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Article

Preparation of VO_2 Nanoparticles with Surface Functionalization for Thermochromic Application

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Abstract. This recent work investigates on the modification of metal oxide particles surface by the addition of amorphous coating layer. This core-shell structure is expected to decrease particles aggregation and increase their distribution in polymer matrix. VO_2 particles were firstly prepared via hydrothermal process with 87% yield and XRD analysis showed that VO_2 monoclinic was obtained with 100% of purity. XPS technique also showed that the surface of VO_2 particles contains -OH group which is promising to form the strong covalent bond with silane coupling agent. The addition of functional groups on the surface of VO_2 particles was then performed by the grafting of (3-Aminopropyl) triethoxysilane (APTES) via the silane anchoring group with 1:10 weight ratio VO_2/APTES. The effect of solvent was also studied by using 10 ml of different solvent such as distilled water, ethanol and chloroform during surface coating. The TEM image clearly shows the presence of the thick organic layer on VO_2 particles and as a result, the core-shell structure was perfectly identified. The round shape of coated VO_2 particles was detected with small aggregation by SEM imageries. Furthermore, the presence of characteristic absorption band of C-H, Si-O-C, Si-O-Si and NH stretching in the FTIR spectra of coated VO_2 particles confirmed the existence of APTES on the surface of VO_2 particles prepared in distilled water and ethanol.

Keywords: Surface functionalization, silane, thermochromic composite film, vanadium dioxide.

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1. Introduction

The conservation of energy becomes nowadays the center of interest in many research fields, especially in sustainable energy developments which emphasize in the increase of an energy efficiency to reduce the use of energy as much as possible. "Smart window" [1] has received widespread consideration for this purpose, especially in the modern architectures. The smart window has the intelligent control when receiving external stimulation such as heat and sunlight. This smart window could be produced by coating some specific material on the glass surface which could reflect the heat radiation from the sunlight in responsive of these external factors. The thermochromic material is one of the most appealing materials to be used in this aspect. In this case, thermochromic material could switch the reflection properties when the temperature change across critical temperature (T_c) and decrease the transmitted radiation passing to inside the building. In consideration of thermochromic properties, Vanadium dioxide (VO_2) is one of the most promising to the glass coating material because of its low critical temperature (68°C) [2]. For practical application, thermochromic VO_2 particles could be directly deposited on the glass substrate by physical or chemical process such as sputtering or chemical vapor deposition [3]. These coating processes could be in-situ incorporated in the glass during manufacturing process. Nevertheless, the direct in-situ coating suffers from some inconvenient and lacks of flexibility. There still remains another important challenge in improving the practical application of a VO_2 based polymeric smart film for smart window application. In this point of view, thermochromic VO_2 particles should be separately fabricated and then mixed with the selected polymeric matrix. The melt process allows the formation of VO_2 polymer composite film which retains the thermochromic properties and could be cut to any shape and size, therefore very flexible for the usage. The major problem of nanoparticle application is the lack of chemical bonding between metal oxide and the polymer chain. Similar to another metal oxide nanoparticle, when VO_2 particles are reduced in size, the effective surface area highly increases. Therefore, metal oxide nanoparticle tends to form large agglomeration because of their tremendously high surface area/particle size ratio. As described in the previous work [4], mechanical properties and thermochromic properties of the VO_2/polymer composite are strongly affected by the dispersion of the metal oxide particles in polymer matrix. This effectively correlates to interfacial adhesion, the size of nanoparticles agglomeration and the interaction between nanoparticles surface and polymer chain. This interaction between individual nanoparticle is thus much stronger than the small interaction between inorganic material and organic polymeric material host [5], resulting to very weak adhesion strength. In order to overcome this limitation, many attempts were achieved, considering method for enhancement of nanoparticles-polymer adhesion and for acquirement of better compatibility.

