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Optically active-thermally stable multi-dyes encapsulated mesoporous silica aerogel: A potential pH sensing nanomatrix

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ABSTRACT

Owing to the pH sensing applications, a mixture of four pH dyes (phenol red, bromophenol blue, creosol red, and phenolphthalein) is encapsulated in mesoporous silica aerogel by sol-gel method. FE-SEM analysis shows that dyes have great influence on the morphology of silica matrix. After encapsulation, silica aerogel matrix has low surface roughness ∼ 1.76 nm, ultra-thin layer 8.26 nm, high surface area of 433 m^2/g, high optical transparency 77%, low refractive index ∼1.37 at 550 nm and thermally stable. The sensor response is optimized at pH 1–12 with the high value of pKa ∼8.35 at 565 nm without any leaching traces. The fast response time 0.71s in acidic medium (pH 1) and 0.36 s in basic medium (pH 12) is observed. From experimental findings, it can be concluded that fusion of sol-gel and nano-technologies can thus open a new way to synthesize thermally stable, high quality nano-porous optical material for sensing applications at dynamic pH range.

1. Introduction

Currently, the interest in silica aerogels based nanostructured materials has been stimulated due to the small size of the building blocks (particle, grain, or phase), high surface-to-volume ratios, a low thermal conductivity (0.01–0.03 W/mK), a high porosity (75–99%), low bulk density (up to 95% of their volume is air), hydrophobicity, and a low index of refraction [1,2]. These materials are expected to use as transparent thermal insulators, inter-metal dielectric materials, and space industry, for optical, acoustic and sensing applications [1,3,4].

Opto-chemical sensor applications include explosive detection to prevent the ecological environmental damage, food industry, security (detection of bioterrorist threats) and many more [3,5]. However, the opto-chemical sensors especially pH sensor requires modification such as easily synthesized nano-porous structures materials for their integration in complex environments. The high surface-to-volume ratio and nano-porous structured materials can improve the sensitivity of the sensors towards the harsh aqueous media. Due to the unique properties of the sol-gel method, this technology has exhibited its diversity and potential applications in many frontiers materials science such as biocatalysts, electrochemistry, biosensors, thin film coatings, high-quality glasses for optical components and fibers, fine oxide powders and opto-chemical sensors [2,6]. Sol-gel based silica porous materials/aerogels is an attractive sensing material research applications worldwide because it enhanced the stability of encapsulated molecules by virtue of the rigidity of the inorganic cage, and prevent leaching of encapsulated organic species due to the effective caging. Furthermore, surfactant CTAB was used as pore-forming and structure directing agent to increase the porosity of the silica matrix for good encapsulation towards good sensing performance. For sensing applications/responses, four different pH indicator 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 ($C_{20}H_{14}O_4$) were selected due to their effective behavior towards the ionic strength and more specifically their spectral similarities in absorption and emission properties. Moreover, these dyes have a wide range from near UV to the near-IR regions of the spectrum.

In the present report, a simple low temperature one step sol-gel method was processed to synthesize the silica matrix aerogels and four different pH dyes (phenol red, bromophenol blue, cresol red, and phenolphthalein) were encapsulated in the silica matrix aerogel. The effect of dyes encapsulation on structural, thermal and optical properties of silica matrix aerogel was studied and is proposed to obtain fast responsive sensing material at dynamic pH range. Moreover, the combination of four indicators dyes within silica aerogel matrix can be a

