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High surface area SiO_2-TiO_2 nano-composite as pH sensor

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ABSTRACT

The mesoporous SiO_2-TiO_2 nano-composite was obtained via the sol – gel method. The presence of surfactant additive CTAB as structure-directing agent leads to the textural modification of composite network after heat treatment at 150°C for 2 hrs. The both samples before and after heat treatment were characterized by BET method, nitrogen adsorption–desorption methods and UV-Vis Spectroscopy. N2 adsorption isotherms of the annealed sample explaining the high surface area value of silica-titania nano-composite is $401m^2/g$ with a pore size of 3.3 nm and pore volume of 0.33 cm^3/g. The influence of surfactant CTAB on the pore structure and surface area of sol-gel based silica-titania nano-composite for pH sensing applications were also investigated. Furthermore, the EDX analysis substantiated the stiociomatric formation of encapsulated silica-titania nano-composites.
Keywords: Mesoporous; sol-gel; encapsulated hybrid

1. INTRODUCTION

The advancement of inorganic encapsulated indicators silica based porous materials are now a wide field of investigation in many fields especially for sensing purposes (Nivens 1998, Beltrán-Pérez, López-Huerta et al. 2006). The thermally stable inorganic network incoperate with organic component to possess the stable chemical behavior in the sensing media (Hoffmann, Cornelius et al. 2006).

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In the inorganic matrix, the presence of the heteroatoms can broaden the potentials of interesting characteristics. Those varieties of hybrid materials that possess positively charged organic groups with exchangeable anions of indicators, have drawn considerable interest in potential applications such as coatings, sensor devices, photocatalysis and biomedical technology (Arenas 2008, Gu¨ngo¨r 2011, Godlisten N. Shaoa 2012). The anion-exchange properties of hybrid materials served as adsorbent for pH sensing anionic dyes. One of the benefits of the sol–gel method, it leads the incorporation of organic species in the inorganic matrices without degradation and allowing the formation of hybrid network (Pabón, Retuert et al. 2007). This modified hybrid material was encapsulated with co-indicators which used for pH sensing. Sensitive sol-gel films are porous structures, which incorporate with sensitive dyes. However, the sensing mechanism was discussed based on their microstructures, such as surface area, pore size and mesopore volume. The porosity (i.e., pore volume, pore size, and surface area) of hybrid depends on the structure and size of particles formed by hydrolysis and condensation reactions, after drying the aggregation of these particles form a gel (Brinker, Sehgal et al. 1994). In this work the fabrication of silica-titania nano-composites by the sol-gel process and the relationships between processing condition, microstructure of porous materials and sensing properties were systematically investigated. This nano-composites were characterized by BET, FESEM, EDX, TGA and UV-Vis spectroscopy analysis.

2. EXPERIMENTAL

2.1. SYNTHESIS OF THE SOLS

To prepare encapsulated indicators silica-titania stable matrix, the two sols A (SiO_2) and B (TiO_2) were mixed in 1:1 volume ratio of silica to titania sol. The detailed analysis of the sol was explained elVHZKHUH 1DVHHP POORI 0 concentration of co-indicators and 1ml of 0.5M concentration of CTAB solution were mixed into a solution of two sols. This mixture was stirred and heated at 80ºC to ensure the proper combination of the constituents. After mixing, the solution turned reddish in color. Then the mixture was left for several days for appropriate aging cycles to increase the viscosity of the solution and removal of volatile components at room temperature. For uniform and adhesive coatings, the glass slides were thoroughly cleaned with acetone for 15 minutes and propanol for 10 minutes in an ultrasonic bath in separate runs to remove any adsorbed gases or contaminants and then dried at room temperature (Islam, Rahman et al. 2013).

3. CHARACTERIZATION:

The surface areas of hybrid matrices were determined from the BET (Brunauer,Emmett and Teller) multipoint method and the pore size distribution was obtained using the BJH (Barret, Joyner and Halenda) method. EDX spectrum (Oxford Silicon Drift Detecto SDD) was used to know the percentage of elements present in the sample. The absorption analysis for sol was performed using a Perkin Elmer Lambda 25 spectrometer over 250-900 nm range.

4. RESULTS AND DISCUSSION:

Mesoporous as-synthesized encapsulated indicators hybrid matrix has specific surface area, pore diameter and pore volume, but after heat treatment at 150°C for 2 hr, it has larger pore diameters and high surface area values. Table.1 shows the values corresponding to surface area, pore diameter and pore volume. The prepared nano-composites after heat treatment have a very high pore volume, which is advantageous for sensing and catalytic applications. Both samples showed a pronounced peak in the mesoporous region (20-200Å). This confirms that the hybrid nano-composite structures are preserved by drying at room temperature.

