



A methanol sensor based on stimulus-responsive magnetic nanoemulsions

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ARTICLE INFO

Article history:

Received 21 March 2013

Received in revised form 7 May 2013

Accepted 9 May 2013

Available online xxx

Keywords:

Methanol sensor

Optical

Chemical sensor

Nanofluid

Nano-emulsion

ABSTRACT

We demonstrate the methanol detection ability of stimulus-responsive magnetically polarizable nanoemulsions. The oil-in-water type of nanoemulsions of droplet radius ~ 100 nm is produced by emulsification of Fe_3O_4 based magnetic nanofluid in presence of water, oil and an anionic surfactant. The nano-emulsion droplets in a cylindrical vial or cuvette placed inside a small solenoid that produces a magnetic field of ~ 100 Gauss constitute the sensor assembly. It is observed that the presence of methanol in ppm level produces strong changes in the repulsive forces between the nanoemulsion droplets, giving rise to a red shift in the incident white light and a visually perceptible color change of the nanoemulsion. The origin of the red shift is studied by measuring the subtle changes in the intermolecular forces between the emulsion droplets in presence of methanol molecules. We observe that the diffusion of methanol molecules significantly alters the onset of electrostatic repulsion between nanodroplets. The sensor showed a linear detection range of 0–2250 ppm and a response time of ~ 1 s. The present approach is a simple, inexpensive and useful for sensitive detection of methanol in aqueous solution.

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1. Introduction

Detection of organic compounds is important for environmental protection, health care and safety during manufacturing of several industrial products [1–4]. Different kinds of sensors have been developed for sensing of toxic [4,5] and biologically important molecules. The most widely used technique for the accurate and reliable detection of volatile organic compounds (VOC) is gas chromatography combined with mass spectrometry [6]. Other VOC sensing approaches are based on piezo resistive techniques [7], hydrogels [8–10], inverse opal [5], carbon/carbon nanotube (CNT) nanocomposite [11], polyimide light guide based optical sensor [12], laterally-oriented ZnO nanowires based sensors [13], photonic crystals based hydrogels, [14–16] hydrogen-bridged cholesteric liquid crystal [17] etc., In recent years, several other semiconductor metal oxide based sensors have been developed for detection of VOCs [18–20]. One of the main drawbacks of many of the VOC sensors is that they work at temperature above $\sim 200^\circ\text{C}$. This warrants the need to develop a room temperature, inexpensive and user friendly approach for VOC molecular sensing with high sensitivity and selectivity. Another major challenge in the molecular recognition of organic materials in aqueous solutions is the interference from water [21]. We tried to address these issues by developing a response-stimulus magnetic nanoemulsion suitable for detection methanol at room temperature [22–24]. Existing methanol sensing

methods, materials used in those sensors, dynamic range, response time and the references are listed in Table 1.

The approach of self assembly is robust and allows creation of new materials and structures [26–28]. The colloidal dispersions offer tunable interaction to go from hard sphere to soft and dipolar ones [25,29–33]. Such tunable properties of magnetic colloids made them wonderful model systems [34–38]. In this paper, we demonstrate that the stimulus-responsive magnetically polarizable nano-emulsion is an ideal candidate for sensing methanol [39,40]. We show that the changes in the organic molecular concentrations produce visually perceptible color changes in the emulsions due to red-shift of the incident light. Further, we also obtain insight into the reasons for the red shift by measuring the intermolecular forces in the presence of methanol molecules.

2. Experimental

2.1. Materials used

Sodium dodecyl sulphate ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4^- \text{Na}^+$) is purchased from Aldrich and is used without further purification. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Oleic acid, 30% NH_4OH used in our experiments were GR grade with 99% purity and were used without any further purification. The Fe_3O_4 nanoparticles and oil-in-water emulsions are produced in our laboratory using well established procedures and the details of the preparation methods are briefly discussed below. Milli-Q water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ is used for all the experiments.

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Table 1
Existing methanol sensing materials, measurement parameter, dynamic range, response time and references.

Material	Measurement parameter	Methanol phase	Dynamic range	Response time (s)	Reference
Polymer based Fiber optics chemical sensor	Optical absorption	Liquid	1 v%	80–100	[65]
Electrochemiluminescence of hydroxyl compounds	Electrochemiluminescence	Liquid	0.01–0.1 M/480.64–806.4 ppm	900	[66]
Polyimide lightguides	Optical-birefringence	Vapour	20%	20–500	[12]
ZnO nanoparticle modified IR internal reflection elements	IR peak intensity	Liquid	1 μ l	~480	[1]
Optical fiber sensing based on xerogel	Reflectance power	Vapour	1.6 mM/48064 ppm	120–440	[67]
Al-doped ZnO thin film	Change in resistance	Vapour	~500 ppm	~200	[68]
Mesoporous photonic crystals	Diffraction peak shift	Vapour	1200–54400 ppmv	~1000	[69]
cyclodextrin derived QCM	Frequency shift	Vapour	3–160 ppm	–	[70]
polymer coated piezoresistive Si bridge	Voltage change	Vapour	0–5000 ppm	60	[7]
Hydrogen-bridged cholestric polymer network	Transmission wavelength	Liquid	40%	–	[17]
Inverse opal hydrogel	Diffraction peak shift	Liquid	0–90%	–	[9]
Magnetic nanoemulsion	Diffraction peak shift	Liquid	0–2250 ppm	~1	Present work

