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Thermally and optically functionalized titania nanoparticles for pH sensing

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Thermally and optically functionalized titania nanoparticles for pH sensing

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Abstract. Owing to the sensing applications, titania nanoparticles (TNPs) are synthesized by sol-gel route at low temperature (80 °C). For pH sensing response, four different pH dyes (phenol red, bromophenol blue, cresol red, and phenolphthalein) mixture is immobilized within TNPs. Thermal and structural behaviour of synthesized TNPs is observed by Thermo-gravimetric analysis (TGA), Fourier transmission infrared spectroscopy (FTIR), and Field emission scanning electron microscopy (FESEM). Thermally stable co-dyes immobilized TNPs confirms void-free surface morphology with heterogeneous chemical bonding. Furthermore, prepared sensing device has linear response with determination coefficient (R2) ~ 0.97 and sensitivity is calculated as ~154 I/pH at 431 nm. The response is optimized at pH 11.

1. Introduction

In the field of sensing applications, a promising tactic is the formation of nano-structures compared to the single component-based sensors. In opto-chemical fiber optic sensor, high sensitivity, repeatability, reversibility, low response time, and noise immunity are required parameters. Moreover, the simple geometry, small size, dynamic range and sensitivity of optical sensors are advantageous over conventional electrochemical sensors. These parameters make fiber optic sensors a suitable choice for practical industrial applications where electronic or acoustic ones are not appropriate [1]. TNPs due to photocatalytic activity, chemical stability, non-toxicity, and dielectric properties were are as chemical/gas sensors, photo-oxidation processes, solar cells [2], and functional coatings [3, 4]. Generally, particle aggregation caused stress in the coating leads the crack surface and limits the sensor response. Indeed, a smooth nanostructured surface coating is required to overcome this issue. TNPs and dopants into the TNPs matrix by different methods have been investigated intensively, however, synthesis of TNPs at low processing temperature is still a challenging task [5]. Sol-gel method permits synthesis of nanomaterials with homogeneity, porosity, tunable grain size morphology at low temperature. The use of surfactant accompanied with this method provides the self-organized nano-porous structures. Furthermore, a mixture of indicator dyes i.e., phenol red, bromophenol blue, creosol red, and phenolphthalein, exhibited distinctive properties like non-toxic, non-carcinogenic, bio-degradable materials and for dynamic pH range [6]. Herein, in this study, a mixture of indicator dyes was immobilized in TNPs to explored interaction between the sensitive coating and analytes at dynamic pH range up to pH 11.

2. Experimental

2.1. Synthesis and coating process

For titania nanoparticles sol, 10 ml of titanium tetra-butoxide was dissolved in mixture solution of 30 ml isopropanol and 30 ml of deionized water. 1ml of HNO_3 was mixed in the solution dropwise. The mixture was stirred vigorously at 80 °C for 30 mints. For proper constituent reactions, the TNPs sol was left at room temperature for 1 day. For immobilization, 1 ml of 0.005 M concentrated mixture of phenol red, bromophenol blue, cresol red, and phenolphthalein was mixed along with 1 ml of 0.005 M concentrated CTAB solution in the TNPs solution. The solution was stirred and heated at 80 °C for 30 min. Afterwords, reddish color sol was aged at room temperature for 2 days. DHT11 humidity sensor was used to measure the rel. humidity ~ 76 ± 1%.

For sensing device, 25 cm long, 1012 µm core diameter, numerical aperture 0.37 ± 0.02, Plastic Clad Silica (PCS) optical fiber was used. Middle region (5 cm) of fiber was decladded and cleaned with isopropanol for contamination removal. The cleaned decladded region was coated by dripped the 100 µL synthesized co-immobilized TNPs sol. The fiber was then kept for 2 days at room temperature in order to get the inert and adhesive coating.

3. Characterizations

Thermo gravimetric analysis (TGA) was performed by thermometer (Mettler Toledo TGA851). Weight mass loss was recorded within 30-1000 °C temperature range at the rate of 10 °C/min under nitrogen atmosphere. The chemical bonding between TNPs and indicator dyes species was observed by Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy using PerkinElmer Series L160000A spectrophotometer. The spectra were recorded at room temperature within the range of 650-4000 cm^{-1}. Surface morphology was observed by field emission scanning electron microscope (Carl-Zeiss). For sensing valuation, intensity based signals were recorded by Ocean Optics USB2000 miniature spectrometer. Whereas, white light emitting diode was used as light source.