Surface modification of metal oxide nanoparticles is clearly one of effective way to reduce its surface energy and to improve its distribution in solvent and also in polymer matrix. Especially the grafting of functional group onto the surface can increase the chemical bonding between modified particle and polymer, in that way increasing their adhesion. When the proper surface modification is achieved by forming the strong physical and chemical interaction between two phases, better distribution and better affinity of particle in polymer matrix could be attained. To do so, the organic layer could be grafted on the surface by polymerization reaction or by means of using coupling agent and anchoring group. Rich with surface bound-hydroxyl group (OH) in exposure to air or upon some activation process, metal oxide surface can undergo functionalization process through anchoring group. Many organic structures could be covalently grafted on the oxides by different attachment groups possible, such as silanes, phosphonates, carboxylates, catechols and alkenes. Among these features, surface modification with alkylsilanes is one of the most promising for preparation of organic layer on metal oxides [6]. The silane anchoring group is appealing because of the strong interaction between organosilane ($RSiX_3$, $RSiX_2$ or R_3SiX) and metal oxide and also it was confirmed that the bonding of functional groups was realized through Si-O-M bonds [7]. This covalent linkage between the substrate and the anchoring group affords organic monolayer or multilayer which is sufficiently stable to undergo further chemical modification and prevent the particles aggregation. Due to the promising application on photocatalytic, most of research on metal oxide surface coating mainly focuses on TiO_2 nanoparticle. Polymer such as polyurethane [5] and fluoropolymer [8] has been successfully mixed with formerly surface modified TiO_2 particles. Various alkoxysilane such as (3-Aminopropyl) trimethoxysilane (APTMS) and (3-Aminopropyl) triethoxysilane (APTES or KH-550) were grafted on the TiO_2 surface, improving the nanoparticles dispersion and mechanical properties of the polymer composite. In the other hand, surface modification of VO_2 particles was barely investigated.

The core-shell structure of VO_2 particles is mainly based on inorganic surface coating such as VO_2@TiO_2 [8], VO_2@Fe [9], VO_2@Al-O [10] and VO_2@ZnO [11]. Most of these previous researches have mostly concentrated on improving thermochromic properties of VO_2 particles, including luminous transmittance and solar regulation efficiency, along with the particle durability which could effectively increase when VO_2 particles is protected by these inorganic layers. As aforementioned, the core-shell structure is demonstrated to be an effective way to stabilize the nanoparticle in the polymer suspension and to protect the nanoparticle. Herein, this work presents one approach to obtain robust surface modification of the VO_2 particles to be ready for further incorporation to polymeric matrix. In this paper, we prepared VO_2 nanoparticles from hydrothermal process and modified the surface with organosilane such as (3-Aminopropyl) triethoxysilane (APTES). The effect of coating solvent was thoroughly investigated by using FTIR spectrometer, X-Ray diffractometer, Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM). This work is expected to shorten the distance of VO_2 particles to real VO_2 polymer films composite application.

2. Materials and Methods

2.1. Materials

Vanadium (V) oxide (98%, Sigma-Aldrich), citric acid (99.5%, Loba chemie) and ethanol (Grade AR, RCI) were used without any purification for the synthesis of VO_2 particles. (3-Aminopropyl) triethoxysilane (98%, Sigma-Aldrich) were used for the modification VO_2. Distilled water, ethanol (Grade AR, RCI) and chloroform (99%, Sigma-Aldrich) were used for investigation of effect of grafting solvent.

2.2. Preparation of VO_2 Nanoparticles via a Hydrothermal Process

VO_2 particles were synthesized via a hydrothermal process. 1.81 g of Vanadium (V) oxide was suspended with 50 ml of distilled water and added by 5.76 g of citric acid solution in 50 ml of distilled water, drop by drop. The yellow suspension was stirred until the homogeneous solution occurs and then kept at 80 °C for 24 h. The blue clear solution was filtered before transferred to the stainless Teflon-lined Parr autoclave which was heated at 200°C for 24 h in hot air oven. After the black suspension was completely cooled down to room temperature, the black solid particle was recovered by filtration and then washed three times by distilled water and ethanol. The obtained blue black precipitate was then dried in vacuum oven at 80°C for 3 h and ignited in the tube furnace under the nitrogen atmosphere at 700 °C for 1 h. Hydrothermal process followed by calcination is demonstrated in Fig. 1.

