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Research Article

Manufacturing and Morphological Analysis of Composite Material of Polystyrene Nanospheres/Cadmium Metal Nanoparticles

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Abstract

A very simple nanocomposite material has been in-situ manufactured from an aqueous polystyrene nanospheres dispersion and cadmium (Cd) metal nanoparticles. The manufacturing was performed by using a high frequency of 40 kHz ultrasonic (US) agitation for 45 minute at atmospheric pressure and at room temperature 20 ^{o}C. No chemical reducing agent and surfactant added in this manufacturing technique due to the US could reduce Cd^{2+} ions of cadmium nitrate tetrahydrate to Cd atomic metals nanoparticles whereas water molecules could act as a pseudo stabilizer for the manufactured material. A thin film was manufactured from aqueous colloidal nanocomposite material of Polystyrene nanospheres/Cd metal nanoparticles (PSNs/CdMNp) fabricated on a hydrophilic silicon wafer. The thin film was then characterized by a JEOL-FESEM for its surface morphology characteristic and by ATR-FTIR spectrometry for its molecular change investigation. It could be clearly observed that surface morphology of the thin film material was not significantly changed under 633 nm wavelength continuous laser radiation exposure for 20 minute. In addition, its ATR-FTIR spectra of wave number peaks around 3400 cm^{-1} have been totally disappeared under the laser exposure whereas that at around 699 cm^{-1} and 668 cm^{-1} have not been significantly changed. The first phenomenon indicated that the hydrogen bond existed in PSNs/CdMNp material was collapsed by the laser exposure. The second phenomena indicated that the PSNs phenyl ring moiety was not totally destroyed under the laser exposure. It was suspected due to the existence of Cd nanoparticles covered throughout the spherical surface of PSNs/CdMNp material particles. Therefore a nice model of material structure of the mentioned PSNs/CdMNp nanocomposite material could be suggested in this research. It could be concluded that this research have been performed since the material structure model of the manufactured PSNs/CdMNp nanocomposite could be drawn and proposed. (*Selected Paper from International Conference on Chemical and Material Engineering (ICCME) 2012*)

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1. Introduction

The composite material of Polystryrene nanospheres/Metal nanoparticles (PSNs/MNp) is a part of metal-incorporated organic polymeric materials that have great deal attention from many researchers who focusing his study on material engineering and its application. It is because of at least two reasons, i.e. (i) the metal nanoparticles (MNp) that existed in the polymer matrixes could commonly add unique physical properties to the associated matrixes such as responsivness to mechanical, optical, thermal, barrier, sound, magnetic, electric stimulation, etc to produce very useful nanocomposites [1]; and (ii) organic polymeric-based nanocomposites are relatively not costly in the point of view of the processing techniques and manufacturing materials compared to the expensive materials widely used in semiconductor processing industry [2].

In the last decade various many useful nanocomposite have been produced through physical incorporation of metal nanoparticles with a suitable organic polymeric matrix for various applications practical. For examples, Zhao *et al* [3] have successful synthesized a nanocomposite of gold nanoparticles/ hydrogel poly(*N*-isopropylacrylamide) (PNIPAm) through copolymerization of functional Au nanoparticles with monomer *N*-isopropylacrylamide. They found that the electrical conductivity of the nanocomposite had been changed by two orders of magnitude at moderate temperature upon temperature stimuli. Tseng *et al* [4] succeeded in preparing both nanocomposite of gold and palladium/styrene oligomer through single thermal process without adding extra reducing agents and surfactants. They observed that thermal stability of styrene oligomer/gold is slightly higher about of 12-15 ^{o}C than that of original styrene oligomer. Muraviev *et al* [5] had also successful synthesized metal-polymer nanocomposite membranes containing metal nanoparticles of either palladium (Pd), platinum (Pt), cobalt (Co), nickel (Ni), or copper (Cu) using polyeter keton matrix through *in-situ* reduction technique. They used this nanocomposite as hydrogen peroxide sensor. Kamrupi *et al* [6] reported their achievement for nanocomposite synthesis of silver/polystyrene in water-super critical carbon dioxide medium through *ex-situ* silver addition method. They showed that the thermal stability of the silver/polystyrene nanocomposite that have been synthesized could be enhanced significantly up to around 30 ^{o}C. They also demonstrated the antimicrobial activity of the nanocomposite against some species of bacteria and found that it has high antimicrobial activity to *Bacillus circulens* BP2 culture type. In relation to that, a very interesting useful phenomenon had been reported by references [7-9] that ultrasonic energy of 20 kHz-10 MHz frequency could be applied to reduce metal precursor to be its according metal nanoparticles.

It is very interesting phenomena that all the metals nanoparticles that have used as nanocomposite with organic polymeric matrixes were actually being existed as metal nanoparticles with zero electrical charge or without real electrical charges (M^0). However, as far as we know cadmium metal nanoparticles (CdMNp) have never used as pure metals of without real electrical charge in nanocomposite synthesis which employ it, but it is always used as its substance form, i.e. cadmium sulfide (CdS) nanoparticles instead of its metal form [2, 10-12]. Moreover, the organic polymeric matrixes used in the nanocomposites that already synthesized were always synthesized from its according monomer either with or without an active functional group [3-6]. It never used straightforward as its polymeric form. Thus, it of course will be more complicated in handling, manufacturing process, have long pathway in the manufacturing, time consuming, etc. because of it requires many hazards chemicals with more quantity by commonly in milliliter even liter volume scale or gram scale of mass, so it will be very costly and have more danger.

