron microscope model Philip XL40 and with pressure of 5 bars. Electron source was attained from tungsten filament. The FESEM micrograph was recorded with resolution of 10 kV for certain times of magnification. A JEOL JEM-2100 Transmission Electron Microscope (TEM) was used for analyzing the particle size of the nano composites. In preparation of the samples for TEM analysis, the CdS/SO$_3$H-P(S-DVB) nano composites was dispersed in ethanol by ultrasonic stirring. Then a drop of the suspension was placed on the grid with Formvar thin film, before carrying out the TEM analysis.

Location of Research

Physical and Inorganic of Chemistry Laboratory-UTM, IbnuSina Institute for Fundamental Science Studies-UTM, Eijkman Institute-Jakarta, Pharmaceutical and Medical Technology Laboratory-BPPT-Puspiptek,Serpong, Tangerang.

Dielectric Property (Constant)

The capacitance of CdS/SO$_3$H-P(S-DVB) nano composites were determined using Impedance Analyzer. Pellets of 2-4 mm thick were prepared by placing sufficient amount of sample (~50 mg) in a steel die measuring 13 mm in diameter, and a pressure of 5 psi were applied and held for 30 seconds. The dielectric constants (ε_r) of the pellet prepared were calculated from the measured capacitance at various frequencies (0.1 kHz to 1,000 kHz) using AC Impedance Analyzer using the equation: C = $\varepsilon_r \varepsilon_o$ A/d, where ε_o is the dielectric constant of the free space (8.854 x 10^{-12} F/m); "A" the area of the electrical conductor; and "d" the thickness of material.

Ionic Conductivity

The ionic conductivity was studied using AC Impedance Analyzer with frequency response analyzer (Auto Lab POST AT 30). The resistances of the specimens were measured at frequency of

0.1 kHz-1,000 kHz using AC Impedance Analyzer. The ionic conductivity, σ, of the CdS/SO$_3$H-P(S-DVB) nano composites were calculated from the resistance data.

RESULTS AND DISCUSSIONS

Synthesis of P(S-DVB), SO$_3$H-P(S-DVB) and CdS/SO$_3$H-P(S-DVB) Nano Composites

Schematic representation of the reaction of polymerization and sulfonation reaction is illustrated in Figure 1. The *in-situ* polymerization in mini emulsion
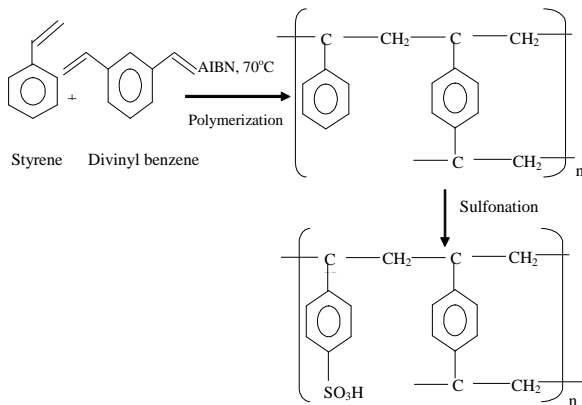

Figure 1. Reaction of styrene and divinyl benzene by free radical polymerization and sulfonation process to form SO$_3$H/P(S-DVB).
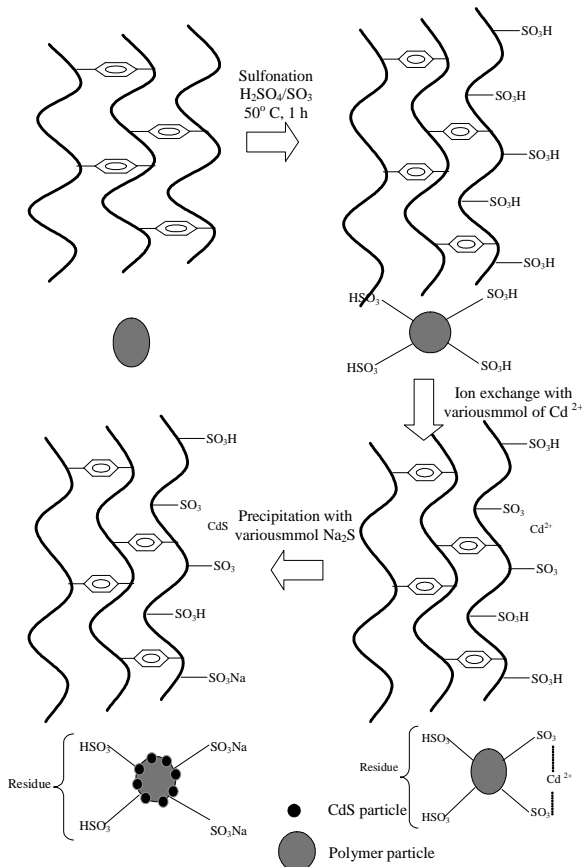
Figure 2. Schematic representation of the synthesis CdS/SO$_3$H-P(S-DVB) nano composites.