Table.1 Surface area, pore diameter and pore volume distribution of silica-titania hybrid matrix encapsulated with co- indicators as-synthesized and heat treated samples

Samples	**Surface area (m^2/g)**	**Pore Diameter (nm)**	**Pore Volume (Cm^3/g)**	**BJA Pore Diameter (nm)**
As-synthesized	341.88	2.8	0.24	3.2
After heat treatment	400.67	3.3	0.337	3.6

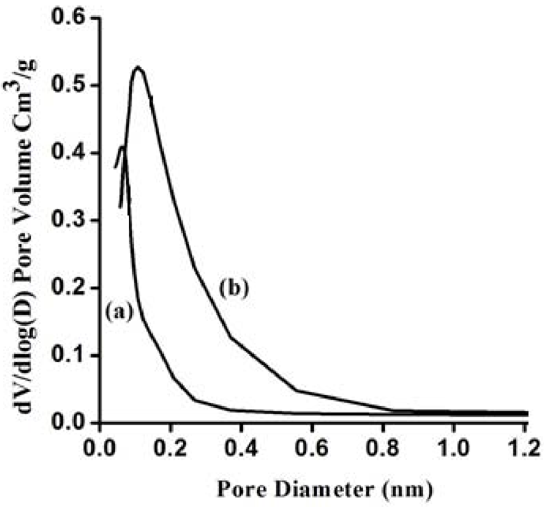

Fig.1 Shows pore size distribution curves obtained by BJH (a) As-synthesized (b) after heat treatment

The adsorption-desorption isotherms of hybrid as-synthesized and annealed one are provided in Fig. 2. The presence of a hysteresis loop indicates type IV behaviour, particularly of mesoporous nature and the hysterisis loops appear at P/Po range of with H2 type associated with ink-bottle pores is due to capillary condensation in the pores of the matrix gel (Abdel-Azim, Aboul-Gheit et al. 2014). The samples have the maximum area under the hysteresis loop indicating that it has the maximum uniform pore size distribution in the mesopore region. The adsorption isotherms of the annealed sample lie below indicating the lower pore volume, but have a similar pattern as that observed in as-deposited sample.

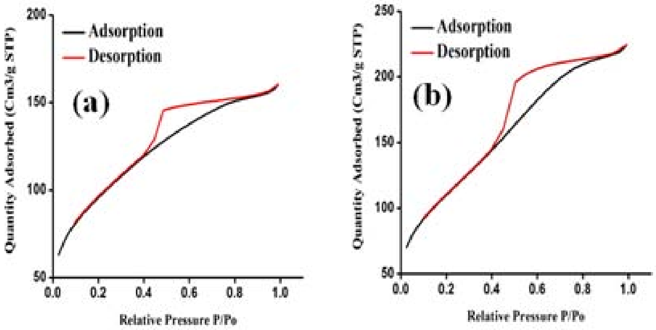

Fig.2 N2 Adsorption isotherms of (a) As-synthesized (b) after heat treatment

Energy dispersive X-ray analysis was used to determine the elemental analysis and to check the indicators had been incorporated into the hybrid lattices. EDX analysis revealed that indicators were successfully incorporated into the host matrix and showed the presence of N, S, Br, Na which are elements of indicators and shows variations after heat treatment. The values of elements summarized in Table.2. The variation in Si and Ti values increased after heat treatment owing to the growth of particles. The amount of carbon incorporated into the matrix lattice is 5.44 % after heat treatment which is a significant constituent of indicators and surfactant. Therefore, encapsulation of indicators within the matrix is successfully carried out.

Table. 2. represents EDX analysis of hybrid matrix encapsulated with indicators before and after heat treatment

Elements wt(%)	Encapsulated Hybrid	After 2 hr heat treatment
C	6.57	5.44
N	2.12	0.64
O	40.66	43.69
Na	5.79	4.27
Si	36.51	38.10
S	0.52	0.7
Ti	5.97	6.23
Br	1.86	0.93

For the sensing purpose of broadening range, mixture of co-immobilized dyes namely (Phenolphthalein ($C_{20}H_{14}O_4$), phenol red ($C_{19}H_{14}O_5S$), bromophenol blue ($C_{19}H_{10}Br_4O_5S$) and cresol red ($C_{21}H_{17}NaO_5S$)) were selected. The absorption spectra of the hybrid, hybrid-CTAB and mixture of indicators after immersion in different pH solutions (3-12) can be seen in Fig. 5. The surfactant was used to examine the absorbance behavior of hybrid sol. Mostly; the absorbance has increased in the presence of surfactant. This is perhaps due to modification of hybrid structure with highest porosity, and therefore the host capacity of the hybrid matrix is enhanced for filling indicators. It is observed that surfactant has the significant change in terms of highest absorbance (315nm) than hybrid (308nm). The absorption bands around 20-300 nm and 550-600 nm were clearly observed [Fig. 3]. These bands correspond to the different pH values. The maximum absorption observed at lower pH values. However, when the sol is treated with pH 9-13, the absorption band occurs in the range of 550-590 nm with the presence of an isosbestic point at 490 nm. The shifting of absorption bands towards higher and lower energy values are probably corresponds to a change from the acidic form to the basic form of indicators (Zaggout, El-Ashgar et al. 2005).