4. Results and Discussions

Figure 1 shows the TGA and DTA profile of co-dyes immobilized TNPs. Mass loss is observed in four steps. The first step mass loss around 3% is calculated from 30 °C to 170 °C, probably due to adsorbed water elimination from inner walls of TNPs matrix and evaporation of organic solvents from the grain surface, as observed by other researchers [7]. The second step mass loss around 5 % within the temperature range of 175 °C - 300 °C is assigned to decomposition of butoxy groups from precursor and elimination of organic species, accompanied to the exothermal process, also reported previously [8]. Whereas, the third mass weight loss around 6 % within the temperature range of 305 °C - 478 °C accompanied with exothermal process attributed to dehydroxylation of Ti–OH groups. Moreover, the last step weight mass loss around 15 % upto1000 °C, ascribed to the carbonaceous residual resistant from dye species to oxidize.

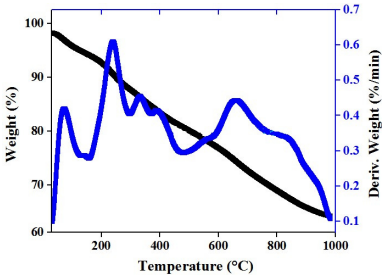

Figure 1. Weight (%) against temperature (°C) and derivative of weight (%/min) of co-dyes immobilized TNPs.

Figure 2 shows the FTIR spectrum of co-dyes immobilized TNPs. The band ~ 753 cm^{-1} that is assigned to the stretching vibration of Ti–O–Ti [9]. A little intense band ~ 950 cm^{-1} is ascribed to the =C–H bending vibrations, as reported by other researchers [10]. The bands ~ 1148 cm^{-1} and ~ 1351 cm^{-1} are attributed to the Ti-O-C bond and C-O-C stretching vibrations, respectively [11, 12]. Whereas, the band at 1638 cm^{-1} is ascribed to the bending modes of Ti-OH [4]. The little intense feature ~ 2115 cm^{-1} is allocated to the stretching vibrations of $–CH_2$ and $–CH_3$ from surfactant CTAB [13]. The broad band at 3277 cm^{-1} is ascribed to O-H hydroxyl group stretching vibrations. Furthermore, figure 3 shows the FESEM pattern of co-dyes immobilized TNPs. The surface shows porous, void-free morphology. The micrograph also indicate the nanoparticles formation. The porous surface is advantageous for sensing evaluation because the analytes diffuse through the pores and interacts with the dye species [14].

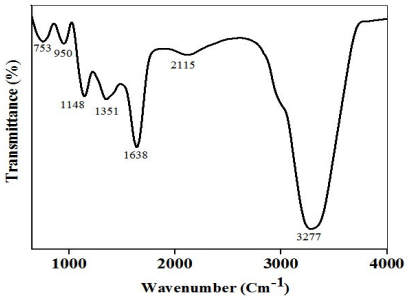

Figure 2. FTIR spectrum of co-dyes immobilized TNPs.

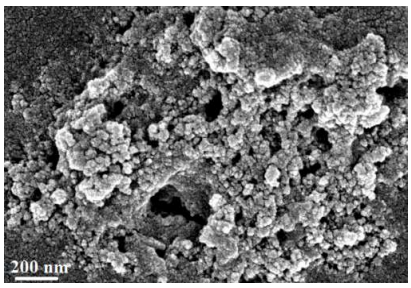

Figure 3. FESEM micrograph of co-dyes immobilized TNPs.