was produced P(S-DVB)polymer particles with a dimension in the micrometer range.The SO$_3$H-P(S-DVB) was synthesized by sulfonation reaction of P(S-DVB) with fuming sulfuric acid (H$_2$SO$_4$/SO$_3$) at 50 °C for 1 hour. The degree of sulfonation of SO$_3$H-P(S-DVB) which was determined by volumetric method was 39.10 %.

Meanwhile, the CdS/SO$_3$-P(S-DVB) nano composites were synthesized from SO$_3$H-P(S-DVB) by ion exchange and precipitation process with various concentrations of cadmium ion, followed by reaction with sulfide ion. The mechanism of ion exchange and precipitation process occurred with replacement of hydrogen ion at sulfonic acid groups by cadmium ion with various concentrations which was then followed by precipitation by sulfide ion at various concentrations and producing CdS nanoparticles on the surface of polymer matrix. The ion exchange, precipitation process and functional groups of the polymer helped to control particle size and formation of CdS nanoparticles on the surface of polymer matrix and produced the yellow CdS/SO$_3$H-P(S-DVB) nano composites. Schematic representation of the synthesis of CdS/SO$_3$H-P(S-DVB) nano composites is illustrated in Figure 2.

UV – Vis Diffuse Reflectance and Fourier-Transform Infrared Spectroscopy of CdS/SO$_3$H-P(S-DVB) Nano Composites

The CdS/SO$_3$H-P(S-DVB) nano composites with various amounts of CdSnanoparticles were characterized by UV-Vis DR spectroscopy (see Figure 3). The absorption onset wavelength of CdS nanoparticles in the CdS/SO$_3$H-P(S-DVB) nano composites was determined using the obtained UV-Vis DR spectra and it was found to be significantly blue-shifted compared to bulk CdS. The direction of the blue shifting is in agreement with quantum confinement effect due to decreasing particle size. The results also suggested that the ion exchange-precipitation processes could control the growth, nucleation
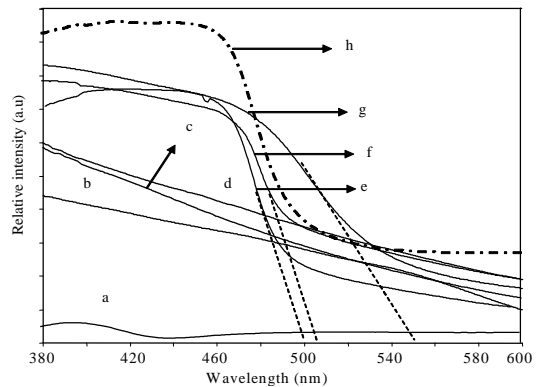

Figure 3. UV-Vis DR spectra of (a) Pure P(S-DVB), (b) SO$_3$H-P(S-DVB), (c) 2.56 % CdS/SO$_3$H-P(S-DVB), (d) 3.34 % CdS/SO$_3$H-P(S-DVB), (e) 7.64 % CdS/SO$_3$H-P(S-DVB), (f) 14.65%CdS/SO$_3$H-P(S-DVB), (g) 16.56 % CdS/SO$_3$H-P(S-DVB) and (h) CdS nanoparticles.

