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STRUCTURAL AND OPTICAL PROPERTIES OF SURFACTANT ASSISTED SiO_2-TiO_2 HYBRID MATRIX FOR pH SENSING: SOL-GEL APPROACH

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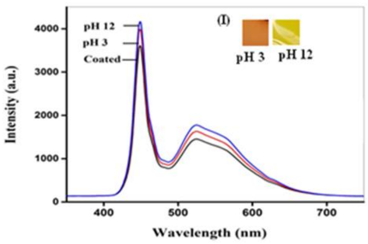
Graphical abstract



Abstract

Structural and optical properties of surfactant-assisted SiO_2-TiO_2 hybrid matrix as a highly responsive optical sensing material by sol-gel method are investigated. Microscopic results indicate the uniform morphology with large pores without any cracks. Matrices have a high surface area (489–342 m^2/g), which has more capability to sense the broader pH range. From UV–visible spectroscopy, it is found that after encapsulation, matrix has ~ 78 % optical transparency with low refractive index of 1.44 corresponding to thickness 138.7 nm. Sensing analysis revealed that the prepared coating has good sensitivity at pH 12 and fast response time. Low refractive index and highly porous matrix, combined for achieving a good responsive optical chemical sensors. This research also opens an aveanue for ths material to be considered as a functional coating.

Keywords: Sol-gel; SiO_2-TiO_2 hybrid, surfactant, coating, optochemical sensor

Abstrak

Struktur dan sifat optik bagi metrik hibrid pembantu-surfaktan SiO_2-TiO_2 sebagai bahan penderia optik dengan gerak-balas yang tinggi melalui kaedah sol-gel telah dikaji. Keputusan mikroskopi menunjukkan morfologi yang sekata diperoleh dengan liang yang besar tanpa sebarang retak. Matriks mempunyai luas permukaan (489 – 342 m^2/g) yang lebih mampu untuk menderia dalam julat pH yang lebar. Daripada spektroskopi UV-Vis, didapati bahawa selepas disaluti, matrik mempunyi ketelusan optik dengan indeks biasan yang rendah 1.44 sepadan dengan ketebalan 138.7 nm. Analisis penderia melahirkan penyediaan salutan yang mempunyi sensitifan yang baik pada pH12 dan mempunyi masa gerakbalas yang pantas. Indeks biasan yang rendah dan matrik yang berliang-liang berpadu untuk mencapai penderia optik yang terbaik tindak-balasnya. Penyelidikan ini juga membuka laluan bagi bahan ini dipertimbangkan sebagai penyalut berfungsi.

Kata kunci: Sol-gel, SiO_2-TiO_2 hybrid, surfactant, salutan, sensor opto-kimia

1.0 INTRODUCTION

In the area of sensing specially to sense the chemical analytes, the optical pH sensors have been gaining attraction among different chemical sensors, due to measurement and pH control in numerous research areas and in a variety of industrial applications. The pH sensor is applicable in aggressive environments like deep-water analysis, wastewater monitoring and chemical reactors[1]. Hence, there is continuity in developing new pH detection techniques with modified materials. Furthermore, high surface area silica-titania hybrid matrix with unique properties obtained by the sol-gel synthesis assigned for various applications like microelectronics, optical coatings, optochemical sensors, host matrices for sensing analysts and environmental monitoring[2, 3]. The sol-gel method possesses an advantage to synthesize the densified, homogeneous and porous material at lower temperatures. This also provides modified network for interaction of particles with the addition of surfactant and dyes for sensing purpose. The surfactant (morphology modifier) Cetyl Trimethyl Ammonium Bromide (CTAB), increases the chemical binding of the heterogeneous species. The reason for the adding surfactant aims at to tailor the modified structural properties and enhance the porosity ratios. Moreover, the refractive index mostly depends on the porosity of the synthesized film and as well as controlled by varying the surfactant ratio[3]. However, at heating the surfactant and residual solvent evaporates to create the microporous on the surface of hybrid, which is responsible for refractive index variation and sensing properties. For opto-chemical sensors, uniform dispersion of mesoporous particles is required in the hybrid network. To address this issue, we used surfactant as stabilizing agent to get the stable disperses hybrid particles. We have studied the effect of surfactant on the structural and optical properties of synthesized hybrid thin film at low temperature heat treatment and then encapsulate it with indicators to observe the response of sensor towards high pHs. For sensing purpose, the PCS (Plastic Clad Silica) optical fiber pH sensor was constructed. The response of the fabricated sensor shows stability and sensitivity towards higher pH values. The colour change observations influences the transmission of light through the optic fiber. So, it can be concluded that the fabricated PCS optic fiber sensors satisfactorily worked in different pH solution without cracking or leaching.

