

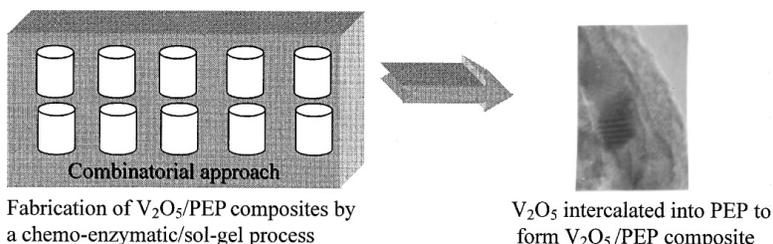
Article

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A Combinatorial Approach for the Synthesis and Characterization of Polymer/Vanadium Oxide Nanocomposites

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Vanadium pentoxide xerogels were prepared by the hydrolysis of $\text{VO}(\text{OC}_3\text{H}_7)_3$ by the sol–gel process. The generation of V_2O_5 was optimized by a combinatorial approach incorporating rapid screening by Raman spectroscopy. The latter revealed crystallites of vanadium oxide. Subsequently poly(*p*-ethylphenol) (PEP)/ V_2O_5 nanocomposites were prepared by the sol–gel process at the optimized molar ratio of $\text{VO}(\text{OC}_3\text{H}_7)_3/\text{H}_2\text{O}/\text{acetone} = 1/45/300$. Evidence from Raman spectra indicated that the presence of PEP did not interfere in the formation of crystalline V_2O_5 in the composites. FTIR also exhibited interaction between PEP and V_2O_5 . TEM showed a fibrous V_2O_5 structure dispersed in the PEP matrix.

Introduction

Hanak's combinatorial approach, which he called the "multiple-sample concept", sparked a revolution in materials research some three decades ago. It involved using sputtering to codeposit two or three elements or compounds on a substrate to create a continuum of composition.¹ It was found that the new method made materials discovery much more efficient. The generation of combinatorial libraries is now a well-established and significant approach in organic chemistry and is now utilized extensively toward the rapid synthesis and screening of biologically active molecules.² However, this technique is being applied in a limited manner to the synthesis of materials with enhanced properties, viz, superconducting, liquid crystalline materials, polymers, and catalysts.³ For the synthesis of materials with enhanced electrooptical properties, such an approach would be highly advantageous due to the large number of variables involved. Instead of approaching this synthesis in a random manner, we are basing our procedure on established theoretical principles which are elaborated below.

Sol–gel processing of glasses and ceramics has attracted scientific and technological interest during the past decade because it provides an effective method for fabricating inorganic nanostructured materials and it has been already applied in a combinatorial approach.⁴ Molecular precursors, e.g., metal alkoxides are used as starting materials. The process begins with the formation of a homogeneous sol with the desired composition. The sol is then converted to a gel, while maintaining its homogeneity and purity. A solid network can be obtained through hydrolysis and condensation reactions. Most sol–gel studies have been reported on silicon, titanium, and zirconium systems.^{5–8} Much less work has been devoted to other transition metal oxides gels. Vanadium pentoxide gels have gained interest during the past few years since the gels can be easily deposited onto a glass or a

polymeric substrate giving layers of large area. They exhibit mixed electronic conduction properties which originate from a proton-hopping process between vanadium ions in different valence states V^{4+} and V^{5+} . As a consequence these vanadium oxide layers are useful materials for antistatic coating, switching and electrochromic devices, and reversible cathodes.^{9–10} Recently, the semiconductor V_2O_5 has been found to exhibit a large nonlinear optical response with a fast response time.¹¹ For many applications, this translates into a third-order nonlinear optical susceptibility, $\chi^{(3)}$, in excess of 10^{-8} esu, and a response time faster than 10 ps. This property is particularly important in electrooptical applications. However, various forms of vanadium oxide such as V_2O_4 , VO_2 , V_2O_3 , V_3O_5 , and V_4O_7 could also exist during sol–gel processing, thus Raman spectroscopy will be used in screening optimal conditions for producing crystalline V_2O_5 in our work.

Polymer/ V_2O_5 xerogel nanocomposites, e.g., polyaniline/ V_2O_5 and polypyrrole/ V_2O_5 , have been reported and exhibited improved conductivity compared to pristine V_2O_5 xerogels.^{12,13} Here we represent a combinatorial approach toward the rapid screening of polyphenol/ V_2O_5 nanocomposite materials for their optical properties. The enzymatic synthesis of polyphenols carried out under ambient conditions has recently been reported.¹⁴ Polyphenols have been used as matrix materials, and their conductivity and optical properties have been studied (ref 15 and references therein). If V_2O_5 is combined with polyphenols with delocalized electrons along its backbone, enhanced optical properties are anticipated.¹⁶ It is here that the combinatorial approach will be especially advantageous in optimizing the synthesis of V_2O_5 /polyphenol nanocomposite materials.

