Chemically Responsive Nanoporous Pigments: Colorimetric Sensor Arrays and the Identification of Aliphatic Amines

Jin Ho Bang[†], **Sung H. Lim**[†], **Erwin Park**, and **Kenneth S. Suslick**[*]
School of Chemical Sciences, University of Illinois at Urbana–Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Abstract

A general method has been developed for the preparation of microspheres of nanoporous pigments, their formulation into chemically responsive pigment inks, and the printing of these inks as calorimetric sensor arrays. Using an ultrasonic-spray aerosol–gel synthesis from chemically responsive dyes and common silica precursors, 16 different nanoporous pigment microspheres have been prepared and characterized. New calorimetric sensor arrays have been created by printing inks of these chemically responsive pigments as primary sensor elements; these arrays have been successfully tested for the detection, identification, and quantitation of toxic aliphatic amines. Among 11 structurally similar amines, complete identification of each analyte without confusion was achieved using hierarchical cluster analysis (HCA). Furthermore, visual identification of ammonia gas was easily made at the IDLH (immediately dangerous to life or health), PEL (permissible exposure limits), and 0.1 PEL concentrations with high reproducibility.

Introduction

For all chemical sensor technology, the sensor surface is obviously critical to the interactions between the sensor and the analyte that are responsible for the sensor response. Especially with the development of sensor arrays for electronic nose applications (which has emerged as a very powerful approach for the selective identification of chemically diverse analytes[1–5]), control of analyte–surface interactions is central to improvements in both sensitivity and selectivity. Sensor arrays do not have highly specific receptors for specific analytes; instead, the array uses cross-responsive sensor elements to mimic the mammalian gustatory and olfactory systems by producing a unique *composite* response for each analyte.[1–4] Prior electronic nose technologies have generally employed physical adsorption onto metal oxide surfaces or absorption into conductive polymers as the primary analyte–sensor interaction,[2] but such interactions are weak (leading to low sensitivity) and nonselective (leading to poor discrimination). In contrast, we have previously reported on the development of a rather different, but quite simple, optoelectronic approach using a calorimetric sensor array of chemically responsive dyes (i.e., soluble colorants whose colors are affected by a wide range of analyte–dye interactions, including Brønsted and Lewis acid–base, Bipolar, and π–π interactions).[4–6]

To make more robust calorimetric arrays, one would prefer a solid-state pigment rather than a soluble dye. Nonpermeable pigments, however, cannot function as sensors: only the surface of a pigment particle will be accessible to analytes. The formation of porous pigments or immobilized permeable polymers from soluble dyes has well-developed precedents for bulk films or monoliths, both in sol–gel matrices[7–11] and in plasticized polymer films.[12] The

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*Corresponding author. E-mail: ksuslick@uiuc.edu.
[†]Contributed equally to this work.

creation of a printable formulation of nanoporous pigments and the use of such nanoporous pigment inks to form a sensor array, however, have not been previously reported.

We have explored a new methodology for the preparation of chemically responsive inks based on nanoporous silica pigments made by an aerosol–gel method. This synthetic method utilizes an ultrasonic spray to generate an aerosol from homogeneous precursor solutions, which is then heated in a gas stream to provide a continuous flow production of dye–silica microspheres. The precursors in the sprayed homogeneous solutions are confined in each micron-sized aerosol droplet, which act as individual microreactors, providing a facile and quite general method of preparing microcomposite materials.[13–17] We report here the application of ultrasonic-spray aerosol–gel synthesis for the preparation of micron-sized spheres of dye-encapsulated nanoporous pigments, demonstrate the use of these inks to print calorimetric sensor arrays, and show their application to the selective identification and detection of amines.