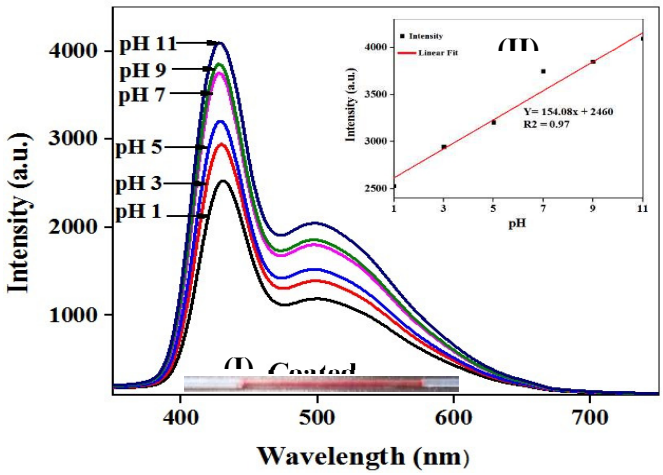

Figure 4. optical spectra of co-dyes immobilized TNPs coated optical fiber within different pH buffer solutions, Inset (I) corresponds to the digital photograph of coated fiber, (II) attributed the intensity variations at 431 nm against different pHs.

Figure 4 shows the optical spectra of co-dyes immobilized TNPs coated optical fiber [Inset (I)] treated against different pH 1, 3, 5, 7, 9 and 11 buffer solutions. It can be clearly observed from the spectra that the intensity in terms of transmission is increased by increasing the pH, probably due to the evanescent field absorption interaction around the sensing region. Inset (II) shows the linear response with determination coefficient (R^2) ~ 0.97. The sensitivity is calculated ~154 I/pH at 431 nm.

5. Conclusions

The titania nanoparticles (TNPs) were successfully synthesized at 80C by sol-gel method for pH sensing evaluation. Mixture of four pH dyes cresol red, phenol red, bromophenol blue, and phenolphthalein was immobilized in TNPs. Thermally stable co-dyes immobilized TNPs matrix exhibited linear sensing response because of void-free coating. Fiber based sensing device shows the good sensitivity ~ 154 I/pH at 431 nm with determination coefficient (R^2) ~ 0.97. Hence, it can be concluded that synthesized material is thermally and optically stable and has potential as opto-chemical pH sensing field.

Acknowledgement

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References

[1] Ghadiry M, Gholami M, Kong L C, Yi C W, Ahmad H and Alias Y 2016 *Sensors* **16** 39
[2] Ye M D, Zheng D J, Lv M Q, Chen C, Lin C J and Lin Z Q 2013 *Adv Mater* **25** 3039-44
[3] Hema M, Arasi A Y, Tamilselvi P and Anbarasan R 2013 *Chem Sci Trans* **2** 239-45
[4] Leon A, Reuquen P, Garin C, Segura R, Vargas P, Zapata P and Orihuela P A 2017 *Appl. Sci.* **7** 49
[5] Surya L, Sheilatina, Praja P V and Sepia N S 2018 *Research Journal of Chemistry and Environment* **22** 48-53
[6] Ashrafi N, Gharanjig K, Hosseinnezhad M, Mehrizi M K, Imani H and Razani N 2018 *Prog. Color Colorants Coat* **11** 79-83
[7] Minga I, Kurajica S, and Mandic V 2015 *acta graphica* **26**11-20
[8] Madarasz J, Braileanu A, Crisan M, and Pokol G 2009 *Journal of Analytical and Applied Pyrolysis* **85** 549
[9] Salamat S, Younesi H and Bahramifar N 2017 *RSC Adv* **7** 19391-405
[10] Rajeshkumar S, Ponnanikajamideen M, Malarkodi C, Malini M and Annadurai G 2014 *J Nanostruct Chem* **4** 96
[11] Mombeshoraa E T, Simoyia R, Nyamoria V O and Ndungu P G 2015 *S. Afr. J. Chem* **68** 153-64
[12] Bozic M, Ban I, Hribernik S, Fakin D and Kleinschek K 2017 *Journal of Sol-Gel Science and Technology* **83** 132-42
[13] Islam S, Bidin N, Riaz S and Naseem S 2016 *Journal of Industrial and Engineering Chemistry* **34** 258-68
[14] Islam S, Rahman R A, Othaman Z, Riaz S and Naseem S 2015 *Journal of Industrial and Engineering Chemistry* **23** 140-4