2.0 EXPERIMENTAL

2.1 For Sol Preparation

The sols are prepared from tetraethyl orthosilicate (TEOS, 98%), Ti(IV) isopropoxide (TTIP, 98%), anhydrous ethanol (99.5%), isopropanol(99.7%), nitric acid (65%) and cetyl-trimethylammonium bromide (CTAB). The molar ratio of reactants was optimized for silica sol TEOS:H_2O:C_2H_5OH:HNO_3=1:2:2:0.5 and as for titania sol TTIP:H_2O:C_3H_7OH:HNO_3= 1:5:5:0.5. The molar ratio of silica and titania sol was 1:1. These silica and titania sol were mixed together with the addition of 0.5 M CTAB and the mixture of pH dyes i.e. phenol red ($C_{19}H_{14}O_5S$), bromophenol blue ($C_{19}H_{10}Br_4O_5S$), cresol red ($C_{21}H_{17}NaO_5S$) and phenolphthalein ($C_{20}H_{14}O_4$), then stirred continuously for one hour. Furthermore, detail procedure was explained in our previous work[4]. The prepared sol was aged for several days to stabilize the components at room temperature. The quartz substrates were spin coated at 4000 rpm for 30 sec and dried them for 24 hrs to stabilize the sol contents. Moreover, the dried films were annealed at 100 °C for 1hr in order to study the surfactant effect at low temperature. Figure 1 summarizes the sample preparation process. Before coating, 30 cm long Plastic Clad Silica (PCS) optical fiber with 5 cm decladed region was washed with HNO3 for 10 min and rinsed several times with de-ionized water to produce hydroxyl groups on the surface which assists bonding of the gel. Coating was done on fiber by dripping the sol onto the decladded region at the middle of the fiber. The fiber was then kept for several days for the stabilization of dyes in the host matrix that helps to reduce leaching of the dye molecules. The dried coatings were then washed with water to remove the excess and unbound dye. The coated region is again dried at room temperature to produce a tough, inert and highly adhesive coating.

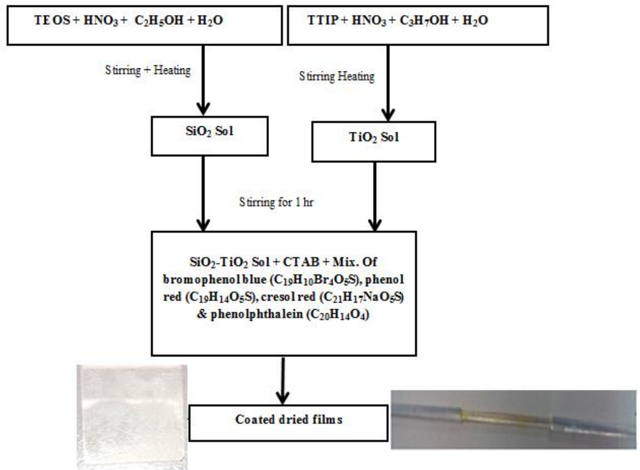


Figure 1 Overall synthesis process

3.0 CHARACTERIZATION

The morphology of the prepared thin films was carried out by using optical microscope Amscope. The average roughness of coating surfaces were characterized by Atomic Force Microscopy (AFM) SPI 3800 N. The surface areas of the prepared materials were determined from the Brunauer, Emmett and Teller (BET) multipoint method and the pore size distribution was obtained using the Barret, Joyner and Halenda (BJH) method. For the calculation of the surface areas, the BET method was used to elaborate N2 adsorption-desorption isotherms. Pore volumes were obtained from the adsorbed amounts of N2 at P/Po = 0.98 desorption curve, supposing the presence of N_2 (density = 0.807 g/cm^3) in the pores under these conditions. Then, BJH method was used to determine the pore size distribution for SiO_2-TiO_2 hybrid matrix. UV-Vis spectrometer (Shimadzu UV-3101PC) was used to record the transmission spectra of the films in the wavelength range from 400-700 nm. The dynamic range and progressive response of the sensor in various pH environments was investigated by a photospectrometer. The white light emitting diode was used as a light source and significant wavelength characteristics were detected by USB2000 miniature fiber optical spectrum analyzer.