Experimental Section

Nanoporous Pigments Preparation and Characterization

All commercial chemicals were used as received unless otherwise specified. Tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), and the organic dyes used in this study were purchased from Sigma-Aldrich. A pictorial representation of a laboratory-scale aerosol–gel setup is shown in Figure 1. In a typical preparation, a precursor solution was made from 2 g of TMOS, 2 g of MTMS, 11 g of ethanol, 28 g of water, and 1 g of 0.1 M aqueous hydrochloric acid and combined with 40 mg of dye; the molar ratio of MTMS to TMOS was 1.1. The precursor solution was introduced into an atomization cell and nebulized by a 1.7 MHz household ultrasonic humidifier (Sunbeam model 696), as described elsewhere.[17] The resulting aerosol was carried through a tube furnace set at a temperature between 200 and 400 °C in an Ar flow at 1.0 SLPM (standard liters per minute). The product was collected in several bubblers containing deionized water and then isolated by centrifugation. After several washings with ethanol and deionized water, the micron-sized powder was dried at room temperature.

For characterization of nanoporous pigments, scanning electron microscopy (SEM) was carried out with a Hitachi S-4700, and transmission electron microscopy (TEM) was performed using a JEOL 2010F with an acceleration voltage of 200 kV. Diffuse reflectance ultraviolet–visible (UV–vis) spectra of the products were obtained using a Hitachi 3300 double monochromator UV–vis spectrophotometer.

Array Preparation and Sensing Experimental Procedure

Prior to the printing, the nanoporous silica-dye pigments were dispersed in 7:3 mixtures of deionized water and 2-methoxyethanol. A calorimetric sensor array was then prepared by spotting suspensions of 16 different pigments onto standard chromatography paper (Whatman Chrl) using a 4 ×4 array of free-floating slotted dip-pins (V & P Scientific, Inc., San Diego, CA). For the detection of aliphatic amines, sensing experiments were performed using a static cells[5] In the ammonia sensing experiments, a certified premixed gas tank from S. J. Smith, Co. (Urbana, IL) was used. Ammonia was mixed with dry and wet nitrogen gas with a manifold of MKS digital mass flow controllers to achieve the desired concentrations and relative humidity. In order to confirm the reproducibility of the array responses, triplicate runs were performed. Difference maps were obtained from the scanned images (cf. Supporting Information, Figure S2, for an example) by digitally subtracting the before image from the after image and averaging the center half of each spot's red, green, and blue (RGB) values using a customized software package, ChemEye (ChemSensing, Inc., Champaign, IL; http://www.chemsensing.com); Adobe PhotoShop may also be used for such analyses. This

results in a 48-dimensional vector with a potential range from −255 to +255 (i.e., 16 changes in red, green, and blue values) that quantitatively represents the calorimetric response of the array.[4] Chemometric analysis (specifically, principal component analysis (PCA) and hierarchical cluster analysis (HCA)[18]) on the difference vectors was carried out using the Multi-Variate Statistical Package (MVSP, v. 3.13i, Kovach Computing).

Results and Discussion

For sensing array applications involving chemoresponsive pigments based on initially soluble dyes, there are four requirements: (1) all colorant centers must be accessible to analytes; (2) the dye must be immobilized in a porous or permeable host material to prevent leaching or blooming of the colorant; (3) the immobilized dye must be solvated in the host matrix to prevent dye crystallization (because solid dye particles are not generally permeable and therefore unresponsive to analytes); and (4) the pigment must be in a printable form. Among various host materials available, ORMOSILs (organically modified silicates) offer additional advantages of high stability, controllable pore size, and ease of modification (e.g., controllable hydrophobicity).[7–11] These features contribute to enhanced analyte adsorption (i.e., effective "preconcentration" of analyte), leading to increased sensitivity.