The variation of absorbance with pH of the solution is shown in Fig. 4 with the calculated pK value 9.3. This corresponds to the pH value at half the maximum absorbance and favored with the presence of indicators anions.

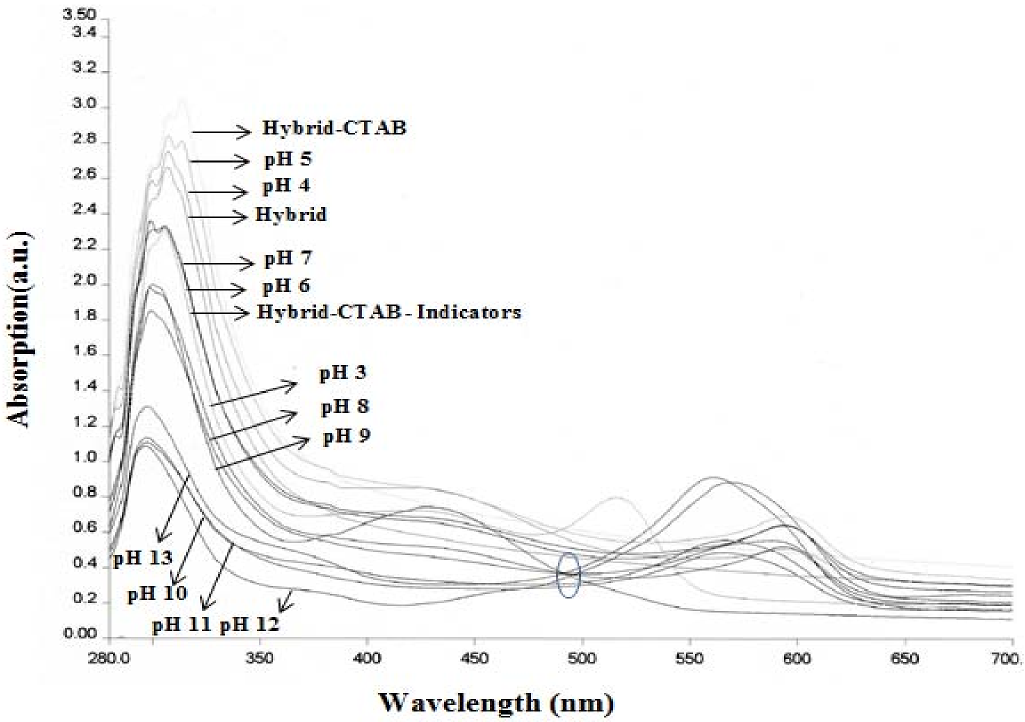

Fig.3 Absorption spectra of hybrid, hybrid-CTAB and hybrid-CTAB-indicators sol at different pH values (3-13).

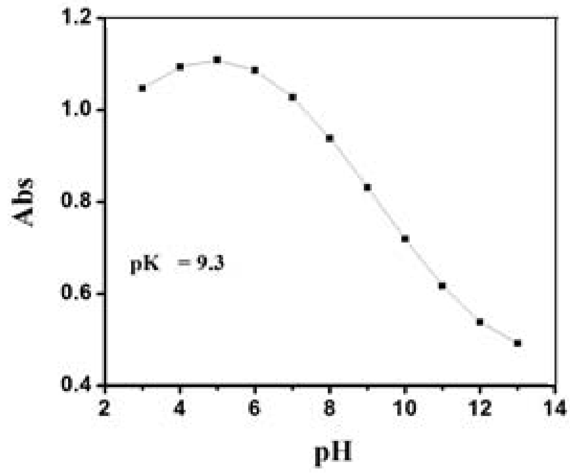

Fig. 4 pK value of encapsulated indicator hybrid sol at pH (3-13).

4. CONCLUSIONS

Encapsulated indicator hybrid silica-titania nano-composite was obtained via the sol-gel method. The materials present mainly mesopores with high surface area values. These materials show anion exchange properties that allowed the immobilization of pH sensing dyes. From the spectroscopic study of hybrid matrix deduced that the organic dye is entrapped in the matrix held by electrostatic interactions and protected against the change of the external pH solution, allowing its use in a large pH range. The encapsulated pH indicator hybrid material after 2hr heating at 150°C shows the good potentiality to be utilized as PH sensor.

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