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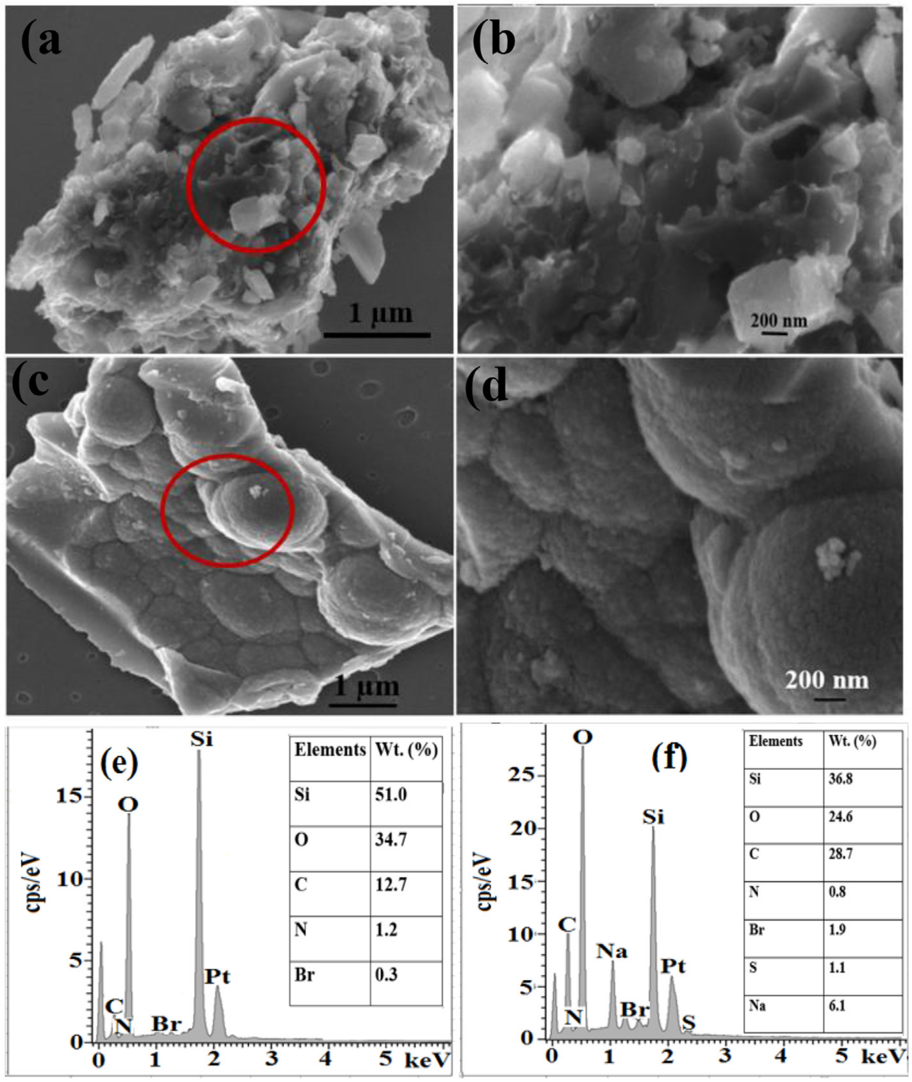

Fig. 1. FE-SEM micrographs of (a) silica matrix aerogel (c) dyes encapsulated silica matrix. (b, d) Corresponding to the zoomed area of marked regions of a and b, respectively. Whereas (e and f) are the EDS spectra of (a, b), Insets corresponding to the elemental compositions in Wt. (%).

novel high surface optical quality material with desirable sensing properties.

2. Experimental procedure

2.1. Chemicals and reagents

The used chemicals i. e, tetraethylorthosilicate (TEOS) [98% Aldrich], ethanol (EtOH), nitric acid (HNO_3) [65% Merck], cetyltrimethylammonium bromide (CTAB), phenol red, bromophenol blue, cresol red, phenolphthalein and standard pH buffer solutions purchased from Sigma–Aldrich and Merck. All these products were used exactly as received without further purifications.

2.2. Synthesis of the sols

For silica sol synthesis, 20 ml of Tetraethylorthosilicate (TEOS) was mixed with 60 ml ethanol, 50 ml deionized water and 1 ml of HNO_3. The molar ratios for TEOS: CH_3CH_2OH: H_2O: HNO_3 was 0.2: 0.4: 0.3: 0.1, respectively. The whole mixture was stirred for 60 min at 60 °C. 5 ml of 0.005 M of surfactant CTAB was added in the above mixture and stirred the solution for another 60 min at 60 °C. The transparent sol was left for appropriate aging cycles at room temperature for 2–3 days. For dyes encapsulation, A 0.005 M concentrated solution of each dye i.e., phenol red, bromophenol blue, cresol red and phenolphthalein was prepared separately. Afterwards, 2 ml from each dye solution was taken and mixed it together vigorously the prepared solution was added to silica sol under continuous stirring for 20 min to ensure the proper combination of the constituents. The whole mixture then stirred and aged at room temperature for 3–4 days. The final product was an orange in color.

Uniform and adhesive films were coated on glass slides for structural and optical characterizations. The glass substrates were chemically cleaned first with acetone for 10 min and then with isopropanol for 20 min in separate runs using an ultrasonic bath for removal of any contaminants and then dried at room temperature. The synthesized sols were spin coated on cleaned glass substrates at a rate of 4000 rpm for 30 s. The coated substrates were aged for 2–3 days at room temperature. Solvent evaporation at room temperature accompanied by further condensation reactions and resulted in solid thin films on the glass substrates.

For sensing analysis, 1 ml of synthesized sol was mixed with 1 ml of each pH solutions 1-12 separately.