

Optical Chemical Sensors on the Base of Arrays of Ink-Jet Printed Micro- and Nanoparticles

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ABSTRACT

Arrays of ammonia and VOCs-sensitive colloidal sensing elements were fabricated using ink-jet printing technology. Three kinds of immobilization techniques were used to entrap fluorescent indicator dyes on the surface of colloidal microparticles. The fluorescence responses of sensor arrays to the vapors of various analytes at the 10 ppm level were studied.

Keywords: fluorescence, microparticle, sensing element, ink-jet, sensor array.

1 INTRODUCTION

The design and development of novel optical chemical sensors are subjects of active research in recent years [1]. In particular, the development of chemical sensors capable of monitoring volatile organic compounds (VOCs) at trace concentrations is driven by the ever-expanding monitoring needs of a wide variety of species in gases.

The concept of cross-reactive sensor array has led to important developments in the analysis of gaseous analytes [2, 3]. Because of its intrinsic sensitivity (down to single molecule level), fluorescence-based sensing occupies a central position in the field of optical chemical sensors.

New approaches to fluorescence sensing continue to appear. For example, colloidal crystals and aggregates made of organic or inorganic microspheres represent a new class of advanced materials that have many potential applications in fields such as photonics and chemical sensing [4, 5].

Fluorescent indicator dye is a key component of fluorescent sensing materials [6, 7]. Colloidal assemblies are promising materials for use in VOC vapor sensors since fluorescent indicator dyes can be immobilized on the surface of latex particles by different methods.

Printing technologies allow deposition of micro- and nanoparticles with high accuracy that can be used for fabricating desired sensing elements and arrays [8]. Self-assembly of dye-containing particles into ordered structures permit one to optimize the functional characteristic of sensor material and, respectively, sensor response by varying properties of components on different levels of hierarchically organized arrays (Fig. 1). For example, the dye structure [9], the sizes of microparticles, the nature of functional groups on the particle surface may be varied.

In addition, the ink-jet printing method holds promise for creating on-chip arrays of miniature sensors for different analytes.

Rational design of sensing materials based on prior knowledge is a very attractive approach but it requires detailed knowledge regarding optical properties of dyes, specific features of their interactions with polymers and analytes, diffusion characteristics for analytes of interest, etc.

In particular, behaviour and properties of dyes entrapped on the particle surface by means of different methods are of great interest.

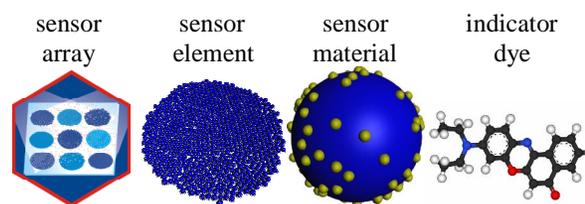


Figure 1: Schematic representation of hierarchical organization of a sensor array.

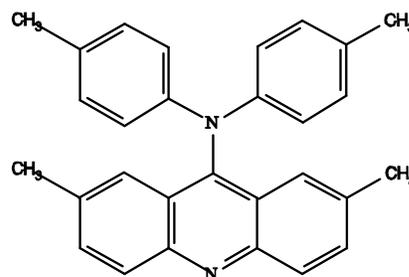


Figure 2: Structure of DTAA molecule.

In this study, vapor-sensitive microarrays of sensing elements containing different fluorescent indicator dyes were investigated. Well-known fluorescent dyes Nile Red and fluorescein, as well as a novel solvatochromic acridinic dye, 2,7-dimethyl-9-ditolylaminoacridine (DTAA, Fig. 2), were used as indicator dyes [10, 11]. Three different kinds of immobilization techniques were used – adsorption, covalent immobilization and photochemical formation of DTAA dye on the surface.

2 EXPERIMENTAL

2.1 Indicator Dyes

Nile Red (NR) and fluorescein isothiocyanate (FITC) purchased from "Aldrich" were used without additional purification. DTAA was formed on the surface of microparticles from p,p'-ditolylamine and CBr₄ under UV light irradiation [10].

2.2 Polymeric dispersions preparation

Styrene (St), methacrylic acid (MAA), N-vinylformamide (VFA), and thioglycolic acid (TGA) were purchased from "Aldrich" and distilled using standard techniques. Potassium persulfate K₂S₂O₈ of technical grade was recrystallized from water. The other initiator – 2,2'-azo-bis-[2-(2-imidazoline-2-yl) propane] dihydrochloride (AIP) ("Wako" Pure Chemical Industries Ltd.) were used without additional purification.