and formation of CdS nanoparticles on the SO_3H-P (S-DVB) polymer surface. Based on the absorption on set wavelength value, the particle size of CdS nanoparticles (see Table 1) was calculated using the Brus Equation (1) [22]:
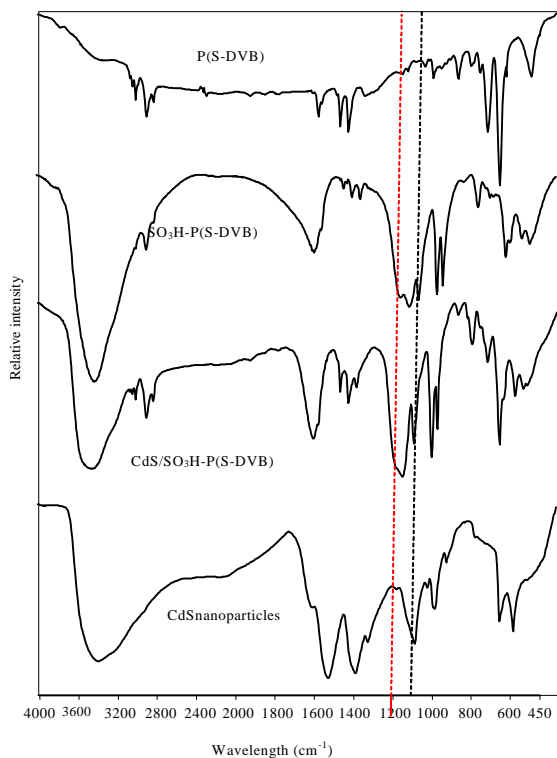
$$E_g(R) = 2.43 + 2.446/R^2 - 0.3031/R \quad \text{............... (1)}$$

The FT-IR spectra of the series of P(S-DVB), SO_3H-P(S-DVB), CdS nanoparticles and CdS/ SO_3H-P(S-DVB) nano composites are shown in Figure 4. These spectra show the main peaks due to the polystyrene component. The P(S-DVB), SO_3H-P(S-DVB) and CdS/SO_3H-P(S-DVB) nano composites show peaks corresponding to the following groups : -OH (at 3,400-3200 cm^{-1}), unsaturated aromatic C-H stretching vibrations (at 3,025 cm^{-1}), CH_2 bending vibration (at 2.920- 2,840 cm^{-1}), aromatic ring (at 1,510 cm^{-1}), CH_2 (at 1475 cm^{-1}), various substitution of benzene ring

Table 1. The absorption onset wavelength and particle size of CdS/SO_3H-P(S-DVB) nano composites

Nanocomposite sample	Onset wavelength (nm)	Particle size of CdS particles (nm)[*]
2.56 % CdS/SO_3H-P(S-DVB)	Not observed	Nd
3.34 % CdS/SO_3H-P(S-DVB)	Not observed	Nd
7.64 % CdS/SO_3H-P(S-DVB)	500	7.0
14.65 % CdS/SO_3H-P(S-DVB)	507	7.3
16.56 % CdS/SO_3H-P(S-DVB)	550	> 8

Nd : not determined, *) determined using Brus equation

**Figure 4.** FT-IR spectra of P(S-DVB), SO_3H-P(S-DVB), CdS nanoparticles and CdS/SO_3H-P(S-DVB) nano composites.

between 900 cm^{-1} and 700 cm^{-1} [23]. Martins *et al.* have studied the characteristic infrared spectra of SO_3H-P(S-DVB) and suggested that the bonding of the sulfonic groups to the aromatic ring of polystyrene out of plane deformation bands assigned to substituted aromatic ring δ (C_{ar}-H) occurs at wavenumbers of approximately 830 cm^{-1} to 850 cm^{-1} [24].

Several new peaks were found in the spectra of SO_3H-P(S-DVB) and CdS/SO_3H-P(S-DVB) at 560 cm^{-1}, 615 cm^{-1}, 1000 cm^{-1}, 1030 cm^{-1}, 1110 cm^{-1}, 1180 cm^{-1} and 1230 cm^{-1} [23]. The absorption peak at 1030 cm^{-1} was attributed to the symmetric stretching vibration of sulfonic acid groups (-SO_3H) and the band at 1110 cm^{-1} was due to a sulfonate anion attached to phenyl ring. The υ_{as} (S-O) vibration at 1180 cm^{-1} appears as broad band at approximately 1200 to 1300 cm^{-1}. An increasing peak at 1110 cm^{-1} and a decreasing peak at 1230 cm^{-1} were observed in the spectrum of CdS/SO_3H-P(S-DVB) are the consequence of the ionization of sulfonic acid groups by cadmium ion. The phenomena clearly showed that the chemical bonding between CdS nanoparticles with sulfonated polymer matrix was quite strong.