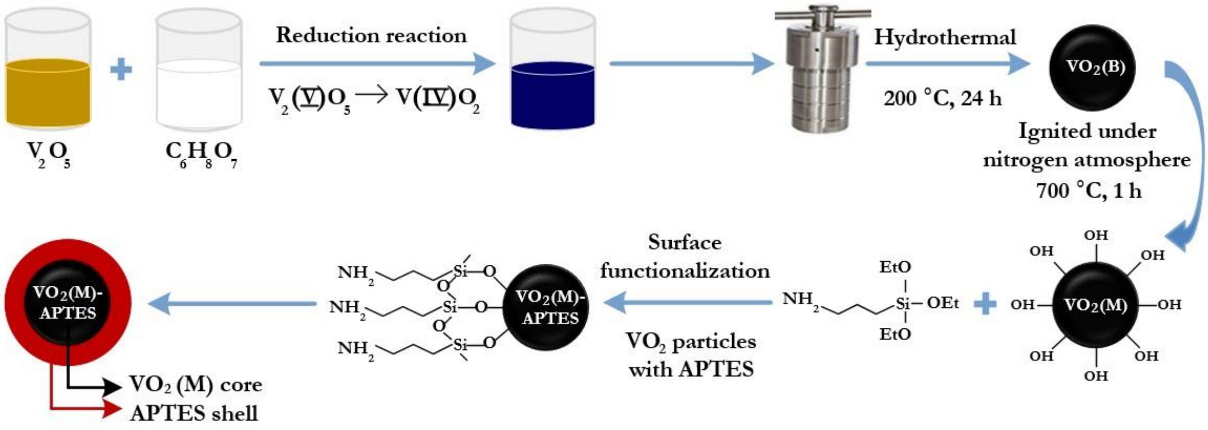

Fig. 1. Schematic of the preparation of VO_2 nanoparticles with surface functionalized for thermochromic application.

2.3. Preparation of Surface Functionalization of Monoclinic VO_2 Particles by (3-Aminopropyl) Triethoxysilane (APTES)

The addition of APTES on the surface of VO_2 particles was performed via silane anchoring group using (3-Aminopropyl) triethoxysilane (APTES) as coupling agent. 0.1 g of previously synthesized VO_2 particles was mixed with 1 g APTES (the ratio between VO_2 and APTES at 1:10 weight ratio) were used for this purpose. In order to study the effect of grafting solvent, 10 mL of various solvent such as distilled water, ethanol and chloroform were employed. VO_2 particles was firstly suspended with 10 ml of solvent and 1 g APTES for 1 h in ultrasonic bath, then separated by centrifugal. The coated VO_2 particles were collected, washed three times with the solvent and dried in vacuum oven under 80°C for 3 h.

2.4. Characterizations of VO_2 Particles

The crystalline structures and crystal sizes of the synthesized VO_2 particles (uncoated and coated with APTES) were studied by using an X-ray diffractometer (XRD, Bruker AXS D8-Discover) in the 2θ range of 10-80 Cu-Kα radiation (λ =1.54178 Å). The accelerating voltage and the current used were 40 kV and 40 mA, respectively.

An X-ray photoelectron spectroscopy (XPS) technique was used to prove the existence of functional group on the surface of VO_2 particles. The XPS data were collected in the V $2p^{3/2}$, O 1s and C 1s binding energy regions, using an AXIS ultra DLD (Kratos Analytical Ltd., Manchester, England), equipped with Avantage Data System software.

In addition, functional groups on the surface of VO_2 particles after grafting with silane anchoring group of APTES, were followed by using an attenuated FTIR spectrophotometer (Thermo instrument, iS5 model). The samples were scanned over wavenumbers ranging between 500 and 4,000 cm^{-1}.

The morphology of the neat VO_2 particles and coated VO_2 particles were examined by using both the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) techniques. The SEM experiment was carried out by using a JEOL (JSM 6610LV) machine, equipped with a secondary electron detector and energy dispersive X-ray detector (EDX). The accelerating voltage used was 10-30 kV. The sample was coated with gold prior to carrying out the SEM experiment. The TEM experiment was carried out by using a JEOL JEM-2100 (JEOL, Peabody, MA, USA) microscope with an accelerating voltage of 200 kV. The TEM specimen was prepared by dissolving 1 mg of the VO_2 particles in 10 ml of isopropanol, followed by sonication for 30 min. The solution was dropped on a copper grid and then dried at 60 °C.

3. Results and Discussion

3.1. Hydrothermal Process of Monoclinic VO_2 Particles

VO_2 particles were prepared from reduction reaction of V_2O_5 by citric acid followed by hydrothermal and calcination process (Eq. (1)) [12].

$$V_2O_5(V^{5+}) \rightarrow V_3O_7(V^{4.67+}) \rightarrow V_4O_9(V^{4.5+}) \rightarrow V_6O_{13}(V^{4.33+}) \rightarrow VO_2(V^{4+}) \tag{1}$$