Experimental Section

Materials. Reversed micellar solutions were prepared using the anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT) from Aldrich. Vanadium oxytripropoxide,

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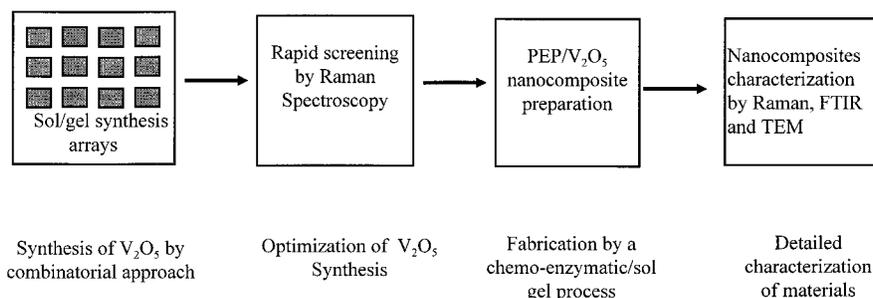


Figure 1. Schematic of the combinatorial process to synthesize PEP/V₂O₅ nanocomposites.

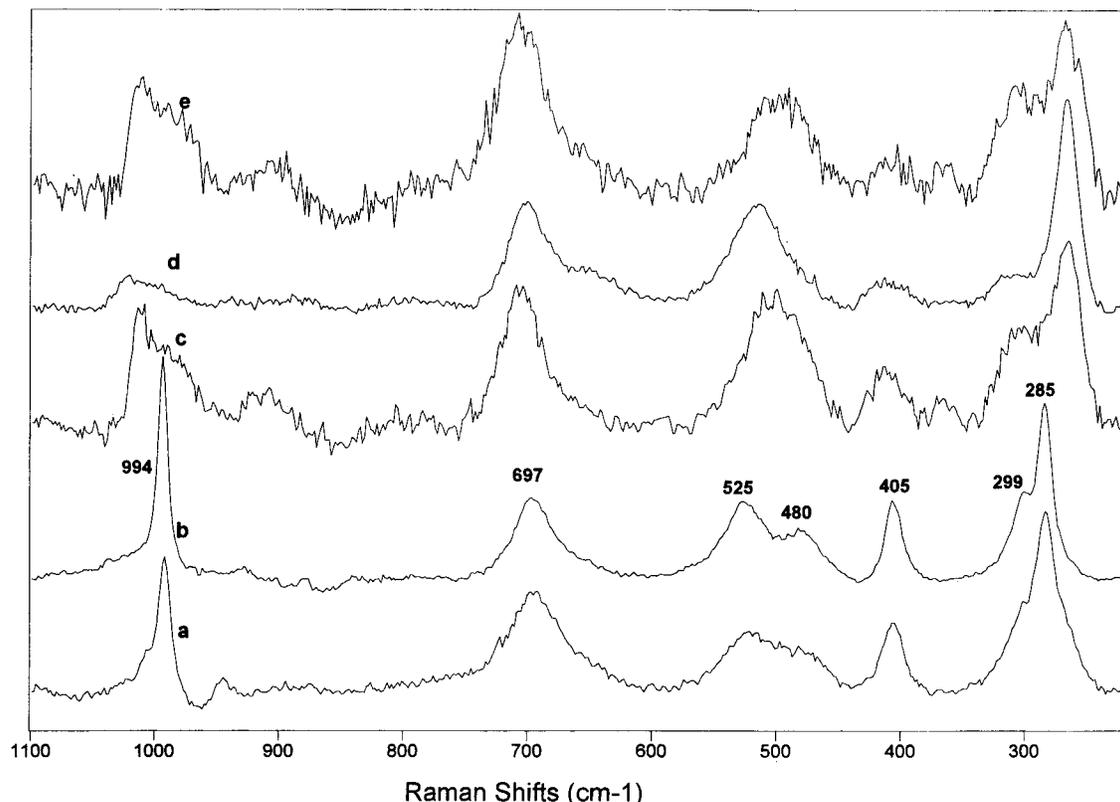


Figure 2. Raman spectra of samples: (a) No. 6; (b) No. 5; (c) No. 15; (d) No. 22, (e) No. 30.

Table 1. Combinatorial Matrix for Vanadate Xerogel Synthesis: Sample Compositions

H ₂ O/VO(OC ₃ H ₇) ₃ (molar ratio)	acetone/VO(OC ₃ H ₇) ₃ (molar ratio)								
	25	40	50	60	75	100	150	245	300
10	No. 14			No. 15			No. 1		
20		No. 17			No. 18	No. 2			No. 4
30	No. 19			No. 20	No. 21			No. 3	
40	No. 22		No. 23		No. 24		No. 40		
45		No. 43		No. 44					No. 5
60		No. 25		No. 26		No. 27			
80			No. 28		No. 29	No. 30		No. 41	
100	No. 31			No. 32			No. 33		No. 6
125		No. 34		No. 35			No. 36		No. 8
150	No. 37				No. 38			No. 39	No. 7

VO(OC₃H₇)₃, was obtained from Aldrich as the alkoxide precursor to prepare V₂O₅.