Structural and Morphological Properties of CdS/SO_3H-P(S-DVB) Nano Composites

The structure and morphology of SO_3H-P(S-DVB) and CdS/SO_3H-P(S-DVB) nano composites were investigated by XRD, SEM and TEM techniques. Figures 5(a)-5(b) and 6 show the XRD patterns of CdS nanoparticles powder, bulk CdS powder, SO_3H-P(S-DVB) powder and CdS/SO_3H-P(S-DVB) powder nano composites with various CdS content respectively.

The XRD patterns of the samples exhibit peaks corresponding to 111, 220, and 311 indicating that CdS nanoparticles are in the cubic phase. The XRD patterns of the CdS/SO_3H-P(S-DVB) nano composites are identical with the XRD patterns of the CdS nanoparticle and also exhibit broad XRD peaks. The broad peaks are attributed to the absence of long-range order in the samples and reflect the small particle sizes. This result agrees with the presence of nanocrystalline CdS, for which quantum size effect are expected. The low intensity peaks indicated that the dimension of CdS nanoparticles was
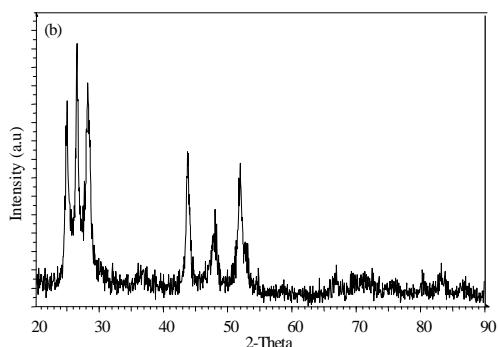
Figure 5. XRD patterns of samples powder (a) CdS nanoparticles and (b) bulk CdS.
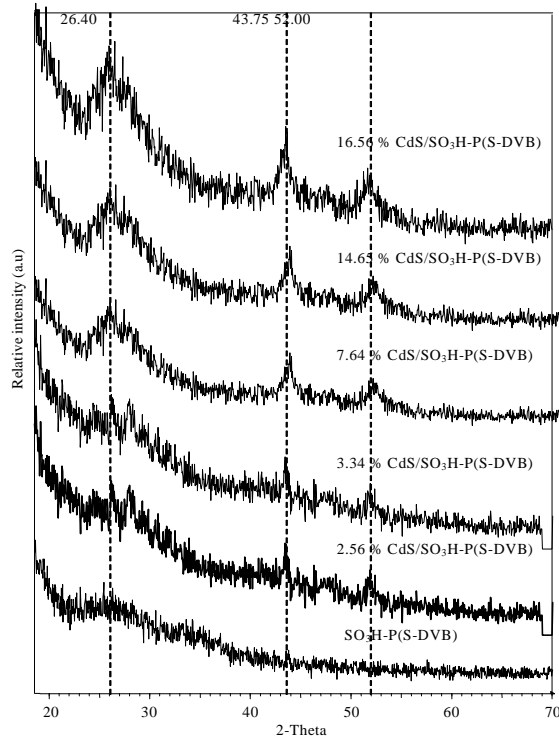
Figure 6. XRD patterns of samples powder SO$_3$H-P(S-DVB) and the various CdS/SO$_3$H-P(S-DVB) nano composites.

homogeneously dispersed in pure polymer matrix. The polymer particles which are amorphous and present in large amount also contribute to the peak broadness.

The morphology of CdS/SO$_3$H-P(S-DVB) nano composites was characterized by SEM and TEM. Figure 7(a)-7(b) shows the typical SEM images of CdS/SO$_3$H-P(S-DVB) nano composites with 1,000 and 100,000
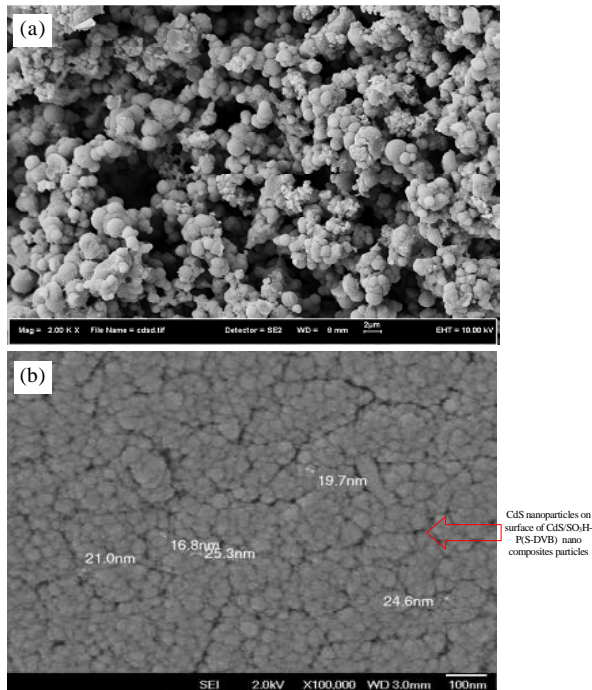