Monoclinic VO_2 particles were obtained with 87 % yield and the purity attained 100 % as shown in Fig. 2. The XRD pattern of initial hydrothermally prepared VO_2 particles showed that the obtained VO_2 particles are highly crystalline with monoclinic phase of 100 %. There are crystalline planes at (011), (200), (210), (220), (022), (013) and (202) at 27.86 °, 37.05 °, 42.23 °, 55.53 °, 57.53 °, 65.00 ° and 70.44° respectively. From these patterns, all peaks correspond to monoclinic VO_2 particles and perfectly correlate with the previous research of Zhang et al.[13] and Valmalette et al. [14]. Moreover, by applying Scherrer's equation, the crystal sizes of the synthesized VO_2 particles were about 26.9 nm [4] which was revealed to be too big for VO_2-based smart window application [15]. To confirm the oxidation state of VO_2 particles surface functional group, X-ray photoelectron spectroscopy (XPS) was carried out and the result is shown in Fig. 3. The corresponding XPS pattern proves the existence of V, O and C. elements, where the carbon of uncoated VO_2 is attributed to surface contamination by organic substance [16]. It could be found that the V $2p^{3/2}$ peak of the nanoparticle is centered at 515.9 eV which is in good agreement with pure VO_2 (516.0 eV) and perfectly corresponds to V^{4+} in VO_2 [17] and [18]. Finally, the peak at 530 eV is assigned to O 1s of O^{2-} ions in the crystal lattice of V ion array [11]. XPS spectrum demonstrated that the surface of particles contains -OH group which is promising to form the strong covalent bond with silanol group of silane coupling agent [6].

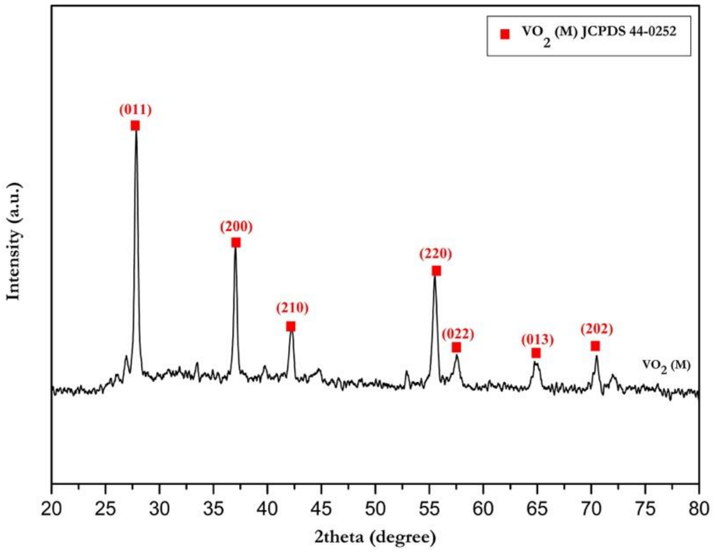

Fig. 2. XRD pattern of the neat VO_2 particles prepared via hydrothermal process.

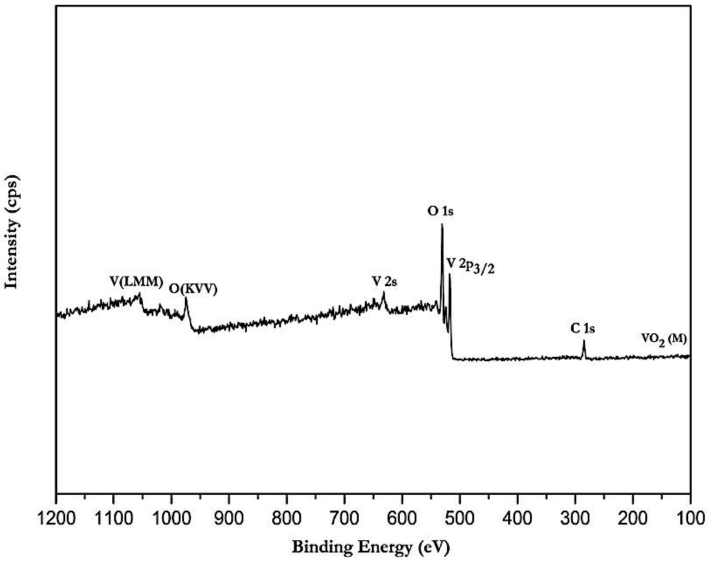

Fig. 3. XPS pattern of the VO_2 particles prepared via hydrothermal process.

The morphology of VO_2 particle was then characterized by SEM images presented in Fig. 4(a) where the large distribution of VO_2 particles with an average diameter of approximate 0.4 μm was identified. This value is however higher than that previously calculated by Scherrer's equation. Moreover, VO_2 particles are all round shape with some agglomeration, caused by the sintering process which could occur during calcinations at very high temperature. As shown in Fig. 4(b), the TEM images gave clear evidence that the particles with an average diameter of approximate 0.3 μm, are clearly round shape and without any coating shell.