4.0 RESULTS AND DISCUSSION

The surface morphology of coated films was studied through optical microscope and Atomic Force Microscopy. The micrographs are presented in Figure 2. Optical micrograph (Figure 2a,) of SiO_2-TiO_2 hybrid reveals that transparent dried films are porous, homogeneous and crack-free, titania particles are well distributed among silica particles. The dispersibility of nanoparticles is due to the adsorption of the modifying agent CTAB surfactant that enhances the inter-particle forces in hybrid materials and prevents formation of any defects like cracks in the films and making dispersion of the particles easier [5]. An agglomeration of particles is due to adsorbed water molecules and hydroxyls ions on the surface of the hybrid films as observed in Figure 2(b). Furthermore, in encapsulated matrix, a noteworthy agglomeration of hybrid nanoparticles takes place with the incorporation of dyes as observed in Figure 2 (c). In order to investigate the morphological features of the encapsulated pH sensing dyes within SiO2-TiO2 matrix thin film on the glass substrate were scanned over 5 × 5 μm2 area. A uniform homogeneous distribution of grains can be observed in all samples [Figure 2(d-f)]. Smooth hybrid films are deposited that exhibit an average surface roughness of 4.30 nm but after heat treatment its value increased upto 7.7 nm that can be attributed to the coalescence into smallest particles. However, after indicators addition the roughness reduced 2.15 nm which shows relatively smooth surface. The variations in roughness are probably due to the entrapment of indicator molecules in the porous voids of the matrix. The indicator molecules fill the pores between the matrix and thus film shows the appearance of clusters, which are enormously closely packed[6].

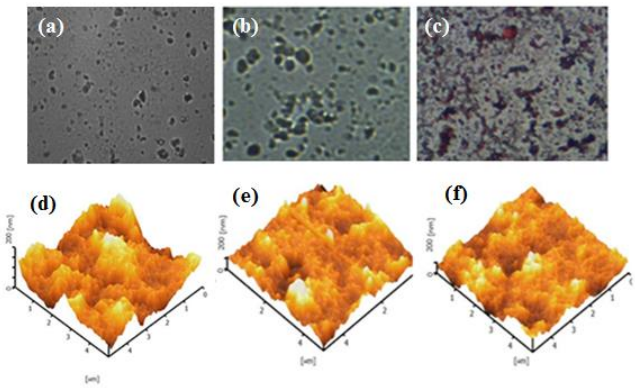


Figure 2 Optical micrographs of SiO_2-TiO_2 hybrid matrix at 10X magnification (a) SiO2-TiO2 hybrid matrix (b) SiO_2-TiO_2 hybrid matrix with surfactant after 100 °C for 1hr heat treatment (c) encapsulated SiO_2-TiO_2 hybrid matrix (d, e & f) are the corresponding 3D AFM images of (a, b & c) respectively

The SiO_2-TiO_2 hybrid matrix has a high surface area 489 m2/g with high pore diameter and pore volume. However, by the addition of surfactant and annealing, surface area and pore volume decrease probably due to the interaction of CTAB molecules with hybrid species. The prepared matrices have a very high pore volume, which is advantageous for sensing and catalytic applications. Table 1 shows the values corresponding to surface area, pore diameter, and pore volume. The adsorption–desorption isotherms of as-synthesized, annealed and encapsulated one are shown in Figure 3. The presence of a hysteresis loop indicates type IV behavior, particularly of mesoporous nature and the hysteresis H2 type associated with ink-bottle pores is due to capillary condensation in the pores of the matrix. The samples have maximum area under the hysteresis loop indicating that it has the maximum uniform pore size distribution in the mesoporous region.