Polymeric dispersions were prepared by emulsifier-free emulsion polymerization carried out in a four-necked glass reactor with a glass paddle-type stirrer, a condenser, an argon inlet, and a temperature controller. One half of hydrophilic monomer (MAA or VFA) was added to the solution of an initiator (K₂S₂O₈ or AIP) in double-distilled water (refluxed and cooled down in argon flow). Then the mixture of styrene with the second part of the hydrophilic monomer and one of chain transfer agents (TGA or *o*-DA) was added and pH of the mixture was adjusted by aqueous NaOH or HCl addition to achieve sufficient ionization degree of reagents. Continuous stirring at 300 rpm and constant temperature varied from 70 to 90°C were maintained during polymerization. After synthesis residual monomers were removed by distillation. Then obtained polymeric particles were washed by successive centrifugation followed by redispersion in double-distilled water to remove water-soluble impurities [12].

2.3 Adsorption of Nile Red on the surface of poly(St-co-MAA) or poly(St-co-VFA) particles

NR solution in ethanol (0.5 mg/mL) was added to 1 wt% polymeric aqueous dispersions (1 mL). Total loaded NR was adsorbed on the particle surface, which was proved by adsorption spectroscopy. The dye surface concentrations are given in Table 1.

2.4 Covalent bonding of FITC on the surface of poly(St-co-VFA) particles

Freshly prepared FITC solution in ethanol (1 mg/mL) was added to 1 wt% polymeric aqueous dispersions (1 mL). Following the interaction between surface aliphatic amino groups and FITC, polymeric particles were washed by successive centrifugation and redispersion in ethanol and

then in double-distilled water to remove unbound dye. The amount of unbound FITC was determined by adsorption spectroscopy. Obtained FITC chemisorption values are given in Table 1.

2.5 Fabrication of sensor microarrays

A tabletop ink-jet printing system Jetlab II (Microfab Inc.) operating in a drop-on-demand mode was used for fabrication of sensor microarrays. A printing device with 50 µm diameter of orifice was installed on the system for deposition of polymeric dispersions.

A typical sample consists of four arrays containing 12 x 60 sensing elements (dots) with the interval between dots about 0.3 mm and the size of a single dot about 50 µm. These arrays were deposited on the hydrophobized surface of a glass slide (18 x 18 mm). The arrays on a slide were fabricated from a given polymeric dispersion and differed in the number of drops per one dot (2, 5, 10, and 20 for first, second, third, and fourth array, respectively). Several tens of samples with different types of particles, surface functional groups, particle sizes and indicator dyes were fabricated.

2.7 Instrumentation

Sizes of polymeric particles were measured by a JEM 100S (JEOL) transmission electron microscope. The particle size distribution was characterized by the root-mean-square deviation, σ . The surface concentration of functional groups was determined by conductometric titration.

The electrophoretic mobility of the particles was studied using standard microelectrophoresis in 10⁻³ mol/L NaCl. Before measurements, the equilibrium between particle surface and the solution was achieved for 24 h. The obtained data were used for calculation of particle ζ -potentials by Smolukhovskiy equation.

A laser confocal scanning microscope Nikon E600 C1 was used for studying the spectral-luminescent properties of arrays and individual sensor elements. The fluorescence spectra were recorded by means of a fiber-optic spectrometer AvaSpec 2048 (Avantes), which was connected to the microscope port. In some cases a Shimadzu-5001 spectrofluorimeter was used.

Packaging of particles in a sensor element was studied with a JSM 6490 (JEOL) scanning electron microscope (SEM) and a Solver-Bio (NT-MDT) atomic-force microscope (AFM) in semicontact mode. Responses of sensor arrays to different analytes and sensor functional characteristics were studied with a test system developed in the Photochemistry Center [13]. In the system, a metrologically certified permeation-tube generator is used for preparation of vapor mixtures. Vapor mixture from the generator goes to analytical cell with experimental sample of a sensor array. For recording array responses, a scientific grade CCD-camera or a fiber-optic spectrometer were used.

Sample	D, nm	σ , %	Surface weak acid or base, $\mu\text{mol}/\text{m}^2$	ζ , mV (pH 6.7)	Dye, $\mu\text{mol}/\text{m}^2$	
					Nile Red	FITC
poly(St-co-MAA)	1	220	2.5	-58	0.47	–
	2	270	0.9	-53	0.57	–
	3	340	0.6	-48	0.57	–
	4	540	2.9	-42	0.63	–
poly(St-co-VFA)	5	130	1.4	+51	0.31	0.24
	6	220	2.8	+45	0.31	0.30
	7	280	3.3	+41	0.31	0.30
	8	1500	1.0	+35	–	0.55

Table 1. Characteristics of poly(St-co-MAA) and poly(St-co-VFA) particles and dye binding.