Therefore in this paper we presented a very simple and safe manufacturing method for composite material of polystyrenes nanospheres

(PSNs)/cadmium metal nanoparticles (PSNs/CdMNp) through straightforward incorporation cadmium metal precursor into the commercial PSNs suspension. In this method, metal precursor would be reducted in-situ employing ultrasonic exposure and the quantity of all chemicals reagents used were in micro scale.

2. Experimentals

The following materials were used: microsphere dispersion of 200 nm Polystyrene nanospheres (PSNs) (199±6 nm, 1.0 % w/v solid concentration, density 1.05 g/ml and index refraction at 589 nm is 1.59, Duku Sci Cooperation USA) used as a main matrix. Cadmium nitrate-4-hydrate ($Cd(NO_3)_2.4H_2O$, Mr = 308.48 gram/mol) of 98 % grade (Cica Reagent-Kanto Chemical Japan) as Cd metal particles precursor. Silicon wafer (100 single crystal orientations, p-doped, resistivity 6.0-9.0 ohm.cm, thickness 675±15 μm, USA) for a hydrophilic solid support material of nanocomposite that would be synthesized. Saturated hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), both in analytical grade, produced J. T. Baker, U.S.A used as received to oxidize properly any oily matter exist on the surface of silicon wafer. Deionized water (DI) that have been produced by our standard laboratory equipment for producing DI used as a general solvent.

2.1. Preparation of PSNs/Cd metal dispersion system

The experiment principle for composite manufacturing of PSNs/CdMNp was performed through dispersion system in water medium according to the following Fig.1. The detail experiment was performed as the following recipe, the amount of 5 μL Polystyrene nanospheres of 200 nm in average size (1.0 % w/v solid concentration, density 1.05 g/ml and index refraction at 589 nm is 1.59, Duku Sci Cooperation USA) was carefully put into a 500 μL eppendorf tube then it was added with cadmium metal precursor of 5 μL 1 % w/v (32.4 mM)(Cadmium nitrate-4-hydrate, Cd(NO3)2.4H2O, Mr = 308.48 gram/mol, 98% grade, Cica Reagent-Kanto Chemical Japan) followed by DI water up to 100 μL total volume. This mixture was then homogenized by vigorous shaking and exposed by 40 kHz ultrasonic wave for 45 minutes (Ultrasonic Cleaner Powersonic 405; SER No.405J411536; made in Korea). On the other hand, a reference sample of the precise recipe as aforementioned was also well prepared according to the same procedure but without exposed with the ultrasonic wave.

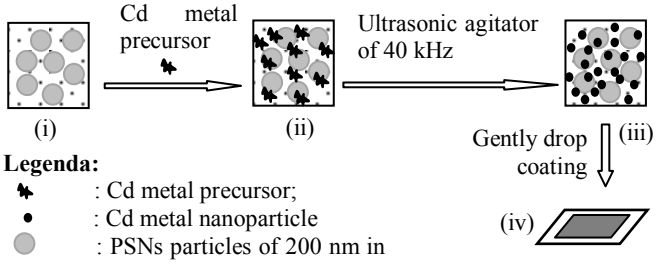


Figure 1. Schematic illustration of the composite manufacturing of PSNs/CdMNp. Here, dispersion system of pristine PSNs of 200 nm in size (i); dispersion system of PSNs/Cd metal precursor (ii); dispersion system of PSNs/CdMNp (iii); and composite of PSNs/CdMNp coated on a hydrophilic silicon wafer (iv).

2.2. Manufacturing composite material of PSNs/CdMNp

It was properly performed as in reference [13], firstly 1 x 1 cm^2 silicon wafers was warmed at 80 ^oC in about 25 mL saturated HCl/H_2O_2 = 3:1 for about 20 minutes to remove any oily matter. This wafer was then taken from the oxidizing solution and subsequently washed up with DI water, finally dried under a laboratory atmospheric air flow. Secondly, 10 μL of the PSN/CdMNp dispersion that already prepared was then coated onto the hydrophilic silicon wafer by gently dropped method. The desirable composite material could be immediately formed after drying in a room temperature through self-assembly process. A reference sample was also manufactured properly from pristine PSNs according the aforementioned procedure. After that, each already manufactured sample was then irradiated by continuous laser beam of 633 nm wave length generated from Helium Light Laser Generator Model 30025 (Serial Number 12187-3408-382, Made in USA.) for 20 minutes under atmospheric pressure and 20^oC room temperature.

2.3. Investigation of surface morphology

By quoting the reference [13] surface morphology of the composite material PSNs/CdMNp as well as pristine PSN that both already manufactured on the silicon wafer, each was then scanned by using a Field Emission Scanning Electron Microscope (FE-SEM) JEOL JSM-7600F Seri No.SM17600053, made in Japan) according the following procedure, the samples were carefully loaded on a FESEM sample holder

then introduced into the FESEM chamber. This chamber was then properly sucked being vacuum at around $10x10^{-5}$Pa. The surface morphology images was then scanned with electron beam source voltage of about 2.00 kV, using LEI SEM detector and scanning wide distance (WD) of about 9.6-9.8 mm. The optimum magnifications scanning of about 10,000 to 50,000 were preferential mode for the best images. Image magnification was defined as the ratio of the length of the scan on the Cathode Ray Tube (LCRT) and the scanned sample specimen (LSpec).