Horseshoe peroxidase (HRP) type II enzyme, HEPES buffer, and hydrogen peroxide were purchased from Sigma Chemical Co. The monomers *p*-ethylphenol (EP) and isooctane were obtained from Acros. All were used as received. Deionized water was used throughout.

Synthesis of Xerogel V₂O₅·*n*H₂O by Sol–Gel Method. The basic material V₂O₅ (with formula V₂O₅·*n*H₂O) was

prepared by the sol–gel process. The alkoxide precursor, vanadium oxytripropoxide, VO(OC₃H₇)₃ (Aldrich), was hydrolyzed in acetone and condensed to form a wet gel as follows: in an array of 20 mL vials, a certain molar ratio of acetone and water was pipetted, mixed, and stirred rigorously, followed by the dropwise addition of VO(OC₃H₇)₃ by syringe. The components were mixed homogeneously, and no catalyst was added. Various molar ratios of VO(OC₃H₇)₃/H₂O/acetone were achieved, and materials were synthesized

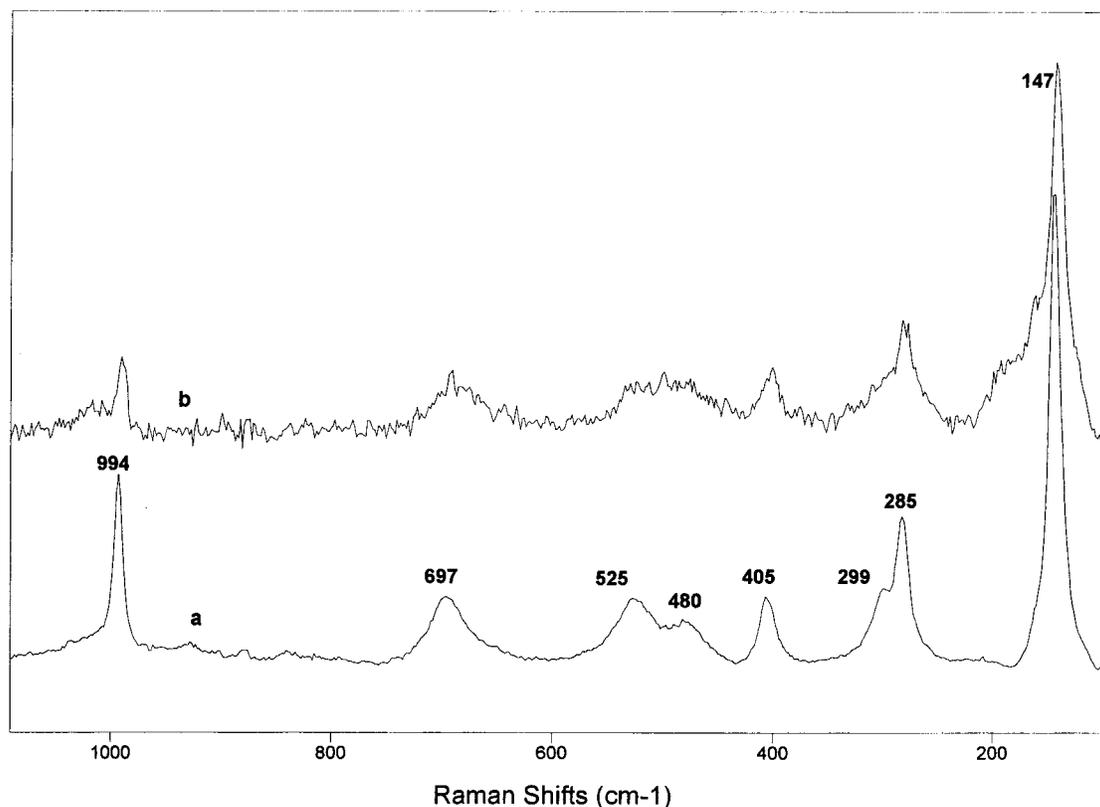


Figure 3. Raman spectra of (a) V_2O_5 (No. 5); (b) PEP/ V_2O_5 (5 wt %:95 wt %).

Table 2. Raman Mode Frequencies and Assignments for Vanadium Oxide in Figures 2 and 3

assignment	a (cm^{-1})	b (cm^{-1})	c (cm^{-1})	d (cm^{-1})	e (cm^{-1})
V–O vibration			1020	1030	1020
V=O stretch	995	994	995	995	995
V–O vibration			900		900
V–O vibration	700	697	700	700	700
V–O vibration	525	525	480–530	480–530	480–530
V–O vibration	480	480			
V–O vibration	406	405	408	408	408
V–O vibration	300	299	300	300	300
V–O vibration	285	285	265	265	265
skeletal vibration	147	147	147	147	147

over a wide composition range as in Table 1. Red viscous V_2O_5 gels were observed instantaneously upon the addition of $VO(OC_3H_7)_3$ into the water/acetone mixture. After 1 h, the V_2O_5 gels were centrifuged, and the upper colorless liquid layer (mostly acetone) was disposed off. A lower layer of concentrated V_2O_5 gel was obtained and lost its water readily at room temperature after 4 days of aging, leading to the xerogel $V_2O_5 \cdot nH_2O$. Longer aging times in open vials lead to denser gels.