We have focused on aliphatic amines as our test analyte to demonstrate the effectiveness of our approach. Aliphatic amines are common pollutants found in industrial wastewater effluents and agricultural runoff due to their wide use in numerous industrial applications.[19] Consequently, the development of selective and rapid sensing technology for aliphatic amines has been an area of great interest. Furthermore, amines are common bacterial metabolic byproducts and can be used as indicators to estimate food freshness.[20] Hence, a practical and robust detection method for amines is of great value in environmental monitoring as well as in food quality control. Several different methods have been previously reported for amine sensing, using various single colorimetric sensors, including the use of metalloporphyrins,[4, 5,21] molecular imprinting,[22] functionalized mesoporous silica,[23] and chromogenic reagents. [24] The ability to distinguish one closely related amine from another, however, requires the use of a sensor array.[4,5]

A total of 16 different nanoporous pigment microspheres were prepared via the ultrasonic-spray aerosol–gel method, formulated into chemoresponsive inks, and dip-pen printed to prepare colorimetric sensor arrays. We used two common silicon alkoxides, TMOS and MTMS, as the matrix-forming precursors to manipulate the porosity of the resulting pigments. When the pigments were prepared using *only* TMOS, the pigments were *not* porous and did *not* show any color change either in response to acidic or basic gases or to acidic or basic aqueous solutions. The pigments obtained using the mixture of TMOS and MTMS, however, were highly porous and exhibited very rapid (subsecond) color changes in response to changes in pH. This indicates that the nanoporous structure resulting from the use of MTMS plays an important role in the diffusion of an analyte into the pigments. As the concentration of MTMS increased, the response time became increasingly more rapid. If MTMS was used alone, however, a significant amount of dye could be leached by aqueous solutions. In our study, a nanoporous pigment prepared with a 1.1 molar ratio of MTMS to TMOS was found to be optimal in terms of response time, consistency, and permanence of dye encapsulation.

We also observed that the furnace temperature had a significant effect on the properties of the pigments microspheres. Representative SEM images of nanoporous pigment microspheres incorporated with bromocresol green (BCG-SiO$_2$) and prepared at 200, 300, and 400 °C are shown in Figure 2. At 200 °C (Figures 2a and 2b), these nanoporous pigment microspheres are smooth-surfaced with diameters ranging from 0.4 to 1.5 µm and are extremely responsive to exposure to a pH 10 aqueous solution (response time < 1 s). As the furnace temperature was

increased to 300 °C (Figure 2c), however, small bumps appeared on the surface of the microspheres, the porosity was diminished, and response time becomes much worse (5–10 min). When the furnace temperature was set to 400 °C (Figure 2d), the formation of these bumps was substantial, the porosity was lost, and the pigment no longer responds to changes in pH even after several hours. We attribute the slow response time observed in pigments obtained at higher temperatures to the collapse of surface pores, which prevents facile diffusion of the analytes to the colorant centers within the silica matrix.

The TEM image (Figure 3a) of a pigment microsphere synthesized at 200 °C shows the nanoporous structure of the silica sphere that results from the amorphous organosilica network formed by the use of MTMS. The incorporation of pH dye molecules into the silica matrix was examined by energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis conducted in scanning transmission electron microscopy (STEM). The X-ray emission from the Br K_α shell, which originates from the bromine in BCG molecules, was observed along with Si K_α and O K_α signals, showing a uniform distribution of BCG molecules throughout the silica microspheres (Figure 3b).

Diffuse reflectance UV–vis spectra of BCG–SiO_2 microspheres are shown in Figure 4 as a function of pH. It is well-known that in an acidic solution, BCG ionizes to give a yellow monoanionic form, but further deprotonation at higher pH confers the blue dianionic form to BCG. As shown in Figure 4, BCG–SiO_2 washed with a acidic solution exhibits strong absorption in the range of 400–600 nm, whereas BCG–SiO_2 washed with a basic solution absorbs visible light mostly in the range of 500–800 nm. The same optical responses were observed in other BCG–SiO_2 synthesized at higher temperatures (i.e.,$\geq$300 °C), but the response time was much slower.