2.4. Investigation of molecular change

The composite material of PSNs/CdMNp and pristine PSNs that have already manufactured on hydrophilic silicon wafer, each was then scanned properly using Fourier Transform Infra Red Spectrometer FTIR (Perkin Elmer FTIR Spectrometer LR 64912C, N3896, FTIR software V1.3.2 Perkin Elmer LX100877-1 made in U.S.A) which was equipped with an ATR sample holder. Subsequently, this sample was put properly on the ATR-FTIR sample stage and scanned carefully under a default set up mode that common used, i.e. peak threshold of 0.5 %T, center of gravity threshold of 0.0022 Absorbance (A), 10.0000 Absorbance Unit (A.U) and center of gravity peak height of 0.2. The generated spectra were then analyzed further under a sequent action of as follows; data Tune-up, ATR correction, Based line correction and the last is Normalization for getting the best ATR-FTIR spectra [13].

3. Results and Discussion

3.1. Analysis of FESEM images surface morphology

Surface morphology of composite of PSNs/CdMNp was depicted in Fig.2. In this context, Fig. 2a clearly shows that a every two PSNs particles adjacent each other was connected by a short bridge-like rod leads to form a very interesting dumbbell-like microstructure material generation. No suitable reasons that can be delivered to explain this interesting phenomenon except we suspect the cluster of agglomerated Cd metal nanoparticles settle in this bridge as a cross-linking facilitator between the both composite particles of PSNs/CdMNp.

This possibility reason was also well supported by both Fig. 2b and 2c. As we can see in Fig. 2b that shows no similar bridge could be formed from the material of pristine PSNs particles since not any Cd metal precursor as well as Cd metal nanoparticles present. Fig. 2c provides more evident that the suspected Cd metal nanoparticles have been clearly incorporated to the PSNs particles material, indeed. Look at the zoom in Fig. 2c, we can see very clear many white colour dots of about 1/5 in size lesser than PSNs particles size of 150 nm (base on the Fig. 2) were settled attached on all PSNs particles surface after the PSNs/CdMNp material irradiated by helium-continuous laser beam for 20 minutes.

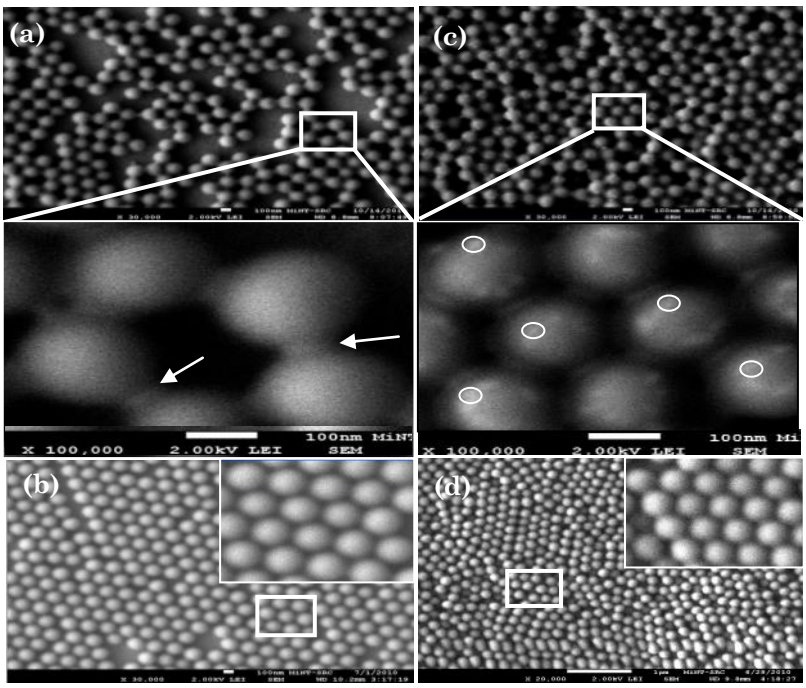
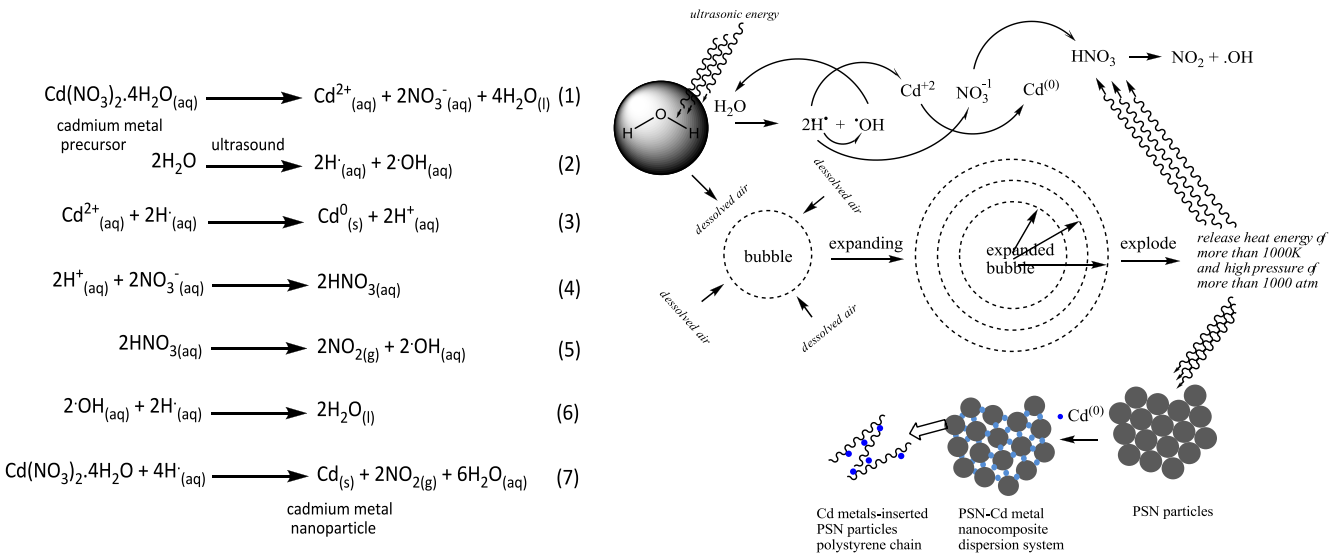