Synthesis of Polyphenol/ V_2O_5 Nanocomposite. The component ratio for No. 5 xerogel was used to make polyphenol/ V_2O_5 composites. Poly(*p*-ethylphenol) was synthesized in a manner similar to our previous study.¹⁵ In a modification of our early procedure, the enzyme horseradish peroxidase (HRP) in water was added to the surfactant (AOT) in isooctane, followed by the addition of EP monomers, to make up the final reaction mixture. The latter reaction condition was $w_0 = 15$ (H_2O/AOT ratio), 0.5 M AOT, 0.15 M monomers, and 0.5 mg/mL HRP. The polymerization was initiated by the dropwise addition of 0.2 M hydrogen peroxide. The above synthesis was maintained for 4 h to

obtain poly(*p*-ethylphenol) (PEP). Then the reaction mixture was centrifuged to collect PEP. The upper liquid was disposed off, and PEP was rinsed with sufficient isooctane to remove AOT. After PEP had been dried in a vacuum oven overnight, it was dissolved in acetone. Subsequently, distilled water and $VO(OC_3H_7)_3$ were added into the acetone solution while stirring, maintaining $H_2O/VO(OC_3H_7)_3/acetone = 45/1/300$. A black viscous gel was formed and dried in air for 4 days.

Screening. Rapid screening of the V_2O_5 xerogels was established via Raman spectroscopy, on a Renishaw ramscope at a wavelength of 514 nm. Before the measurements, a piece of silica wafer was placed on the microscope stage to focus and calibrate the peak position (at 521 nm) as the reference material. The accumulated scanning times and laser power were adjusted to acquire optimum Raman spectra. V_2O_5 spectra were obtained in the range of 1100 to 100 cm^{-1} .

Characterization. After comparing the Raman spectra of V_2O_5 xerogels and selecting the optimized samples, PEP was intercalated into V_2O_5 to form PEP/ V_2O_5 composites. Their

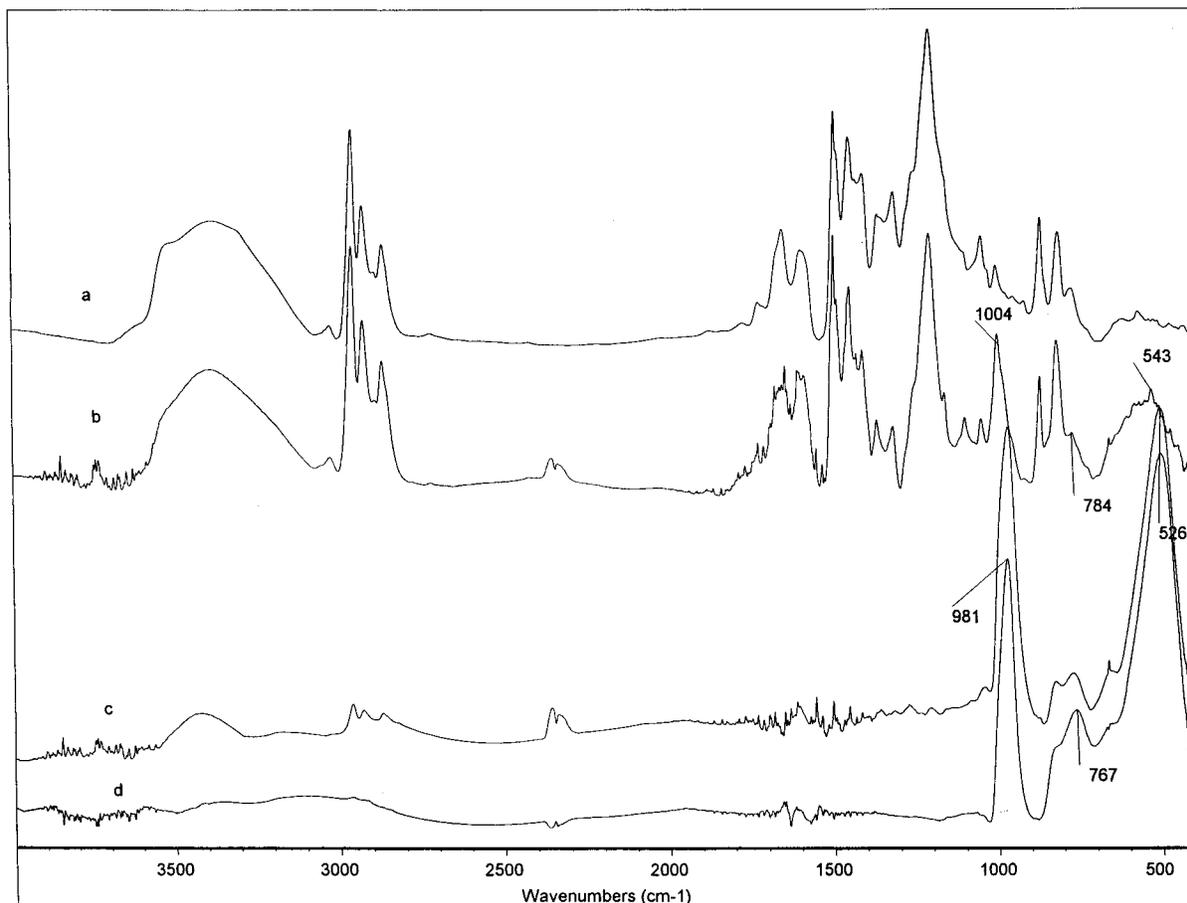


Figure 4. FTIR spectra of (a) PEP; (b) PEP/V₂O₅ (5 wt %:95 wt %); (c) PEP/V₂O₅ (30 wt %:70 wt %); (d) V₂O₅.