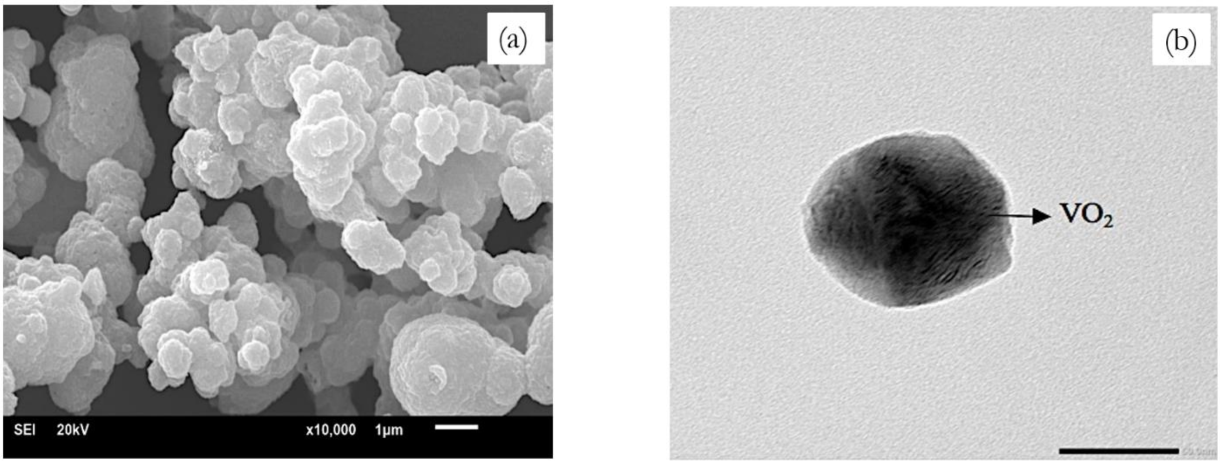

Fig. 4. (a) SEM and (b) TEM images of uncoated monoclinic VO_2 particles prepared via hydrothermal process.

3.2. Surface Functionalization of Monoclinic VO_2 Particles by (3-Aminopropyl) Triethoxysilane (APTES)

The addition of functional groups on the surface of VO_2 particles was performed by grafting the silane anchoring group with VO_2 and APTES with weight ratio at 1:10. To study the effect of solvent, 10 ml of different solvent were used such as distilled water, ethanol and chloroform. Figure 3 presents the proposed three-step mechanism for the formation of monolayers from APTES by Pujari et al. [6]. During the grafting, the polar VO_2 surfaces absorb molecule of water which can undergo subsequence hydrolysis with organosilane to produce hydroxysilane. The Van der Waals force between polar VO_2 surfaces and -OH of silane group yields some aggregation between hydroxysilanes. Approached closely to each other, the condensation between Si-OH groups can take place to form Si-O-Si crosslinked network with the neighboring silanol groups. This Si-O bonding is also the strong connection point between anchoring group and VO_2 surface, consequently forms the thick coating layer on the metal oxide surface. From this mechanism, the presence of water molecule is essential in hydrolysis of ethoxy group to silanol group for subsequent condensation reaction.

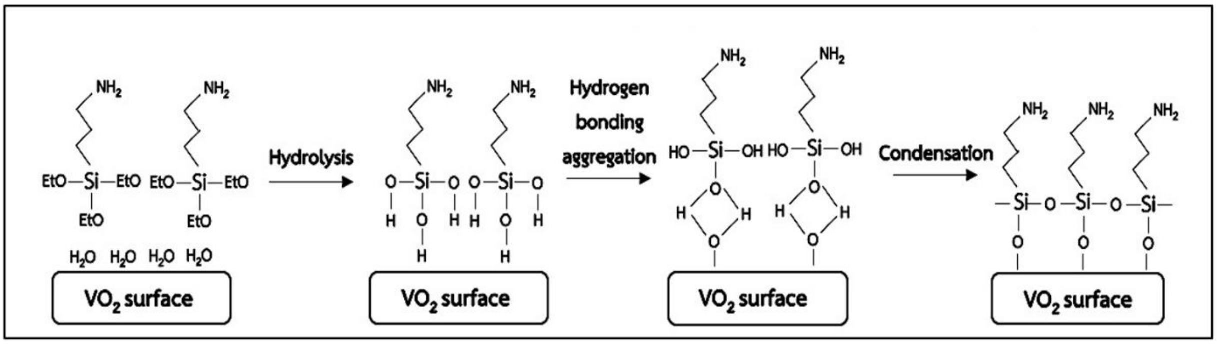

Fig. 5. Reaction scheme for the three-step mechanism for monolayer formation by silanes (APTES) on OH terminated surfaces [6].