Figure 2. FESEM images surface morphology of composite material of PSNs/CdMNp (a), pristine PSNs (b), continues laser-exposed PSNs/CdMNp (c), and continues laser- exposed pristine PSNs (d).



$$Cd(NO_3)_2.4H_2O_{(aq)} \rightarrow Cd^{2+}_{(aq)} + 2NO_3^-{}_{(aq)} + 4H_2O_{(l)} \quad (1)$$

$$2H_2O \xrightarrow{\text{ultrasound}} 2H^{\cdot}_{(aq)} + 2{\cdot}OH_{(aq)} \quad (2)$$

$$Cd^{2+}_{(aq)} + 2H^{\cdot}_{(aq)} \rightarrow Cd^0_{(s)} + 2H^+_{(aq)} \quad (3)$$

$$2H^+_{(aq)} + 2NO_3^-{}_{(aq)} \rightarrow 2HNO_{3(aq)} \quad (4)$$

$$2HNO_{3(aq)} \rightarrow 2NO_{2(g)} + 2{\cdot}OH_{(aq)} \quad (5)$$

$$2{\cdot}OH_{(aq)} + 2H^{\cdot}_{(aq)} \rightarrow 2H_2O_{(l)} \quad (6)$$

$$Cd(NO_3)_2.4H_2O + 4H^{\cdot}_{(aq)} \rightarrow Cd_{(s)} + 2NO_{2(g)} + 6H_2O_{(aq)} \quad (7)$$

Figure 3. Schematic illustration of the reduction reactions of Cd^{2+} through "hot spots" mechanism generated by ultrasonic irradiation of 40 kHz for 45 minute.

In contrary the similar phenomenon cannot be seen at all in Fig. 2d of which material of pristine PSNs were irradiated by the same laser beam also for 20 minutes. These aforementioned facts which represented by both Fig.2a and 2c indicated that Cd metal nanoparticles had been formed during ultrasonic agitation and during laser irradiations respectively. It is of course very interesting because the previous actions were taken place in an aqueous medium as a water dispersion system whereas the later one was taken place in an atmospheric open air as a solid material film, and the both reductions processes were taken place physically *in situ*.

Those conform to the theory of "hot spots" mechanism that agreed and followed by many researchers of various countries in over the world [7-9, 14-17]. According to the theory, it has already well understood that high-intensity ultrasound of 40 kHz could exceed the bonding of water molecule hydrogen and capable to break down homolytically its atomic bonding to produce synchronically high concentration of hydrogen (·H) and hydroxyl (·OH) radicals. Subsequently, sufficient numbers of micro cavitations bubbles can be formed immediately since the water molecules exist in the cavity destructed. These cavitations bubbles would absorb air from the solvent/medium which cause them expand progressively until their maximum critical volume was exceeded so that of course they will be exploded and collapse.

Despite of less than one second exist, the very high heat energy and pressure with temperature more than 5000 K and pressure more than 1000 atm respectively would be produced from the exploding bubbles [7,16,17]. The aforementioned high heat energy and pressure would be able to initiate any suitable chemical reactions and physical change of both PSNs particles and precursor of Cd metal. Adopting the mechanism of "hot spots" aforementioned, we propose a series of chemicals reactions during reduction process which initiated by the ultrasonic wave exposure as equations (1) up to (7). It is clear that every two hydrogen radicals can deliver its electron to one ionic cadmium metal (Cd^{2+}) rather than hydroxyl radical.