Table 3. Infrared-Active Mode Frequencies, Relative Strength, and Assignments for V₂O₅, PEP, and V₂O₅/PEP Composites

assignment	PEP	V ₂ O ₅	PEP/V ₂ O ₅ (5 wt %:95 wt %)	PEP/V ₂ O ₅ (30 wt %:70 wt %)
OH stretch	~3400 (s)		~3400 (w)	~3400 (s)
aromatic CH stretch	3039 (w)			3039 (w)
aliphatic CH stretch	2962 (s)		2962 (w)	2962 (s)
(CH ₃ and CH ₂)	2929 (m)		2929 (w)	2929 (m)
	2871 (m)		2871 (w)	2871 (m)
C=O stretch	1662 (m-w)			1662 (m-w)
aromatic C=C ring stretch	1589 (m), 1504 (s), 1458 (s)			1589 (m), 1504 (s), 1458 (s)
CH ₂ scissor	1458 (s)			1458 (s)
C-OH stretch	1213 (vs)			1213 (vs)
aromatic CH in-plane bend	1061 (w)			1061 (w)
	1014 (w)			1014 (w)
V=O stretch		981 (s)	982 (s)	1004 (m-s)
aromatic CH out-of-plane bend	877 (m)			877 (m)
	823 (m)			823 (m)
V-O-V stretch (γ_{asym} and γ_{sym})		767 (m)	768 (m)	784 (m-w)
		527 (s)	526 (s)	543 (m)

FTIR spectra were obtained on a Nicolet Magna 560 FTIR system and UV-vis absorption spectra on a Perkin-Elmer Lambda 6 spectrophotometer.

The morphology of the polymer/V₂O₅ nanocomposites was characterized by transmission electron microscopy (TEM). For TEM analysis, micrographs were obtained at an acceleration voltage of 200 kV on an analytical Philips CM200-Twin TEM.

Results and Discussion

The combinatorial approach for the optimized rapid synthesis, screening, and fabrication of PEP/V₂O₅ nanocomposites is shown schematically in Figure 1.

The alkoxide precursor, vanadium oxytripropoxide, VO(OC₃H₇)₃, was hydrolyzed in acetone and condensed to form a wet gel which gradually lost water and produced V₂O₅. However, the molar ratios of the components play an important role in the formation of V₂O₅ since vanadium alkoxides are very reactive toward hydrolysis. This arises from the high electrophilic power of the vanadium atom and the possible coordination expansion from 4 to 5 or 6.¹⁷ The hydrolysis ratio $h = \text{H}_2\text{O}/\text{VO}(\text{OC}_3\text{H}_7)_3$ controls the formation of V₂O₅. Here we have extensively varied the molar ratios of the components to obtain the optimized V₂O₅ xerogel. Raman spectroscopy provided a rapid and effective screening