The XRD pattern shown in Fig. 6 exhibits the apparent loss of monoclinic crystallinity of VO_2 particles after coating because all characteristic peaks appear to be flatten. Nevertheless, all characteristics peaks of crystalline planes (011), (200), (210) and (220) at 27.86 °, 37.05 °, 42.23 ° and 55.53 ° respectively, are still presented.

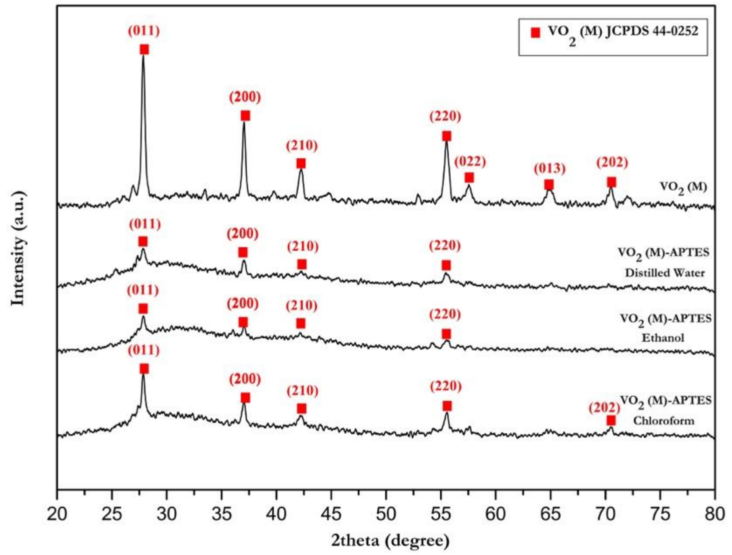

Fig. 6. XRD pattern of VO$_2$ particles coated by APTES using 10 ml of various solvent.

The presence of APTES coating on the surface of VO$_2$ particles in different solvent during the grafting was studied by FTIR spectroscopy as shown in Fig. 7. The characteristic absorption bands from 3200-3400 cm^{-1} and the weak peak at 1616.3 cm^{-1} in the spectrum of the uncoated VO$_2$ particles were attributed to the stretching vibration of hydroxyl groups (O-H) on the particle surface and absorbed water on VO$_2$ particles [19]. The characteristic of C=O and C=C stretching vibrations were observed in distilled water and ethanol at 1707 cm^{-1} and 1633.7 cm^{-1}, respectively. The bands at 1450 cm^{-1} and 1160 cm^{-1} are attributed to deformation vibrations of C-H in CH$_2$ and CH$_3$, respectively. Furthermore, the bands at 780 cm^{-1} was assigned to the stretching vibration of Si-O-C and the band at 995.3 cm^{-1} was assigned to the Si-O-Si link vibrations indicated that some condensation of the silane chains had occurred. The weak peak observed at 3240-3360 cm^{-1} corresponds to N-H stretching from amine group situated at the end of chain. All of characteristic absorption bands were summarized in Table 1.

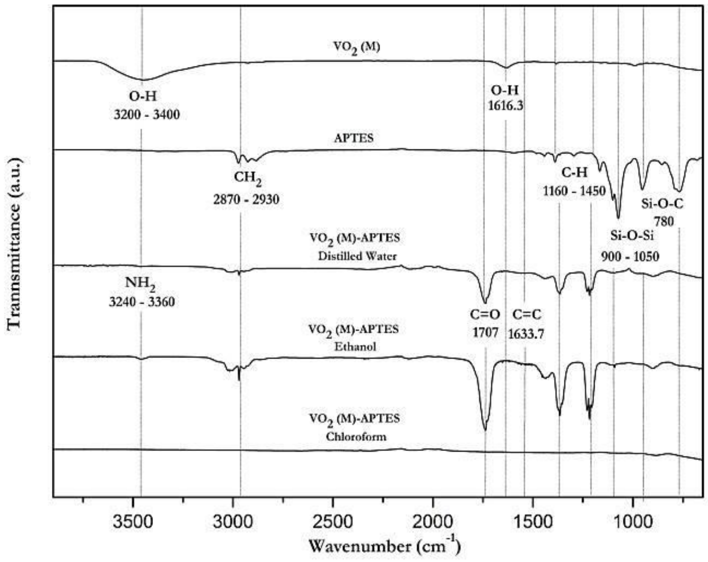

Fig. 7. FTIR spectra of VO$_2$ particles coated by APTES using 10 ml of various solvent.