Donating the electron to Cd^{2+} ion can reduce it become cadmium metal nanoparticles (Cd) coincide leaving ionic hydrogen (H^+) in the aqueous medium. These sequent reactions then would be proceeded to associate the ion H^+ to nitric (NO_3^-) become a nitric acid molecule (HNO_3). Finally these cycles of chemical reactions would be terminated by dissociating synchronically HNO_3 to nitrogen dioxide gas (NO_2) and hydroxyl radical because of heat energy exposure that released from the bubbles explode. Visually, the interesting mechanism of the "hot spot" arguments can be illustrated schematically such as Fig.3.

In addition, Fig.3 is another possibility, here the high temperature heat energy produced from the bubbles explode would affect and excite pi electrons of PSNs benzene ring become more reactive towards Cd^{2+} ions to form coordination covalent bonding pi-Cd^{2+}. In this situation, then the very reactive radical of ·OH would deliver its electron towards ion Cd^{2+} to reduce it become Cd metal nanoparticles. This attractive phenomena would be of course able to drive the formation of a bridge of which connected two PSNs particles adjacent each other. Even it was not impossible to promote the formation of cross linking bonding intra PSNs particle which connected between

polystyrene backbones chains adjacent each other such as Schexnailder's statement of a similar case [1].

On the other hand, it is very attractive since continuous laser beam of 633 nm wave length straightforward that irradiated towards composite material of PSNs/CdMNp could further reduce the rest of Cd metal precursor that hold on the particle surface of PSNs/CdMNp which not been reduced during ultrasonic agitation such as shown in Fig. 2c. We can see very clear in this Figure that many white colour dots settle hold on the particles surface of PSNs/CdMNp. We do suspect these dots are agglomerated Cd metal nanoparticles which formed during laser irradiation. Using the very common and widely well known as formula of photonic energy of electromagnetic wave E that expressed as $E = hc/l$ whereby h, c and l each is a Planck constant (6.62×10^{-34} m^2 kg s^{-1}), speed of light in vacuum space (3.0×10^8 ms^{-1}) [18] and laser beam wave length (633 nm) respectively, we can calculate this laser photonic energy is approximately 1.0×10^{-22} kJ. Hence this energy will be equal to 1.2×10^{-19} kJ for 20 minute laser exposure. It is reasonable that the quantity of the laser photonic energy would just powerful to affect significantly then break down any chemical bond energy or physical interaction of less than 1.2×10^{-19} kJ. In relation to the sequences chemical reactions which expressed in Fig. 3a we can see that actually HNO_3 molecule is an impurities/contaminant that might be produced along the manufacturing process of the composite material of PSNs/CdMNp, see equation (4).

Fortunately bonding energy of O_2NOH-$OHNO_2$ (nitric acid dimer) is less than 1.2×10^{-19} kJ per molecule. This energy value was calculated approximately from O'Donnell *et al*'s reports which stated that dissociation energy bonding of OH-$HONO_2$ was around 5.3 kcal mol^{-1} [19]. Considering the Avogadro number stated that the quantity of 1 mole molecule will be equal to 6.023×10^{23} molecular particles and 1 caloric equal to 4.186 joule [18] so the energy value of 5.3 kcal mol^{-1} will be equal to 3.68×10^{-23} kJ molecule-1≈ 0.4×10^{-23} kJ $molecule^{-1}$. Hence this O_2NOH-$OHNO_2$ contaminant can be dissociated properly by laser irradiation of 633 nm for 20 minutes exposure. As it is well widely known that HNO_3 is a very strong oxidizing agent so we could very easy guess that it will be changed to both hydrogen radical, .H and nitrate radical NO_3· under the laser beam exposure. Furthermore this hydrogen radical would be absorbed by $Cd(NO_3)_2.4H_2O$ that hold on the composite material surface of PSNs/CdMNp and subsequently reduce Cd^{2+} to be Cd metal nanoparticles according the equation (3). While

$$2HNO_{3\,(s)} \xrightarrow{\text{laser beam irradiation}} 2H^{\cdot}_{(g)} + 2NO_3^{\cdot}{}_{(g)} \quad (8)$$

$$Cd(NO_3)_2.4H_2O_{(s)} \xrightarrow{\text{laser beam irradiation}} Cd(NO_3)_{2\,(s)} + 4H_2O_{(g)} \quad (9)$$

$$Cd(NO_3)_{2\,(s)} + 2H^{\cdot}_{(g)} \longrightarrow Cd^0_{(s)} + 2H^+_{(g)} + 2NO_3^{\cdot}{}_{(g)} \quad (10)$$

$$4NO_3^{\cdot}{}_{(g)} + 4O_{n\,(g)} \longrightarrow 4NO_{2\,(g)} + 4O_{2\,(g)} \quad (11)$$

$$2H^+_{(g)} + O_{n\,(g)} \longrightarrow H_2O_{(g)} \quad (12)$$

$$2HNO_{3(s)} + Cd(NO_3)_2.4H_2O_{(s)} + 5O_{n\,(g)} \longrightarrow \underset{\text{cadmium metal nanoparticle}}{Cd^0_{(s)}} + 4NO_2 + 4O_2 + 5H_2O \quad (13)$$

that, radical NO_3· changed synchronically to be NO_2 and O_2 since gaining reactive oxygen O_n from atmospheric air. That is why metal nanoparticles of Cd covered a particle surface of composite material of PSNs/CdMNp. The speculative series of these reactions can be written in the following equations, (8) to (13). Here, equation (13) is the sum of total reactions of the equations of (8) up to (12).