Figure 7. SEM images of samples powder 7.64 % CdS/SO$_3$H-P(S-DVB) nano composites at magnifications (a) 2,000X and (b) 100,000X.
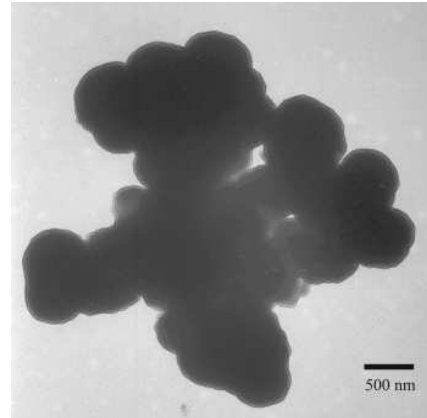

Figure 8. TEM images of samples powder agglomerated of CdS/SO$_3$H-P(S-DVB) nano composites

magnifications under the optimum condition at 10 KV and 2 KV, respectively. The SEM images at Figure 7(a) showed ofCdS/SO$_3$H-P(S-DVB) nanocomposite particles with diameter 300 nm-2 micrometer and the SO$_3$H-P(S-DVB) polymers as host matrices were clearly observed with ball-shape.

SEM images at Figure 7(b) showed the presence of CdS particles attached on the surface of SO$_3$H-P(S-DVB) with particle size between 16.8 – 25.3 nm, suggesting that the CdS nanoparticles were small and dispersed on polymer surface. The dispersionof CdS on the surface of polymer was also identified from the corresponding change in colour of products.

The shape and size of the nanocomposite can be seen in the TEM micrographs of Figure 8, where the micrographis shown the dark center and pale edge of the spheres. Cadmium as heavy element developed a darker color compared to carbon and hydrogen in the polymer structure. The dark domain observed in the TEM image indicates that it originated from CdS nanoparticles, indicating that CdS nanoparticles were small and homogeneously dispersed in the polymer matrix. As can be seen, the spheres exhibit a diameter distribution in the range of 500 nm-1 micrometer. However, it is difficult to observe the particle size and size distribution of CdS nanoparticles by visual inspection of the TEM images, due to the TEM image was obtained by a low accelerating voltage (70 KeV), hence the a statistical description of the size distribution of CdS nanoparticles cannot be carried out.

Dielectric and Ionic Conductivity Properties of CdS/SO$_3$H-P(S-DVB) Nano Composites

Table 2 shows the dielectric constants of SO$_3$H-P(S-DVB) and CdS/SO$_3$H-P(S-DVB) nano composites at various contents of CdS nanoparticles and various frequencies (100, 1,000, 10,000, 100,000 and 1.000.000 Hz). Figure 9 shows the dielectric constants measured at frequency of 100 Hz ofP(S-DVB), CdS nanoparticles, Cd(SO$_3$)$_2$-P(S-DVB), NaSO$_3$-P(S-DVB), SO$_3$H-P(S-DVB) and CdS/SO$_3$H-P(S-DVB) nano composites at various

Table 2. Milliequivalents (meq) H+/gram of SO₃H-P(S-DVB) with degree of sulfonation = 39.10 % and CdS/SO₃H-P(S-DVB) nano composites with several of CdS content.