These absorption bands could firmly confirm the existence of APTES layer on the surface of VO$_2$ particles. These peaks were on the other hand absent by using chloroform as solvent during grafting process. As mentioned before, the silanization step carried out with APTES requires hydrolysis of ethoxy group to silanol group ready for condensation reaction. The presence of water molecule or polar and protic solvent is strongly significant for APTES attachment on the metal oxide surface.

The mechanism of surface attachment of APTES was fully discussed for other metal oxides particles [6] such as silica [20] or magnetic iron oxides nanoparticles [21]. All this previous research justified that the silanization reaction was performed via two-stage reaction kinetics involving adsorption, chemical sorption and intraparticle diffusion process. However the surface coverage of vanadium dioxide has not been reported to the author's knowledge. Despite that the silanization reaction occurred during the grafting of APTES on vanadium oxide surface should be comparable to the other metal oxide particle because of the similar presence of hydroxyl group on the surface, demonstrated by XPS analysis (Fig. 3).

Table 1. The typical functional groups and corresponding wavenumber with the possible compounds.

Wavenumber (cm^{-1})	**Functional groups**	**Compounds**
3200 - 3400	O-H stretching vibrations	Hydroxyl groups
3240 - 3360	N-H stretchings	N-H stretch absorptions
2870 - 2930	C-H vibrations	Alkane chain
1707	C=O stretching vibrations	
1633.7	C=C stretching vibrations	
1616.3	O-H stretching vibrations	Hydroxyl groups
1160 - 1450	C-H vibrations	Alkane chain
900 - 1050	Si-O-Si vibrations	Silane group
780	Si-O-C stretching vibrations	Silane group

The morphology of VO_2 particles coated with APTES was systematically characterized by SEM and TEM instrument. Figure 8a-8c demonstrates the SEM image of coated VO_2 particles in different media. Agglomeration morphology of coated VO_2 particles was still observed in SEM images, and the nanoparticles appear to decrease in uniformity and increase in size after coating by APTES in ethanol and chloroform, when being compared with Fig. 4a. The average diameter of coated VO_2 particles becomes 1.5 μm while using distilled water (Fig. 8a) and ethanol (Fig. 8b) as grafting solvent. The average diameter of coated VO_2 particles becomes 2.5 μm while using chloroform (Fig. 8c) which produces larger VO_2 particles than those using distilled water (Fig. 8a) and ethanol (Fig. 8b) due to the effect of water adsorbed on the surface of the metal oxides. In general, size, uniformity and distribution of particle in polymer matrix are important parameters which strongly affect on the polymer-particle composite properties. Smaller particles have high surface energy and can easily aggregate when surface energy of large particle is reduced and aggregation is also decreased. However, distribution of large and coarse particle in polymer matrix is always difficult due to low dispersion ability, resulting to non-uniform polymer-particle composite. As found in previous work [4] [12], optical and thermochromic property of polymer composite film is strongly influenced by size and distribution of particle, especially visible light transparency and IR transmittance.

Figure 8d presents the TEM image of APTES coated VO_2 particles prepared solely in distilled water. The amorphous or organic coating shell is clearly identified with non-uniform thickness. The average diameter of VO_2 particles is approximately 0.5 μm with the coating thickness of 0.003-0.005 μm. This TEM image reveals the aggregation of core-shell structure of coated VO_2 particles, similar to the results obtained previously by Tong et al. [10], Chen et al. [11] and Srirodpai et al. [12].