3 RESULTS AND DISCUSSION

Some typical examples of obtained experimental data are presented below. Figs. 3 (a) and 3 (b) show the optical micrograph and fluorescence image of fragments of an array of sensing elements based on 220 nm poly((St-co-MMA) particles with immobilized DTAA.

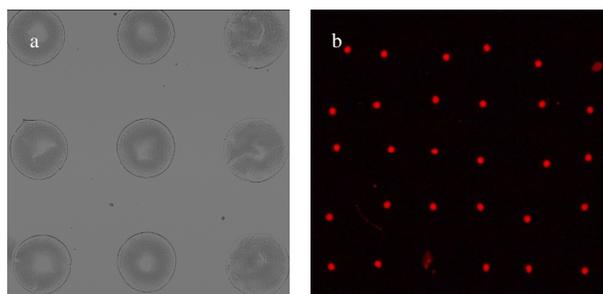


Figure 3: (a) Transmission and (b) confocal fluorescence images of sensor array fragments. Fluorescence image (at 650 nm) was acquired with excitation at 520 nm.

Optical image of an individual sensing element of the order of 50 μm in diameter is shown in Fig. 4 (a).

The microstructure of an individual colloidal aggregate was studied with scanning electron microscope and atomic force microscope. Figs. 4 (b), 4 (c), and 4 (d), shows that the aggregate is an assembly of ordered microparticles and has a hemispherical form.

The fluorescence spectra of sensor elements based on 200 nm poly(St-co-MMA) latex particles with different indicator dyes are presented in Fig. 5.

Fig. 6 illustrates observed hypsochromic shift of the fluorescence spectrum of sensor elements based on poly(St-co-MMA) and DTAA in the presence of 200 ppm ammonia vapor.

Fluorescence responses versus time to acetone vapors of similar elements with immobilized FITS and Nile Red are shown in Fig. 7.

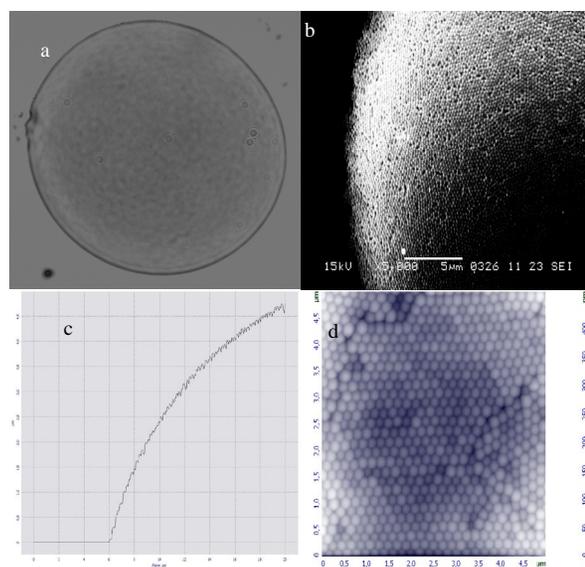


Figure 4: Images of a sensing element: (a) bright field microscope image; (b) SEM image; (c) profile of a sensing element measured by means of AFM; (d) semicontact mode AFM image of the upper layer of latex particles.

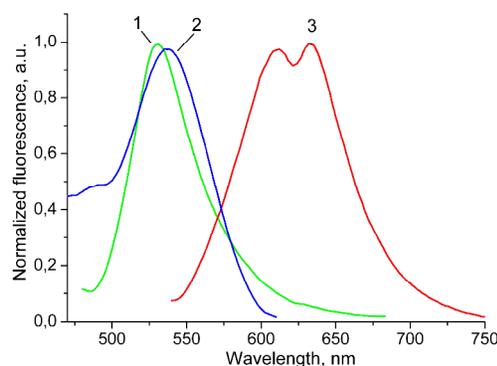


Figure 5: Fluorescence spectra of sensor elements on the base of poly(St-co-MMA) particles dyed with (1) FITC; (2) DTAA; and (3) Nile Red.

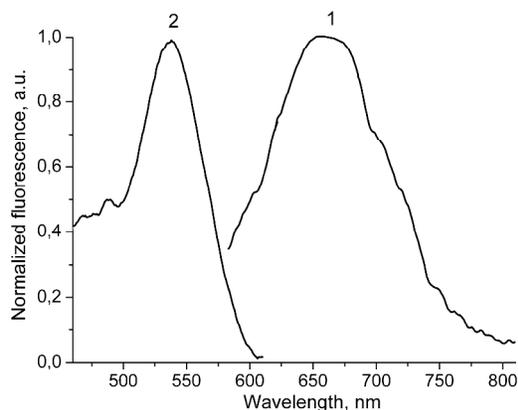


Figure 6: Fluorescence spectra of a sensor element based on poly(St-co-MMA) and 9-DTAA (1) before and (2) after exposure to 200 ppm ammonia vapors.