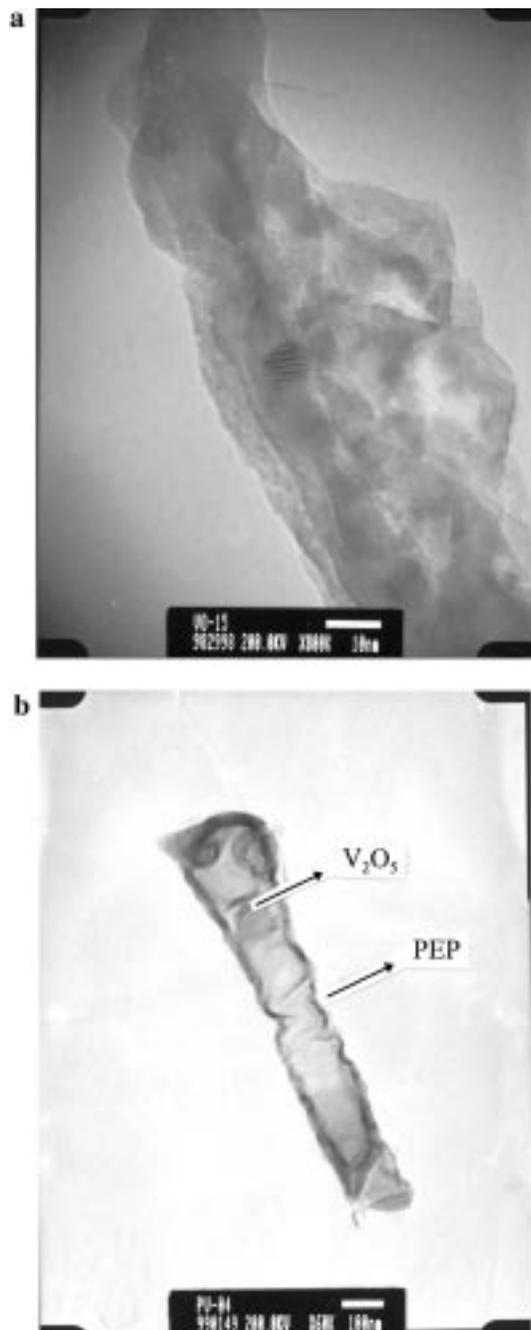


Figure 5. TEM of PEP/ V_2O_5 composites (30 wt %: 70 wt %): (a) high magnification; (b) low magnification.

of products. The Raman spectra of the samples are depicted in Figure 2. The spectrum obtained for pure crystalline V_2O_5 vibrations is quoted here for reference. Pure crystalline V_2O_5 is dominated by strong bands appearing at 995 , 700 cm^{-1} and 285 , 147 cm^{-1} and by less intense bands at 525 , 480 , and 406 cm^{-1} .¹⁸ Parts a and b of Figure 2 show V_2O_5 crystalline characteristics for sample Nos. 5 and 6, respectively, indicating the formation of V_2O_5 : the peaks at 995 cm^{-1} ($V=O$) and 147 cm^{-1} (the skeletal vibration of V_2O_5 , not shown here) indicated the formation of crystalline V_2O_5 . All other samples exhibited a mixture of oxides. A few other sample spectra are presented here (Figure 2c–e) to illustrate the coexistence of vanadium oxides. For example, sample Nos. 15, 22, and 30 gave broad peaks from 990 – 1042 cm^{-1}

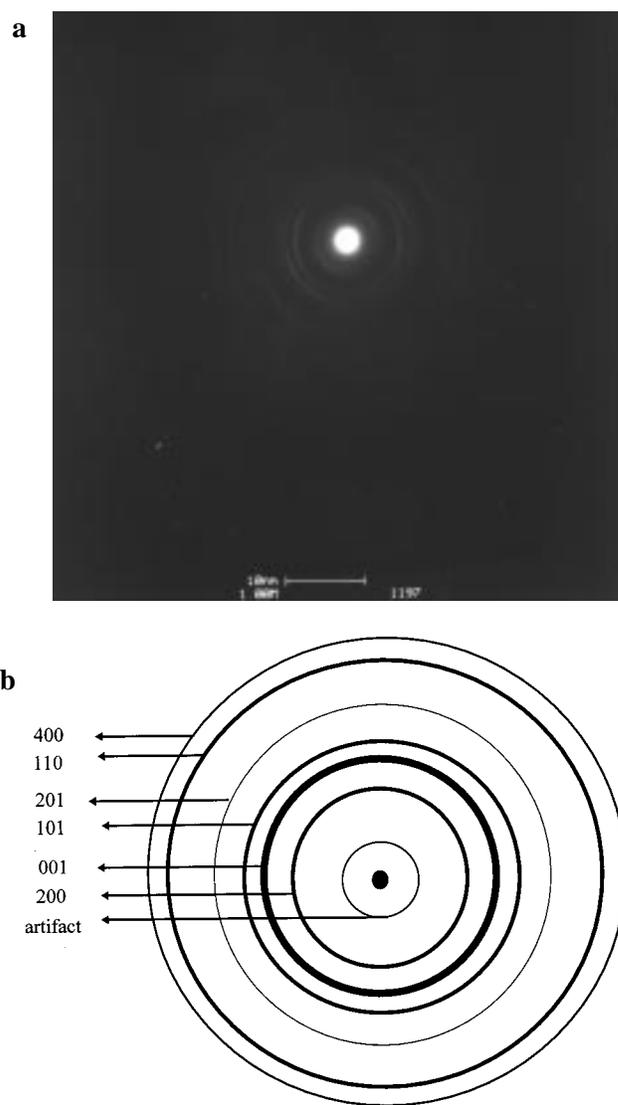


Figure 6. Electron diffraction pattern of V_2O_5 from TEM: (a) original diffraction pattern; (b) schematic diffraction pattern and the assignments of indexes.