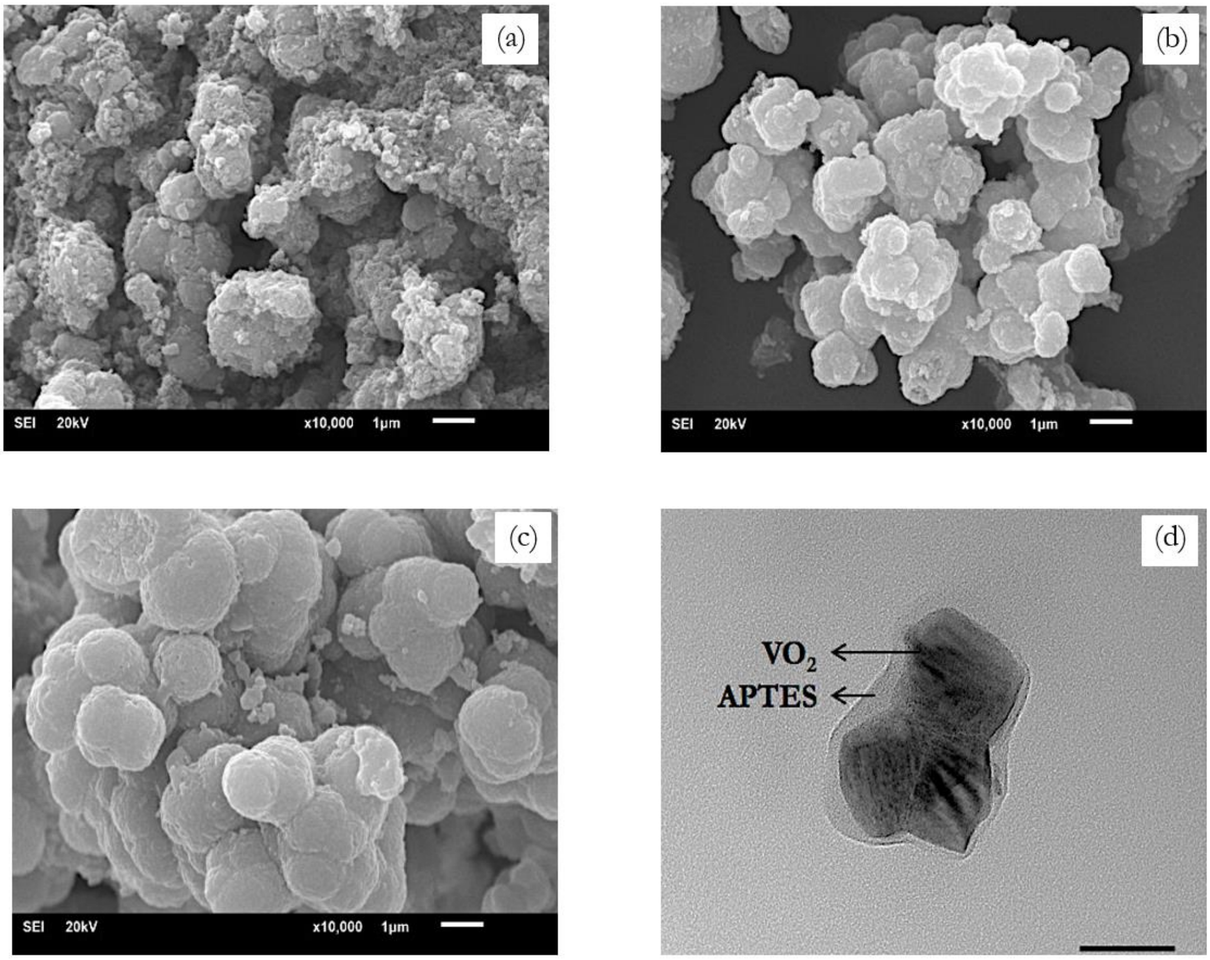

Fig. 8. SEM of VO_2 particles coated by APTES, by 10 ml of various solvent (a) distilled water, (b) ethanol, (c) chloroform and (d) TEM images of coated VO_2 particles prepared in distilled water.

In consideration of obtained thickness of APTES layer, the formation of multilayer [22] is also possible in addition of monolayer coating. This complication could be resulted from the physisorption, hydrogen bonding or electrostatic attachment besides covalent linkage [23] which present between the silane groups.The results show that APTES was successfully grafted on the surface of VO_2 particles and distilled water and ethanol are suitable solvents for APTES grafting. This result is consistent with the research of Daniel et al. [24] and Morrill et al. [25] where distilled water was selected for grafting process.

4. Conclusion

In this research, VO_2 particles were successfully prepared via hydrothermal process with 87 % yield and XRD analysis showed that VO_2 monoclinic was obtained with 100 % of purity. Agglomeration morphology of uncoated VO_2 particles was then confirmed by XPS technique which also showed that the surface of VO_2 particles contains -OH group which is promising to form the strong covalent bond with silane coupling agent.

VO_2 particles coated with APTES were prepared using different solvent such as distilled water, ethanol and chloroform. Various methods were employed for characterization of core-shell structure of VO_2 particles. The presence of characteristic absorption band of C-H, Si-O-C, Si-O-Si and NH stretching in the FTIR spectra of coated VO_2 particles confirmed the existence of APTES on the surface of VO_2 particles prepared in distilled water and ethanol. Moreover, the XRD analysis strongly confirms that VO_2 particles still preserve the monoclinic structure, however, with slightly loss of crystallinity after surface functionalization. Finally, the TEM image clearly shows the thick organic layer on VO_2 particles surface and as a result the core shell structure was perfectly identified. The round shape of coated particle was detected with small aggregation by SEM imageries. Distilled water and ethanol were proved to be the effective solvent for APTES grafting on monoclinic VO_2 particles.

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