Sample	Log frequency (Hz)				
	6	5	4	3	2
P(S-DVB)	1.4	2.9	2.9	3.1	5.9
CdS nanoparticles	4.6	16.2	28.9	49.8	100.0
Cd(SO₃)₂-P(S-DVB)	4.2	39.3	294.7	2145.1	9097.8
NaSO₃-P(S-DVB)	8.6	55	359	1286.8	2016.6
SO₃H-P(S-DVB)	2,338.0	10,947.0	25,345.0	61,634.0	236,190.0
2.56 % CdS/SO₃H-P(S-DVB)	1,989.0	7,425.0	13,931.0	30,069.0	87,118.0
3.34 % CdS/SO₃H-P(S-DVB)	1,281.0	7.702.0	14,933.0	26,988.0	74,394.0
7.64 % CdS/SO₃H-P(S-DVB)	144.0	923.0	2,862.0	6,326.0	22,861.0
14.65 % CdS/SO₃H-P(S-DVB)	46.0	297.0	1,090.0	3,662.0	15,683.0
16.56 % CdS/SO₃H-P(S-DVB)	18.4	39.5	145.0	391.0	1,309.0
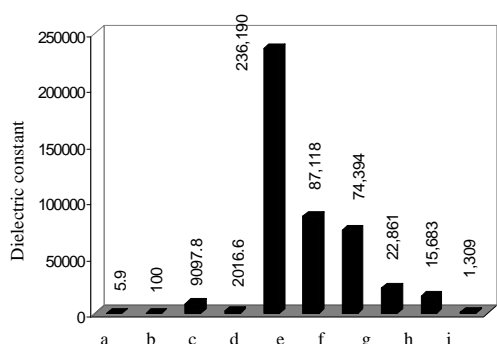
Figure 9. Dielectric constant of (a) P(S-DVB), (b) CdS nanoparticles, (c) Cd(SO₃)2-P(S-DVB), (d) NaSO₃-P (S-DVB), (e) SO₃H-P(S-DVB), (f) 2.56 % CdS/SO₃H-P (S-DVB), (g) 3.34 % CdS/SO₃H-P(S-DVB), (h) 7.64 % CdS/SO₃H-P(S-DVB), (i) 14.65 % CdS/SO₃H-P(S-DVB) and (j) 16.56 % CdS/SO₃H-P(S-DVB) at 100 Hz.

contents ofCdS nanoparticles. The dielectric constants of CdS/SO₃H-P(S-DVB) nano composites decreased with increasing CdS nanoparticles content as compared to SO₃H-P(S-DVB).

On the other hand, the dielectric constants of the CdS/SO₃H-P(S-DVB) nano composites showed higher values than P(S-DVB) (~6 measured at 100 Hz) and CdS nanoparticles (100 measured at 100 Hz). The possible explanation for this result is the higher strength of electrical properties of proton and polarity of SO₃H-P(S-DVB) as a host matrix. The protons at the sulfonic acid functional groups are very easily moved and when parts of the protons were replaced with CdS nanoparticles, the amount of proton was decreased and the dielectric properties of the nano composites decreased correspondly.

This phenomenon was supported by the decreasing milliequivalen (meq) H⁺/gram of CdS/SO₃H-P(S-DVB) nano composites with increasing amounts of CdS nanoparticles (see Table 3). The low dielectric constants of Cd(SO₃)₂-P(S-DVB) and NaSO₃-P(S-DVB) also supported the above explanation.
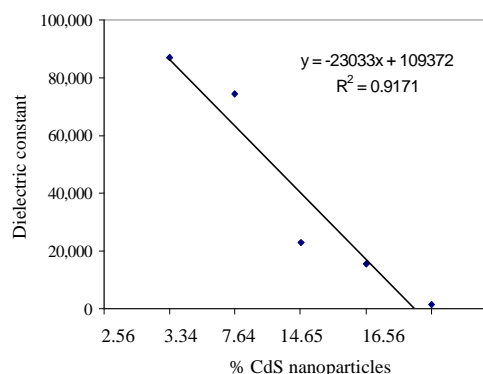
Figure 10 shows a graph of relationship between of dielectric constant versus various contents of *CdS nanoparticles of* CdS/SO₃H-P(S-DVB) nano

compositesat 100 Hz. The curve shows a good correlation with the coefficient correlation of 0.9171.

Figure 11 shows the ionic conductivities of P(S-DVB), SO₃H-P(S-DVB), CdS nanoparticles and CdS/SO₃H-P(S-DVB) nano composites. The ionic conductivity values of CdS/SO₃H-P(S-DVB) nano composites decreased with increasing CdS nanoparticle content as compared to SO₃H-P(S-DVB). The same reason which explained the dielectric properties can also be applied to explain this ionic conductivity property. When some the protons in sulfonic acid were replaced with cadmium ion or CdSand CdS nanoparticles attached on the surface of polymer, the mobility of the proton recidue was hindered. The result was also evidenced by the

Table 3. Dielectric constants of P(S-DVB), CdS nanoparticles, SO₃H-P(S-DVB) and CdS/SO₃H-P(S-DVB) nano composites at various frequencies.