and indicated a mixture of three components: V_2O_5 (285 , 300 , 406 , 480 , 525 , 700 , and 995 cm^{-1}), V_2O_4 (295 , 408 , 430 , 530 , and 695 cm^{-1}) and vanadyl (265 and 1020 cm^{-1}), whereas a single phase of crystalline V_2O_5 is ascribed to the spectra in Figure 2a,b. It has been reported that $V-O-V$ stretching vibrations of polyvanadates appear at 400 – 600 cm^{-1} .¹⁹ The broad peaks at about 500 cm^{-1} are probably due to the $V-O-V$ bond. Figure 2a–d demonstrates that the various compositions of $H_2O/VO(OPr)_3/acetone$ give various inorganic vanadium oxide structures: sample Nos. 5 and 6 give the optimum products. We observed that the optimum molar ratio $h = H_2O/VO(OC_3H_7)_3$ was ca. 40 – 100 . This is a high hydrolysis ratio and it causes the sol–gel products to be mostly V_2O_5 . Probably V_2O_5 resulting from red gels was completely formed due to the presence of sufficient water. On the other hand, low h values (<40) may cause a mixture of gels and colloidal solutions with $VO(OC_3H_7)_3$ and, therefore, a complex mixture of vanadium oxides upon drying. Thus high hydrolysis ratios lead to the formation of V_2O_5 during the sol–gel process. In addition, acetone could assist the formation of a homogeneous red

Table 4. Indexed Diffraction Pattern of Vanadium Pentoxide

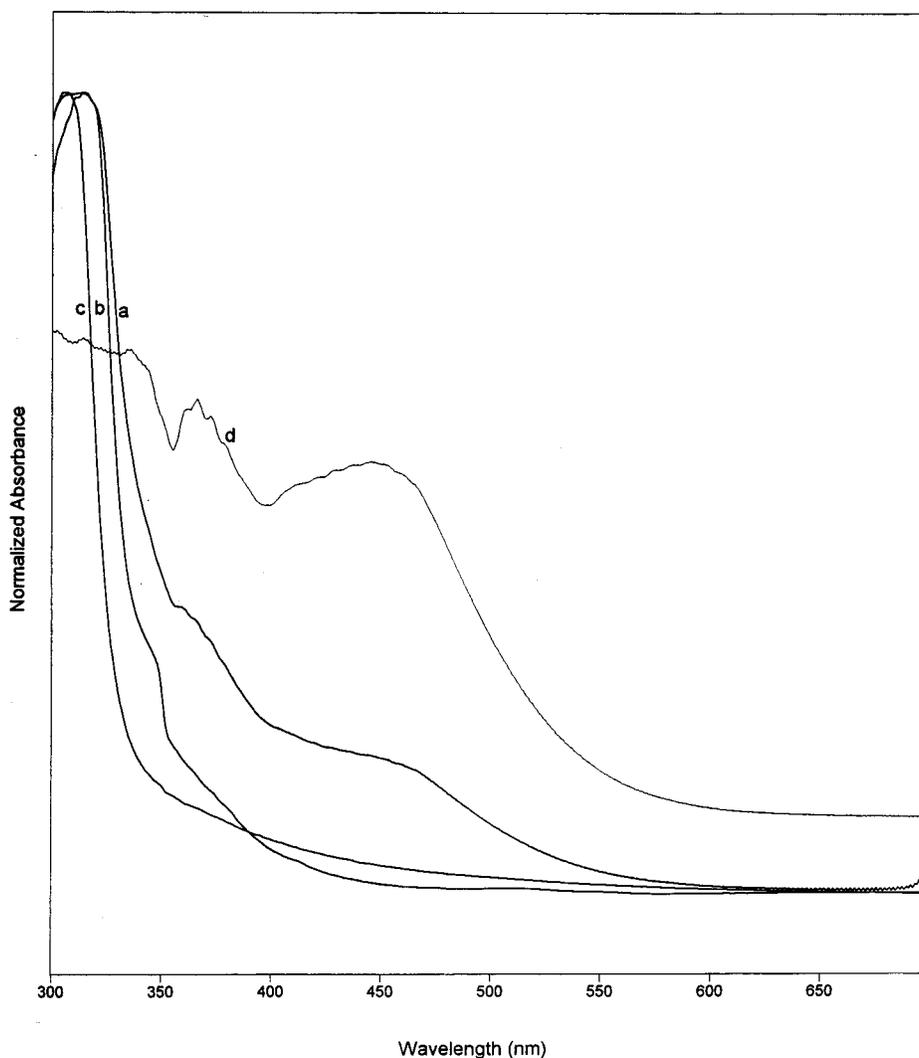
<i>d</i> -spacing from JCDPS file: 41-1426	measured <i>d</i> -spacing	<i>hkl</i>
5.768	5.752	200
4.379	4.308	001
4.090	4.041	101
3.482	3.508	201
3.408	3.318	110
2.882	2.636	400

gel. Higher acetone/VO(OC₃H₇)₃ ratios tend to produce V₂O₅, that is, the nature of the vanadium products depends on acetone amounts as well.

After rapid screening by Raman spectroscopy, the optimized molar ratio of VO(OC₃H₇)₃/H₂O/acetone = 1/45/300 (sample No. 5) was used to prepare PEP/V₂O₅ nanocomposites. Due to the aromatic ring structures in the PEP backbone, fluorescence will significantly interfere with the Raman spectra. To acquire Raman spectra, a PEP/V₂O₅ composite with a minor amount of PEP (5 wt %) was prepared to investigate the nature of vanadium in the composites obtained from the sol-gel process. Figure 3b shows that the PEP/V₂O₅ nanocomposites contain crystalline V₂O₅, although its

Raman spectrum is much weaker than that of pristine V₂O₅ (Figure 3a). This indicates that the presence of PEP does not interfere with the formation of V₂O₅ through the sol-gel process, and PEP can be intercalated into V₂O₅. Table 2 lists the details of Raman mode frequencies and assignments for various vanadium oxide samples.