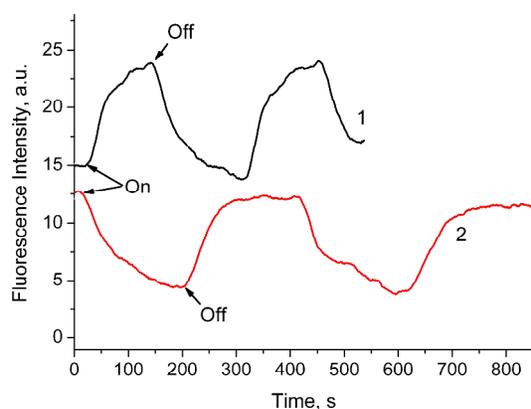


Figure 7: Fluorescence responses of sensor elements to acetone admission-removal cycles: (1) sensor element on the base of FITC and poly(St-co-MMA) particles, the fluorescence intensity was monitored at 530 nm; (2) sensor element on the base of Nile Red and poly(St-co-MMA) particles, the fluorescence intensity was monitored at 600 nm. On: a stream of zero air containing 10 ppm acetone was passed through the sensor element; off: a stream of zero air was passed through the sensor element, flow rate: 73 ml/min.

As follows from the results presented above, all the three methods of dye immobilization are advantageous for creating sensing elements and corresponding sensor arrays.

Figs. 6 and 7 demonstrate that changes in the position of fluorescence bands as well as quenching or enhancement of fluorescence intensity may be used as fluorescence response to the presence of VOC vapors.

In the case of DTAA the observed hypsochromic shift of the fluorescence band is connected with deprotonation of DTAAH^+ due to the reaction of proton transfer from DTAAH^+ to NH_3 .

Mechanisms of the fluorescence quenching and enhancement characteristic of the sensing elements with FITS and Nile Red require further investigations.

4 CONCLUSIONS

Ink-jet printing technology was used to fabricate arrays of vapor-sensitive sensing elements consisting of assemblies of dyed colloidal microparticles. The technology is potentially amenable to fabrication of multianalyte sensors to simultaneously analyze given sets of VOCs. Optical and functional properties of sensing materials and corresponding sensing elements and sensors can be tuned by varying the nature of fluorescent dyes, polymers, sizes of latex particles, methods of dye immobilization, etc.

REFERENCES

- [1] "MNT Gas Sensor Roadmap", MNT Gas Sensor Forum, 3, 2006.
- [2] J. R. Epstein, D. R. Walt, *Chem. Soc. Rev.* 32, 203, 2003.
- [3] N.A. Rakow, K.S. Suslick, *Nature* 406, 710, 2000.
- [4] J. Park, J. Moon, H. Shin, D. Wang, M. Park, *J. Colloid. Interface Sci.* 298, 713, 2006.
- [5] J.C. Carter, R.M. Alvis, S.B. Brown, K.C. Langry, T.S. Wilson, M.T. McBride, M.L. Myrick, W. R. Cox, M.E. Grove, B.W. Colston, *Biosens. Bioelectron.* 21, 1359, 2006.
- [6] V.G. Plotnikov, V.A. Sazhnikov, M.V. Alfimov, *High Energy Chemistry* 41, 299, 2007.
- [7] V.A. Sazhnikov, M.V. Alfimov, *Chem. Eng. Trans.* 15, 267, 2008.
- [8] P. Calvert, *Chem. Mater.* 13, 3299, 2001.
- [9] Y. Urano, M. Kamiya, K. Kanda, T. Ueno, K. Hirose, T. Nagano, *J. Am. Chem. Soc.* 127, 4888, 2005.
- [10] V.A. Sazhnikov, A.A. Khlebunov, M.V. Alfimov, *High Energy Chemistry* 41, 25, 2007.
- [11] L.G. Samsonova, N.I. Selivanov, T.N. Kopylova, V.Y. Artyukhov, G.V. Maier, V.G. Plotnikov, A.A. Khlebunov, V.A. Sazhnikov, M.V. Alfimov, *High Energy Chemistry* 43, 105, 2009.
- [12] A.Yu. Men'shikova, T.G. Evseeva, K.S. Inkin, Yu.O. Skurkis, S.S. Ivanchev, *Russ. J. Appl. Chem.* 79, 1660, 2006.
- [13] A.A. Khlebunov, D.S. Ionov, V.M. Aristarkhov, V.A. Sazhnikov, M.V. Alfimov, *Chem. Eng. Trans.* 15, 293, 2008.