Table 1. Surface area, pore diameter and pore volume distribution of SiO_2-TiO_2 hybrid matrix as-synthesized, heat treated and indicators encapsulated matrix samples

Sample	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	BJH pore diameter (nm)
Hybrid	489	4.3	0.5	4.4
Hybrid-CTAB after annealing	0.3	425	3.4	3.9
Encapsulated indicator matrix	0.2	342	2.8	3.2

The transmittance data were taken by UV–Vis spectroscopy and the refractive indices were calculated by the Fresnel formula[6]. The wavelength used in determination of refractive index is 632.8 nm. Optical thickness are calculated as $nd = \lambda/4$. Where, n is calculated by Fresnel formula. The thickness is calculated with an accuracy of ±3 nm. Transmission spectra are shown in Figure 4-I. All samples are mainly transparent throughout the visible range 400–700 nm. The SiO_2–TiO_2 hybrid sample exhibits a lower transmission ~ 52.84 at 632.8 nm can be seen in Figure 4-I (a), which may be the result of scattering from a few large pores. While higher transmission can be observed after 1 hr heat treatment as shown in Figure 4-I (b). After annealing, CTAB assisted SiO_2-TiO_2 hybrid nanoparticles is highly porous in nature because of the scattered and reflected light, escaping from the coating may trap and restrained in these pores. As a result, the scattered and reflected light is transmitted through the coating. So, annealed sample showed higher transparency in the visible region. However, after encapsulation the transmission value again decreases up to 78.58 nm as shown in Figure 4-I(c), probably due to the smaller grains which result in lower transmission due to the presence of grain boundaries that act as scattering centers for light. Additionally, the scattering from interface also results in decreasing the transmission in the encapsulated dyes matrix. From UV–visible spectroscopy, it is found that coated films have a good optical transparency with tunable refractive index 1.33, 1.32 and 1.44 corresponding to thickness 118.8, 119.7 and 138.7 nm respectively. The variations in refractive index are shown in Figure 4-II. However, the closeness of refractive indices of both samples, i.e., SiO2–TiO2 hybrid matrix and annealed one [Figure 4-II(a, b)], can possibly be attributed to the coalescence of the nanoparticles as reported by Vaccaroet *et al*., [7]. The reduction in refractive index between hybrid (1.33) and surfactant assisted annealed hybrid (1.32) is most probably due to the evaporation of residual solvent that creates porosity on the surface topography of the film. Besides, the refractive index after encapsulation is high due to less porous gel (Figure 4-II(c)), which results probably from shrinkage, densification and encapsulation of indicator dyes molecules[8].

The variation in refractive index is directly related to the variation in thickness, which could be due to the density or polarization of materials[9]. Additionally, the optical properties of hybrid materials can relate to their structural properties, which depend on the process parameters such as substrate, sol, central wavelength, optical thickness, porosity, heat treatment and the composition of the materials used[8].

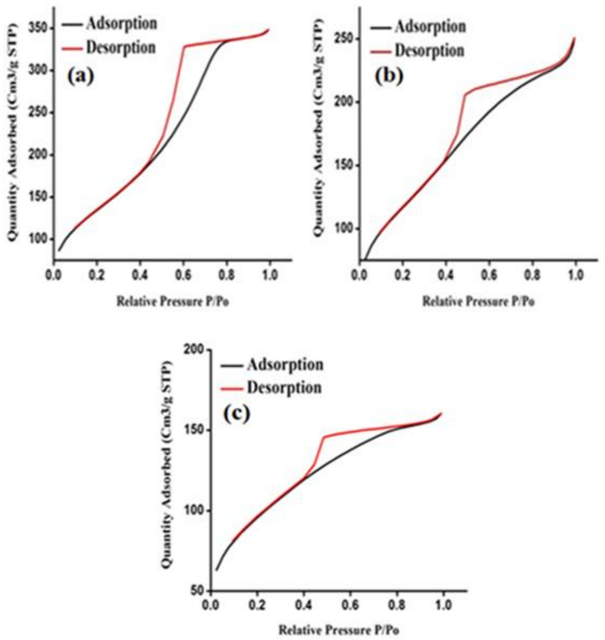


Figure 3 Adsorption-desorption isotherms of (a) as-synthesized (b) annealed one (c) after encapsulation