Further characterization of the xerogels by IR established the formation of V₂O₅ through observation of bands between 1100 and 400 cm⁻¹. The bands in this region are diagnostic of V₂O₅ and are assigned in Figure 4d. Due to the presence of V-O-V in the structure, two vibrational modes exist in the 400–800 cm⁻¹ region, corresponding to the symmetric (γ_{sym}) and asymmetric (γ_{asym}) stretching. They are at 526 and 767 cm⁻¹, respectively. The stretching at 981 cm⁻¹ is assigned to the V=O band ($\gamma_{\text{V=O}}$). The IR spectra of PEP (Figure 4a) and polymer/V₂O₅ (Figure 4b,c) were also examined and indicated the formation of the composite. Comparing the spectra of the composite, pure polymer and V₂O₅, it was observed that the $\gamma_{\text{V=O}}$ (Figure 4d) shifts up from 981 cm⁻¹ in V₂O₅ to 1004 cm⁻¹ in PEP(30 wt %)/V₂O₅ composites (Figure 4b), implying the incorporation of polymer to V₂O₅. Therefore the vibrational frequency of V=O is anticipated to increase, probably due to the strengthened

**Figure 7.** UV-vis spectra of samples in THF: (a) PEP/V₂O₅ (30 wt %:70 wt %); (b) PEP/V₂O₅ (5 wt %:95 wt %); (c) PEP; (d) V₂O₅.

V=O bond resulting from the interaction between polymer and V₂O₅.¹³ Both the V–O–V γ_{sym} and γ_{asym} modes in the composite shift to higher wavenumbers (from 767 to 784 cm⁻¹ and from 526 to 543 cm⁻¹, respectively), compared to the pure inorganic V₂O₅ and implying the interaction between polymer and V₂O₅, and a reduced V–O–V bond length was proposed.¹³ In addition, all three bands exhibited decreasing absorbances because of the existence of polymer in PEP/V₂O₅ nanocomposites. Table 3 lists the details of infrared mode frequencies and assignments for V₂O₅, PEP, and V₂O₅/PEP composites (5 wt % and 30 wt %, respectively).

The molar ratio of VO(OⁿPr)₃/H₂O/acetone = 1/45/300 (sample No. 5) was used to obtain the V₂O₅/PEP composites, and simultaneously the PEP contents were changed to prepare varying PEP:V₂O₅ ratios. Thus we have combined the sol–gel process with a chemo-enzymatic method, to prepare hybrid organic/inorganic materials, optimized by a combinatorial approach.

The morphology of pristine V₂O₅ and PEP/V₂O₅ composites was investigated by TEM. The fibril nature of V₂O₅ was exhibited with the width of ca. 20 nm, which is consistent with the reported V₂O₅ structure,²⁰ that is, four 27 Å wide fibrils consist of a fiber in the *a* axis. The fibril nature of V₂O₅ in the PEP/V₂O₅ nanocomposites has also been illustrated: it is much like pristine V₂O₅, and fibrils have a 27 Å width dimension (Figure 5). Both pristine V₂O₅ and PEP/V₂O₅ nanocomposites give identical electron diffraction patterns shown in Figure 6a. The rings and their assigned indexes are listed in Figure 6b. These indexes are consistent with those reported for crystalline V₂O₅.¹⁶ The first ring is an artifact from the microscope optics. The diffuse nature of the electron diffraction peaks could be indicative of the presence of small domain sizes. It was observed that the rings are more pronounced along a certain direction; this would suggest that the particles are elongated, i.e., fibrillar, along that direction. The diffraction pattern indexes are listed in Table 4.

Figure 7 compares the optical absorbance for V₂O₅, PEP/V₂O₅ (30 wt % and 5 wt % of PEP), and PEP in THF. The V₂O₅ exhibited an optical absorption edge between 400 and 500 nm with a peak absorption above 400 nm and a minimum in the high absorption region near 370 nm. The PEP/V₂O₅ composite shows an absorption edge at 400 nm, which is attributed to the V₂O₅ component in the composite, and a higher absorbance in the UV region compared with the pristine PEP due to the introduction of V₂O₅. Because the photo energy of ultraviolet light corresponds to the energy gap of semiconducting oxides,^{21,22} the absorption of the

composites increases as the wavelength approaches the UV region. The absorbance edge is red-shifted by the nano-sized V₂O₅.

Conclusion

Nanocrystalline V₂O₅ was synthesized by the sol–gel process via a combinatorial approach. V₂O₅ products were screened and optimized by Raman spectroscopy. Subsequently PEP/V₂O₅ nanocomposites were also obtained by the sol–gel method. Both FTIR and Raman spectroscopies verified the formation of the PEP/V₂O₅ composites. TEM illustrated the possible nanofeatures of PEP/V₂O₅ composites.

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