Sample	meq H⁺/gram
SO₃H-P(S-DVB)	3.50
2.56 % CdS/SO₃H-P(S-DVB)	2.64
3.34 % CdS/SO₃H-P(S-DVB)	2.35
7.64 % CdS/SO₃H-P(S-DVB)	1.53
14.65 % CdS/SO₃H-P(S-DVB)	0.66
16.56 % CdS/SO₃H-P(S-DVB)	0.24

$$y = -23033x + 109372$$
$$R^2 = 0.9171$$

Figure 10. A graph of the relationship between of dielectric constant and of several CdS nanoparticles contentsofCdS/SO₃H-P(S-DVB) nano composites at 100 Hz
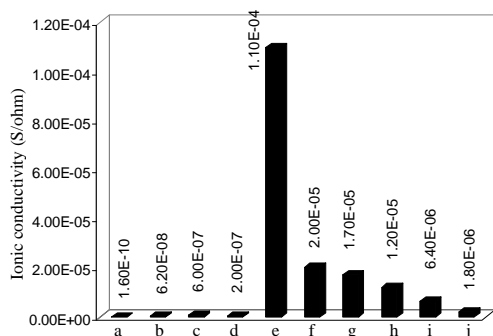
Figure 11. Ionic conductivity of (a) Pure P(S-DVB), (b) CdS nanoparticles, (c) Cd(SO$_3$)2-P(S-DVB), (d) NaSO$_3$-P(S-DVB), (e) SO$_3$H-P(S-DVB), (f) 2.36 % CdS/SO$_3$H-P(S-DVB), (g) 3.34 %CdS/SO$_3$H-P(S-DVB), (h) 7.64 % CdS/SO$_3$H-P(S-DVB), (i) 14.65 % CdS/SO$_3$H-P(S-DVB) and (j) 16.56 % CdS/SO$_3$H-P(S-DVB).
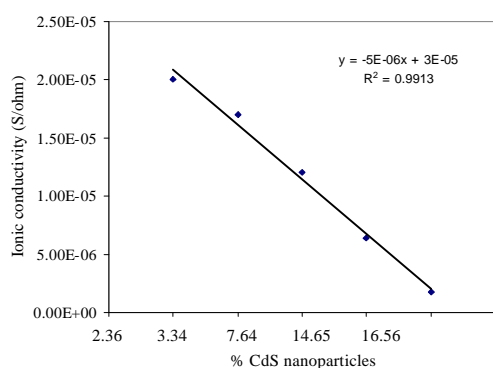
Figure 12. A graph of the relationship between ionic conductivity and amount of CdS nanoparticles of CdS/SO$_3$H-P(S-DVB) nano composites.

decrease of meq H$^+$ in the CdS/SO$_3$H-P(S-DVB) nanocomposite with increasing amount of CdS nanoparticles (see Figure 12).

Figure 12 shows the relationship between % CdS nanoparticles in the CdS/SO$_3$H-P(S-DVB)nano composites with ionic conductivity of CdS/SO$_3$H-P(S-DVB) nano composites. The curve shows a good correlation between % CdSnanoparticles and decreasing the ionic conductivity of the CdS/SO$_3$H-P(S-DVB) nano composites with coefficient correlation of 0.9913.

CONCLUSION

The CdS/SO$_3$H-P(S-DVB) nano composites was successfully prepared by ion exchange and precipitation process CdSto SO$_3$H-P(S-DVB) polymer matrix. The dielectric property and ionic conductivity of nano compositeschanged compared to the pure polymer SO$_3$H-P(S-DVB) due to the presence of CdS nanoparticles in polymer matrices.The dielectric of constant and ionic conductivity of CdS/SO$_3$H-P(S-DVB) nano composites was decrease as compare to the pure polymerSO$_3$H-P(S-DVB). As SO$_3$H-P(S-DVB) contains mobile proton which is responsible for high dielectric constant, the attachment of CdSnanoparticles reduced the dielectric constant and ionic conductivity

due to the replacement of proton with CdS nano particles.Based on the above results, one concludes that the attachment of CdS nanoparticles on the surface of SO$_3$H-P(S-DVB) polymers can influence and control of the dielectric property and ionic conductivity of thenano composites.

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