In addition, another very attractive phenomenon can be shown when we put a square border on each morphology surface of Fig. 2 to find how many particles inside the square border aforementioned. In this case, based on the magnification scale that displayed in the Fig. 2, i.e. every 1 mm long in the figure represented 100 nm real size of composite material of PSNs/CdMNp, so when we determine 5 mm length as a basic square to calculate particle density of the composite, it would be approximately equivalent to 5×10^2nm length in nanoparticle scale. Hence we can see every $(5\times10^2\,nm)^2$ wide area of white color-marked square in Fig. 2a, 2b, 2c and 2d could loading 6 units of PSNs/CdMNp, 8 units of pristine PSNs, 7

$$\frac{d_{1000}}{(10^3\,\text{nm})} = \frac{P_{500}}{(5\times10^2\,\text{nm})} \quad (1a)$$

$$d_{1000} = \frac{(P_{500})(10^3\,\text{nm})}{(5\times10^2\,\text{nm})} \quad (1b)$$

$$d_{1000} = 4.0 \times (P_{500}) \quad (1c)$$

units of laser-exposed PSNs/CdMNp and 13 units of laser-exposed pristine PSNs respectively. These phenomena will be more interesting quantitatively if the terminology of particles density of PSNs or PSNs/CdMNp could be applied. In this situation, the particles density could be defined as the total amount of PSNs particles or PSNs/CdMNp that fully loaded by the

Table 1. Particles density of some fabricated PSN-based materials

Figure	Material	P_{500}/ particle*	d_{1000} / particle nm^{-2}**
2a	The composite material of PSNs/CdMNp	6	24
2b	Pristine PSNs	8	32
2c	Laser-exposed composite material of PSNs/CdMNp	7	28
2d	Laser-exposed pristine PSNs	13	52

**The particles amount of every (500 nm)^2 wide of area*
***It was defined as the particles number of every (10^{3}nm)^2 wide.*

wide area of (10^3 nm)^2, so the that intended density could be calculated by applying equations 1c, whereby d_{1000} and p_{500} each is the intended particles density of PSNs in wide area of (10^3 nm)^2; and the amount of PSNs particles in wide area of (5x10^2 nm)^2 of the associated square area respectively.

Those indicated that the Cd nanoparticles that incorporated in PSNs can enlarge significantly the distance of inter particles PSNs or PSNs interface in line with the particles density of PSNs/CdMNp that lower compared to that of pristine PSNs. This fact has a very important implication for porous material fabrication which is widely used in technological processes associated with adsorption and catalysis phenomena [13,20]. Moreover, here, we propose a constant of 4.0 as constant of conversion to calculate nanoparticles density in either every square or circle area with 500 nm side lengths or 500 nm diameter lengths. Therefore by applying equation 1c, we found that the particles density of composite of PSNs/CdMNp; pristine PSNs; laser-exposed composite of PSNs/CdMNp; and laser exposed-pristine PSNs could be summarized in Table 1.

3.2. Analysis of ATTTR-FTIR spectra

It can be very clear seen in Fig.4 that wave number peaks of around 3400 cm^{-1} which representing bonding stretching vibration of SiO-H [13, 21] (see Fig.4a and 4b), had been disappeared at all due to 633 nm laser beam irradiation for 20 minute exposure (see Fig.4c). Because the bonding of SiO-H (more precise SiO….H) might a chemical bonding that occurred between silicon wafer surface of the supporting material and hydrogen atom of a phenyl (*ph*) ring moiety of PSNs polystyrene, i.e. C-H$_{sp2}$ (Fig. 4d) so the chemical bond which occurred between the supporting material and the comopsite of PSNs/ CdMNp have been totally lost under the laser irradiation. In line to the aforementioned bond collapsing we see wave number peaks 3060 cm^{-1} and 2900 cm^{-1} which is representing stretching vibration of a phenyl atomic hydrogen, C-H$_{sp2}$ (Fig.4d) and a polystyrene backbone hydrogen, C-H$_{sp3}$ (Fig.4d) [13,22] respectively almost went disappeared (see Fig. 4c). These interesting phenomena might indicate that both bonding C-H$_{sp2}$ and C-H$_{sp3}$ undergone collapsed drastically so that it could not respond the infrared beam that hit it. In this situation the associated phenyl ring structure became unstable and then it might undergo self-rearrangement to be more stable non-aromatic cycloalkene (see Fig.4e). This phenomenon possibility was attractively indicated by the fact of disappearing wave number peaks 1600 cm-1 which represented bonding stretching vibration of phenyl moiety C=C$_{sp2}$ (see Fig.4d), and bending vibration of bonding C-H$_{sp3}$ which was expressed as wave number peaks of around 1450 cm^{-1} [13, 22] were still appear sharply after laser irradiation (see Fig. 4e).