2.2. Preparation of stimulus-responsive magnetically polarizable oil-in-water emulsion

Magnetite (Fe_3O_4) nanoparticles used in the preparation of nanoemulsion was synthesized by a simple co-precipitation technique [41–43]. The freshly prepared iron salt solutions of 0.2 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.4 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were mixed with a 1:1 ratio at a constant stirring speed of 1000 rpm. After the addition of ammonia solution, the pH of the solution reached a value of 10. When the solution turned to black, 20 mL of oleic acid was added and the dispersion pH was adjusted to 9.5. Then the temperature was increased to 70 °C. At the same pH, temperature and stirring speed, the solution was kept for 30 min to finish the coating process. The surfactant coated particles were washed with triply distilled water at 60 °C and then dispersed in hexane. The surfactant-coated magnetite nanoparticles were dried at 35 °C for 48 h in inert atmosphere and then the dried particles were dispersed in octane.

The magnetically polarizable nanoemulsion droplet was prepared by a simple emulsification procedure that involves shearing of magnetic nanofluid (octane based ferrimagnetic nanoparticles of Fe_3O_4 with particle size ~10 nm) in presence of an anionic surfactant of sodium dodecyl sulphate (SDS) and water.[44] SDS is used to stabilize the emulsions, owing to their metastable nature. The crude polydisperse emulsion, produced by the emulsification process, is then converted to a fairly monodisperse one with narrow droplet size distribution using fractionation technique that exploits the depletion flocculation under added surfactant micelles [45]. The depletion flocculation occurs when the interdroplet spacing is smaller than the micellar diameter, where small micelles are excluded from the gap between the droplets. The inherent coupling between the repulsive forces and micelles leads to an existence of this extra thickness that enhances the depletion force [46]. After depletion flocculation, the dilute phase of emulsion droplet is separated and the dense emulsion phase is used for the experiments.

2.3. Characterization of nanoparticles and nanoemulsions

The prepared Fe_3O_4 samples were characterized by X-ray diffraction using Rigaku Ultima IV X-ray diffractometer. The crystallite size (d) was calculated using the Scherrer formula, $d = k\lambda/\beta\cos\theta$, where, $k = 0.89$, $\lambda = 1.5418 \text{ \AA}$, β is the peak width at half the height of highest peak (FWHM) and θ is the half of diffraction angle. The magnetic properties of nanoparticles were studied using cryogen free mini VSM (Cryogenics, UK) for applied field strengths between –2.5 and 2.5 Tesla. The thermo-gravimetric analysis of particles was carried out using a Mettler-Toledo TGA/DSC system under inert

atmosphere from 30–600 °C at a heating rate of 5 °C/min. Small angle X-ray scattering (SAXS) studies were carried out using Rigaku Ultima IV instrument. The scattering intensity $I(q)$ was measured as a function of the scattering vector ($q = 4\pi \sin\theta/\lambda$). The scattering intensity plot was fitted with the spherical model equation, $I(q) = |\Delta\rho|^2 \{ (4\pi/q^3) [\sin(qD/2) - (qD/2)\cos(qD/2)] \}^2$ where, D is the diameter of the particle and $\Delta\rho$ is the difference in electron density of the particle and the suspended medium (i.e. octane). The most probable particle size was obtained from the distance distribution function. Fourier transform infrared spectroscopy (FTIR) studies were done using ABB Bomem MB 3000 instrument. The spectrum was obtained in the wave number range of 400 to 3600 cm^{-1} . The size distribution of the nanoparticles and emulsion were determined by dynamic light scattering using a Zetasizer-Nano (Malvern Instrument). The hydrodynamic radius (R_H) of the solute particles is calculated from the diffusion coefficient (D), using the Stokes–Einstein equation $R_H = k_B T/6\pi\eta D$ where k_B is the Boltzmann constant and η is the viscosity of the solvent. The zeta potential (ζ) is obtained from the electrophoretic mobility (u) using the Smoluchowsky equation $\zeta = u\eta/\epsilon$, where η and ϵ are the solution viscosity and dielectric constant of the medium respectively. The force measuring apparatus comprises of a solenoid type electromagnet, programmable variable current source, white light source and a spectrograph. The details of the force apparatus is discussed elsewhere [47,48]. By varying the magnetic field strength, the distance between the colloidal particles is precisely controlled. The force apparatus is capable of measuring very weak forces between the droplets in the range of 10^{-11} to 10^{-14} N, with a sensitivity in the inter-particle spacing of 0.2 nm. This is a unique technique that allows in situ measurement of forces between the droplets or particle in solutions [49,50].

3. Results and discussion

3.1. Properties of nanoparticles and stimulus-responsive nano-emulsions

The room temperature XRD pattern of Fe_3O_4 nanoparticles (Figure S1a–supporting information) shows diffraction peaks of 220, 311, 400, 422, 511, and 440 that are indexed to a cubic spinel structure and the pattern matches well with Fe_3O_4 phase of JCPDS no. 19–0629. The average crystallite size obtained from Scherrer formula was ~10 nm. The magnetization data of nanoparticles shows superparamagnetic nature with a zero remanence and coercivity. (Figure S1b–supporting information). The parallel alignment

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