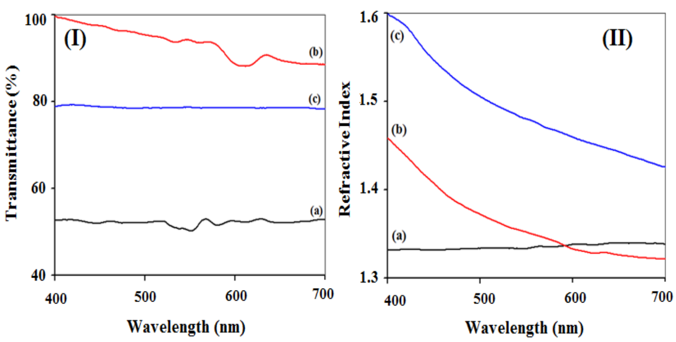


Figure 4 Transmission spectra of (a) SiO_2-TiO_2 hybrid matrix (b) annealed (c) encapsulated indicators SiO_2-TiO_2 hybrid matrix. (II) Refractive index (a) SiO_2-TiO_2 hybrid matrix (b) annealed (c) encapsulated indicators SiO_2-TiO_2 hybrid matrix

For sensing analysis, a mixture of dye indicators i.e. bromophenol blue ($C_{19}H_{10}Br_4O_5S$), cresol red ($C_{21}H_{17}NaO_5S$), phenol red ($C_{19}H_{14}O_5S$) and phenolphthalein ($C_{20}H_{14}O_4$) was encapsulated within annealed SiO_2-TiO_2 matrix. This mixture exhibited a red color in an acidic solution pH 3 and yellow color in basic solution pH 12 by protonation or deprotonation of carboxyl group and OH group on the molecule[10]. The variation in colour within different pH medium is due to OH^- ions, which freely penetrating into the porous matrix and reacting with indicators, resulting in the change in coating colouration as shown in Figure 5 inset (I). The colour change was fast within seconds (1-2) when immersed in pH solutions. This is a significant improvement over previous work reported in the literature and the stated response times were in the order of 20-100 minutes[10]. The response of the device is found to be high at pH 12 in terms of output intensity as shown in Figure 5. It is evident from the spectra that the response increases with the increase in pH values. In sensing process, the analytes diffuse through the pores of the coated layer and interacts with the indicator molecules. Hence, the inter connectivity between pores has a significant role in the increased sensitivity of the optochemical pH sensor. No leaching is observed when the samples were treated with high pHs, which exhibited the strong interaction of indicators with SiO_2-TiO_2 hybrid matrix.

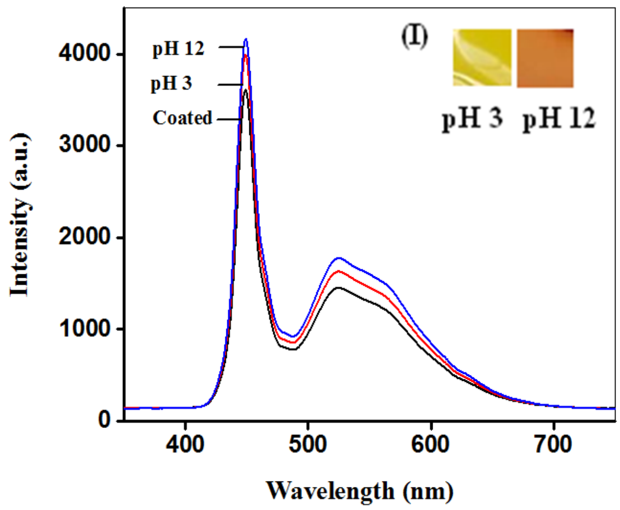


Figure 5 Response of the sensor within different pH values 3 and 12. Inset (I) is showing the color variations in pH 3 and 12 solutions

5.0 CONCLUSIONS

In conclusion, we have demonstrated the synthesis of SiO_2-TiO_2 hybrid matrix in the presence of surfactant at low temperature 100 °C by sol-gel method. The microscopic analysis indicates that the particles are uniformly distributed without any cracks or defects. It can also be observed that the interconnectivity of indicators with matrix has a significant role in the increased stability and sensitivity of the present sensor. After encapsulation, matrix has mesoporous nature with high surface area

342 m^2/g, a pore size of 2.8 nm and pore volume of 0.2 cm^3/g. The optical properties of mesostructured hybrid thin films were directly correlated to their composition and structural properties. The highly porous nature with low roughness values makes SiO_2–TiO_2 matrix network to excellent host for sensing molecules. Furthermore, UV-Vis spectroscopy revealed that the prepared surfactant assisted SiO_2-TiO_2 hybrid matrix shows good sensitivity at pH 12 within 2 seconds. So, it can be concluded that the fabricated matrix is an excellent material for binding organic compounds for optical pH sensing and has great potential for opto-chemical pH sensor due to its stability and fast response time.

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