Of the aforementioned phenomena above we found the uniqueness properties of composite material of PSNs/CdMNp, that is despite of C-H$_{sp2}$ phenyl moiety collapsed which is indicated by its wave number representative peaks, i.e. 3060 cm^{-1} was not appeared during laser beam irradiation, but wave number peaks 699 cm^{-1} and 668 cm^{-1} of which representing vibration of phenyl wagging and twisting respectively [13, 22] were still significantly appear during the laser irradiation (see Fig.4c). The uniqueness properties was attributed that probable the aromatic ring of phenyl moiety actually did not totally destructed but it was just transformed to be non-aromatic during the laser exposure. This possibility was clearly confirmed by its surface morphology image that still exist as a spherical shape as shown in Fig. 2c.

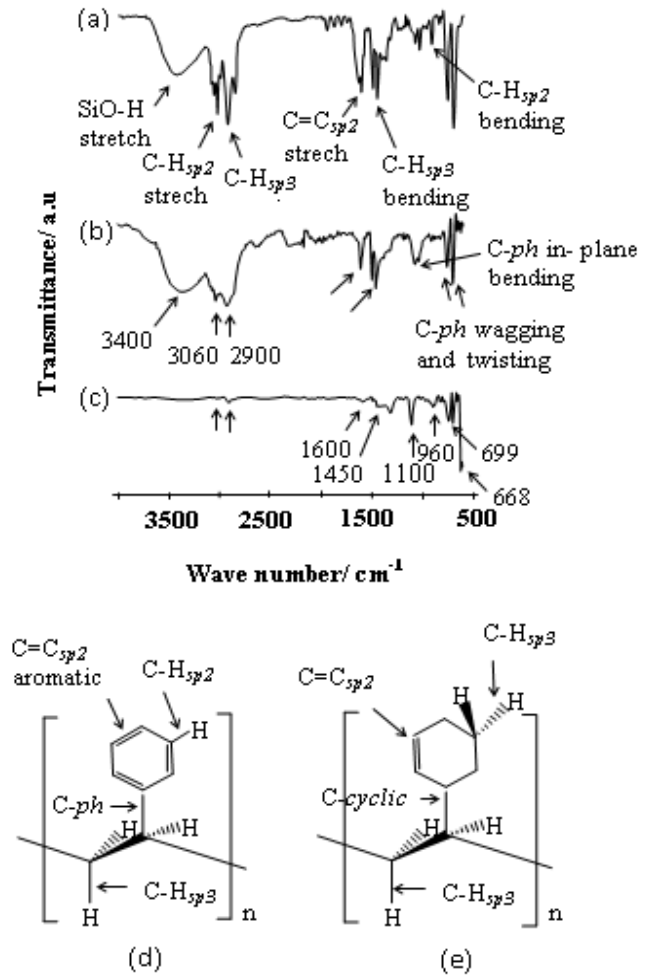


Figure 4. ATR-FTIR spectra of pristine PSNs (a), composite material of PSNs/CdMNp (b), and Laser-exposed composite material of PSNs/CdMNp (c). These spectra were asdopted from reference [13] for spectra (b) and (c). Illustration of Polystyrene molecular structure unit (d) and (e).

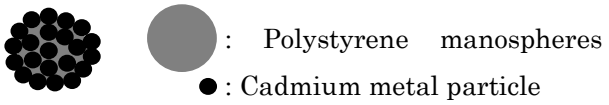


Figure 5. Proposed model for the composite material structure unit of PSNs/CdMNp. Here, surface of PSNs particle was fully covered by agglomerated Cd metal nanoparticles.

This phenomenon might be very unique due to the Cd metal nanoparticles that settled therein could act as a powerful shield that selectively prevent a lot of covalent bonds collapsed under laser radiation exposure of 633 nm wavelength for at least 20 minute at atmospheric pressure and room temperature of about 20 ^{o}C. Those facts lead to a very attractive material structure of composite material of PSNs/CdMNp where in this case the surface of PSNs particles have been successful covered by agglomerated Cd metal nanoparticles. Thus, we could propose the structure of a unique nanomaterial model of composite material of PSNs/CdMNp as that depicted in Fig. 5 of which will be have very important prospect especially for the engineering and manufacturing strategy of porous nanocomposite material.

4. Conclusions

It can be concluded that the basic molecular structure of polystyrene framework that construct the composite material of PSNs/CdMNp did not change significantly compared to that of pristine PSNs. The existence of Cd metal nanoparticles which covered the surface of PSNs could provide at least two impacts especially to its physical properties, those are (1) make capable to form a dumbbell-like structure between two units adjacent particles of the composite of PSNs/CdMNp, and (2) capable to enhance the porosity of the PSNs-based composite material compare to the pristine PSNs.

The most important and interesting phenomenon was the existence of Cd metal nanoparticles on the surface of PSNs which might able to act selectively as a powerful shield to prevent certain covalent bond of polystyrene framework to collapse during continuous laser exposure of 633 nm wavelength for at least 20 minute at atmospheric pressure and room temperature of about 20^{o}C. This research was successfully performed since the throughout surface morphology of the composite material of PSNs/CdMNp could be well analyzed and further explored to create a structure material model of the aforementioned composite.

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References

[1] Schexnailder, P. and Schmidt, G. (2009). Nanocomposite polymer hydrogels, *Colloidal and Polymer Science* 287: 1-11.

