

FABRICATION OF FLUORESCENT AMMONIA SENSOR USING POLYMER NANO- AND MICROPARTICLES

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1. INTRODUCTION

The opportunity to control of ammonia is important in different application areas such as environmental gas analysis, automotive and chemical industry, medical diagnostics, etc. Some monitoring systems require very low detection limits (for example, 50 ppb for diagnostic breath analysis) [1].

Ink-jet printing is known to be one of the most promising methods for controlled deposition of functional materials [2]. For example, arrays of the colloidal photonic crystals may be directly fabricated using an ink-jet printing [3]. Development of optical sensor materials based on micro and nanoparticles with dyes immobilized on their surface was pointed out to be very important for further optical chemical sensors and electronic nose systems progress [3]. It is obvious that a wide range of materials can be created by combining different dyes, particles and methods of immobilization and that a chemical modification of the indicator dye and the surface of the particle permit functional characteristics of material to be tailored for a specific analyte or a group of analytes.

Many features make fluorescence one of the most powerful transduction. Therefore, an array of sensor elements each of which represents an ensemble of fluorescent functional micro- or nanoparticles is a perspective transduction platform [5, 6].

In this study, the results of studying fluorescent sensor microarrays fabricated by inkjet printing and application of the arrays to ammonia detection are presented.

2. EXPERIMENTAL

2.1 Materials

Styrene (St), methacrylic acid (MAA), N-vinylformamide (VFA), and thioglycolic acid (TGA) were purchased from Aldrich and distilled using standard techniques. Potassium persulfate $K_2S_2O_8$ of technical grade was recrystallized from water. Chemical Industries Ltd.) as well as dyes – Nile

The other initiator – 2,2'-azo-bis-[2-(2-imidazoline-2-yl) propane] dihydrochloride (AIP) ("Wako" Pure). Carbon tetrabromide (Merck) and ditolylamine (Aldrich) were used as received.

2.2 Polymeric dispersions preparation

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 ($K_2S_2O_8$ 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 [7]. Information about particles properties are presented on Fig. 1. and in Table 1.

2.3 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 μ m diameter of orifice was installed on the system for deposition of polymeric dispersions.

A typical sample consists of four 12x60 sensor elements (dots) arrays with the interval between dots about 0.3 mm and the size of a single dot about 50 μ m. These arrays were deposited on the

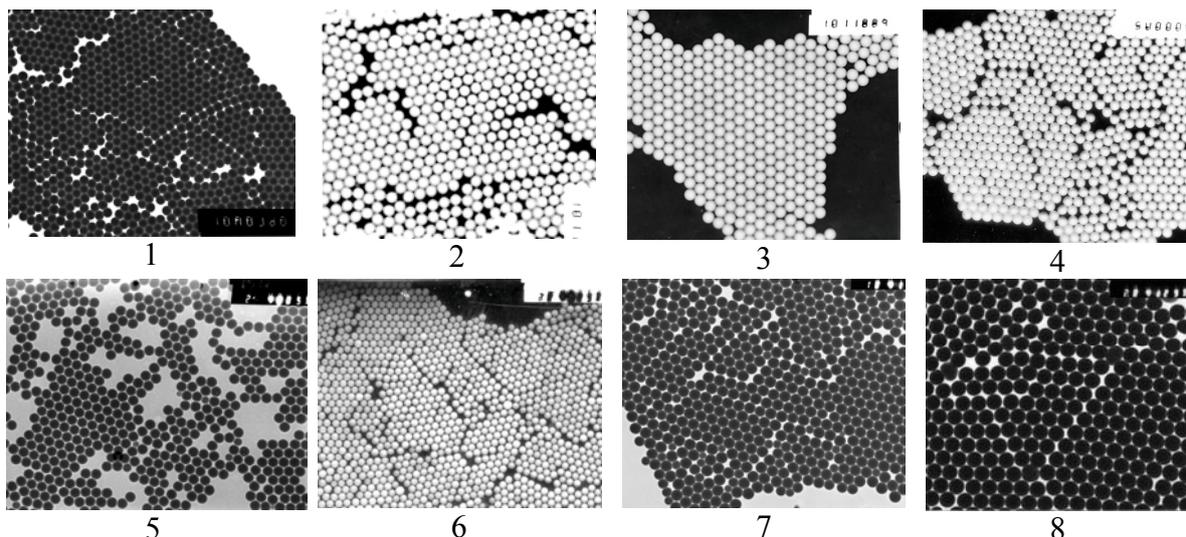


Fig. 1. TEM micrographs of poly(St-co-MAA) (1-4) and poly(St-co-VFA) (5-8) particles.

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

Sample	D, nm	σ , %	Surface weak acid or base, $\mu\text{mol}/\text{m}^2$	ζ , mV (pH 6.7)	
poly(St-co-MAA)	1	220	2.5	1.5	-58
	2	270	0.9	1.2	-53
	3	340	0.6	1.4	-48
	4	540	2.9	1.7	-42
poly(St-co-VFA)	5	130	1.4	1.1	+51
	6	220	2.8	0.3	+45
	7	280	3.3	0.7	+41
	8	1500	1.0	0.5	+35

hydrophobic surface of a glass slide (18x18 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.

Some of experimental samples were fabricated from dispersions containing no indicator dye. These samples were used for photochemical synthesis of a fluorescent dye. After drying, samples were kept in the atmosphere of ditolylamine and carbon tetrabromide vapor and then irradiated using a UV/visible light source. As a result, a solvatofluorochromic dye, 2,7-dimethyl-9-(ditolylamino)acridine (9-DTAA) (Fig 1.), was formed on the surface of microparticles [8,9].

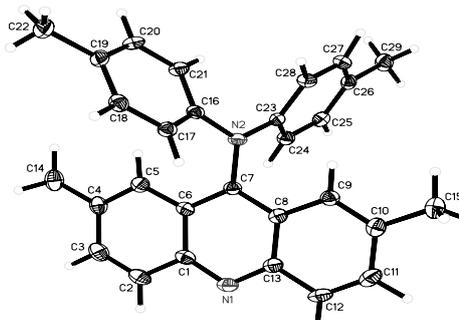


Figure 2. Molecular structure of 9-DTAA.

2.4 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 Smolukhovsky 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 its functional characteristics were studied with a test system developed in the Photochemistry Center [10]. 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 of array responses, a scientific grade CCD-camera or a fiber-optic spectrometer were used.

3. RESULTS AND DISCUSSION

Fig. 1 shows, as an example, TEM micrographs of different types of synthesized particles.

In Fig. 3, a fragment of a sensor array fabricated from poly(St-co-MAA) particles (diameter 220 nm) containing 9-DTAA is shown.

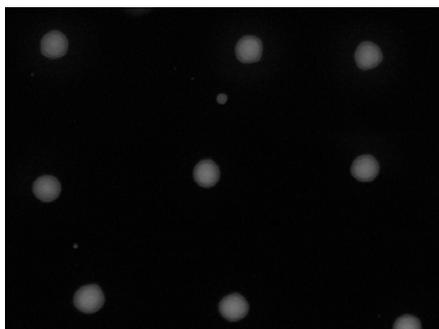


Figure 3. Fragment of a sensor array. Diameter of a sensor element is 50 μ m, distance between elements is about 0.3 mm.

Figs. 4 and 5 show the SEM and AFM images of a sensor element of the array, respectively.

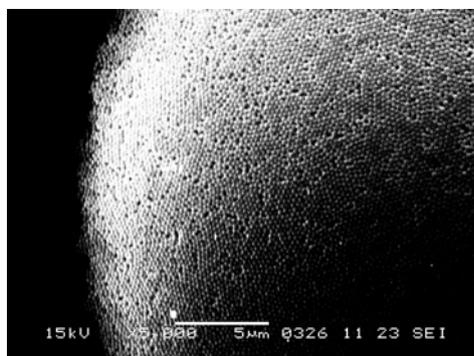


Figure 4. SEM image of a sensor element.

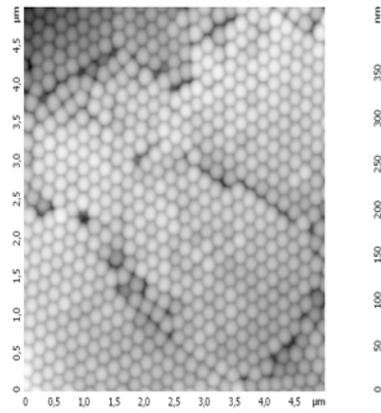


Figure 5. AFM image of the surface of a sensor element.

It is seen that particles after deposition onto hydrophobic surfaces are assembled into ordered structures like photonic crystals. It was stated that the structure of particle ensembles is independent of the number of drops deposited per one sensor element and the particle size.

Fig. 7 shows the fluorescent signals of individual sensor elements fabricated from poly(St-co-MAA) and poly(St-co-VFA) particles (diameter 220 nm) with immobilized 9-DTAA upon exposure of ammonia vapors.

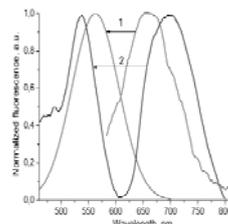


Figure 7: Responses of sensor elements upon ammonia vapors: 1 – 9-DTAA and poly (St-co-MMA), 2 – 9-DTAA and poly (St-co-VFA).

Responses of obtained sensor arrays to different analytes were studied, as well as some functional characteristics such as response time,

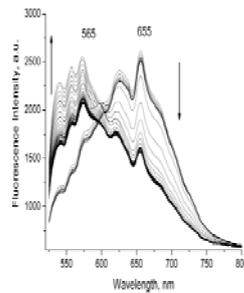


Figure 8. Response of a sensor array doped with 9-DTAA to ammonia vapor.

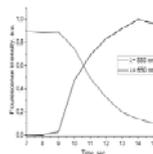


Figure 9. Kinetics of response of sensor array.

recovery time and limit of detection of sensor arrays were determined. In Fig. 8 and Fig. 9, the response of a sensor array (poly(St-co-MAA) particles, diameter 220 nm, indicator dye 9-DTAA) to ammonia can be seen. The concentration of ammonia vapor was 200 ppm, the exposure time was 30 s. It is seen that the fluorescence intensity at 655 nm is decreased whereas the intensity at 565 nm is increased. This is due to deprotonation of 9-DTAA in the presence of ammonia. The response time is about 15 seconds.

5. Conclusions

Sensor microarrays composed of dyed colloidal particles were fabricated by inkjet printing. Microstructural observations indicate that in some cases the colloidal assemblies have the structure like photonic crystals. It was shown that different dyeing procedures can be used for fabrication of sensor arrays. It was observed that obtained arrays exhibit sensitivity to ammonia.

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