[2] Yon, H.; Lee, J.; Park, D. W.; Hong, C. K.; and Shim, S. F. (2010). Preparation and electrorheological characteristic of CdS/Polystyrene composite particles, *Colloidal and Polymer Science* 288: 613-619.

[3] Zhao, X.; Ding, X.; Deng, Z.; Zheng, Z.; Peng, Y.; and Long, X. (2005). Thermoswitchable Electronic Properties of a Gold Nanoparticle/ Hydrogel Composite, *Macromolecular Rapid Communications* 26(22): 1784-1787

[4] Tseng, C.C.; Chang, C.P.; Ou, J.L.; Sung, Y.; and Ger, M.D. (2008). The preparation of metal-styrene oligomer and metal-SSNa nanocomposites through single thermal process, *Colloids and Surface A: Physicochemical and Engineering Aspects* 330: 42-48.

[5] Muraviev, D. N; Ruiz, P.; Munõz, M; and Macanás, J. (2008). Novel strategies for preparation and characterization of functional polymer-metal nanocomposite for electrochemical applications, *Pure Applied Chemistry* 80(11): 2425-2437.

[6] Kamrupi, I.R; Phukon, P; Konwer, B.K; and Dolul, S.K. (2011). Synthesis of silver-polystyrene nanocomposite particles using water in supercritical carbon dioxide medium and its antimicrobial activity, *The Journal of Supercritical Fluids* 55: 1089-1094.

[7] Zhang, K.; Park, B.J.; Fang, F.F.; and Choi, H. J. (2009). Sonochemical Preparation of Polymer Nanocomposite, *Molecules* 14: 2095-2110.

[8] Gedanken, A (2004). Using Sonochemitry for the Fabrication of Nanomaterials, *Ultrasonics Sonochemistry* 11: 47-55.

[9] Gedanken, A (2003). Sonochemistry and its application to nanochemistry, *Current Science* 85(12): 1720-1722.

[10] Wei, G.; Wen, F.; Zhang, X.; Zhang, W.; Jiang, X.; Zheng, P.; and Shi, L. (2007). A general method to synthesis of amphiphilic colloidal nanoparticles of CdS and noble metals, *Journal of Colloid and Interface Science* 316: 53-58.

[11] Antolini, F; Pentimali, M; Luccio, T.D; Terzi, R; Schioppa, M; Re, M; Mirenghi, L; and Tapfer, L. (2005). Structural characterization of CdS nanoparticles grown in polystyrene matrix by thermalytic synthesis, *Materials Letters* 59: 3181-3187.

[12] Wu, D.; Ge, X.; Huang, Y.; Zhang, Z.; and Ye, Q. (2003). g-Radiation synthesis of silver-polystyrene and cadmium sulfide-polystyrene nanocomposite micropoheres, *Materials Letters* 57: 3549-3553.

[13] Wibawa, P. J.; Saim, H.; Agam, M.A.; Nur, H. (2011). Design, Preparation and Characterization of Polystyrene Nanospheres Based-Porous Structure towards UV-Vis and Infrared Light Absorption, 2011 International Conference on Physics Science and Technology (ICPST 2011), *Physics Procedia* 22: 524 – 531.

[14] Xiao, G.; Gao, P.; Wang, L.; Chen, Y.; Wang, Y.; and Zhang, G. (2011). Ultrasonochemical-Assisted Synthesis of CuO Nanorods with High Hydrogen Storage Ability, *Journal of Nanomaterials* 2011: 1-6.

[15] Novik, A.A. (2010). Applying of Ultrasound for Production of Nanomaterials, *XXII Session of the Russian Acoustic Society, Session of the Scientific Council of Russian Academy of Science on Acoustic*, 15-17, Moscow.

[16] Campos, M.D.; Muller, F.A.; Bressiani, A.H.A.; Bressiani, J.C. and Greil, P. (2007). Sonochemical Synthesis of Calcium Phosphate Powders, *Journal of Material Science: Materials in Medicine* 18: 669-675.

[17] Naddeoa, V.; Belgiornoa, V. and Napolib, R.M.A. (2007). Behaviour of Natural Organic Matter during Ultrasonic Irradiation. *Desalination* 8: 40-44

[18] Mohr, P. J; Taylor, B.N; and Newel, D.B. (2008). CODATA Recommended Values of the Fundamental Physical Constants 2006, *Reviews of Modern Physics* 80(2): 633-730.

[19] O'Donnell, B. A; Li, E.X.J; Lester, M.I; and Fransisco, J. S. (2008). Spetroscopic identification and stability of the intermediate in the OH + $HONO_2$ reaction, *Proceeding of the National Academy of Science* 105(35): 12678-12683.

[20] Hua, M.Y.; Chen, C.J., Chen, H.C., Tsai, R.Y.; Cheng, W.; Cheng, C.L.; and Liu, Y.C. (2011). Preparation of a Porous Composite Film for the Fabrication of a Hydrogen Peroxide Sensor, *Sensor* 11: 5873-5885.

[21] Socrates, G. 3rd Ed. (2001). *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons: 52-75.

[22] Luo, H. L. Sheng, J. and Wan, Y. Z. (2008). Preparation and characterization of TiO_2/polystyrene core–shell nanospheres via microwave-assisted emulsion polymerization, *Materials Letters* 62: 37– 40.