The reversible characteristics of the chemical response of the nanoporous pigments led us to exploit them in sensing applications. To demonstrate the utility of these nanoporous pigments in calorimetric sensor arrays, 16 different nanoporous pigment microspheres (incorporating 14 different pH dyes and 2 solvatochromic dyes, Table 1) were prepared using the same procedures as for BCG–SiO_2 (i.e., furnace temperature at 200 °C) and resulting in very similar microspheres. For fabrication of the calorimetric sensor arrays, chemoresponsive inks were made from the nanoporous pigment microspheres by dispersal in an aqueous solution of 2-methoxyethanol, printed on standard chromatography paper using slotted dip-pins, and dried under vacuum.

The resulting sensor arrays were used for the analysis of vapors of 11 structurally similar aliphatic amines; average color change profiles were acquired for each amine, as shown graphically in Figure 5. As is obvious even to the eye, the calorimetric sensor array shows a unique color change for each amine. The color change profiles are actually digital data (16 changes in red, green, and blue values ranging from −255 to +255) and were compiled into a library of 48-dimensional vectors. For statistical analyses (Figure 6), PCA and HCA were used to analyze this digital database (Supporting Information, Table S1). PCA provides a quantitative evaluation of the analytical dispersion of a technique based on its number of independent dimensions of variance.[18] Prior electronic nose technologies have very few independent dimensions: 95–99% of the total variance among analytes is typically achieved with their first two dimensions. In comparison, there is a very high level of dimensionality (i.e., dispersion) with the pigment-based calorimetric sensor arrays. When PCA is applied even to this family of intimately related analytes, there are still eight dimensions required to capture 90% of the total variance, as shown in Figure 6a, which exemplifies the extraordinary discrimination ability of the colorimetric sensor arrays. To examine the multivariate distances between the analyte responses in this 48-dimensional RGB color space, HCA was performed using the minimum variance ("Ward's") method. A response dendrogram was generated as

shown in Figure 6b. Remarkably, all of the aliphatic amines were accurately classified and identified against one another without error among the 36 trials.

The nanoporous pigment-based array was further evaluated for its sensitivity for the detection of ammonia at various concentrations: 5 ppm, 50 ppm (the permissible exposure limit, PEL), and 300 ppm (the immediately dangerous to life or health concentration, IDLH) at 33% relative humidity (the digital data of the array response is provided in Supporting Information, Table S2). Ammonia vapor is of particular interest because even low concentrations of the gas can lead to serious toxicological consequences.[25] In this respect, the development of a simple and sensitive sensor array for gas-phase detection of ammonia is a potentially valuable tool in environmental monitoring. The difference maps of the arrays (shown in Figure 7 after 2 min of NH$_3$ exposure) are, as expected, unique to each concentration of the analyte. Distinct and highly reproducible patterns were obtained at all NH$_3$ concentrations, even at one-tenth of the PEL, with no confusion as shown by HCA (Supporting Information, Figure S2), thus demonstrating an easy method to quantify ammonia concentrations at low detection limits. From the SIN ratio observed at 5 ppm, we estimate that our limit of detection (defined as 5*S/N) is well below 100 ppb (i.e.,<0.2% of the PEL).

Conclusions

The preparation of nanoporous pigment microspheres and their formulation into a chemoresponsive inks has been demonstrated for the first time. The chemically responsive microspheres were prepared via an aerosol–gel synthesis and incorporated into a colorimetric sensor array using dip-pen printing. The use of TMOS and MTMS as silica precursors with the incorporation of pH and solvatochromic dyes provides robust silica microspheres having a nanoporous structure, which not only facilitates the diffusion of analytes for rapid color changes, but also effectively stabilizes the colorants and prevents leaching of dyes from the silica microspheres upon contact with liquids. Colorimetric sensor arrays prepared using these nanoporous pigments are able to discriminate among 11 structurally similar aliphatic amines as well as ammonia gas at various concentrations with detection limits well below the PEL.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Acknowledgment
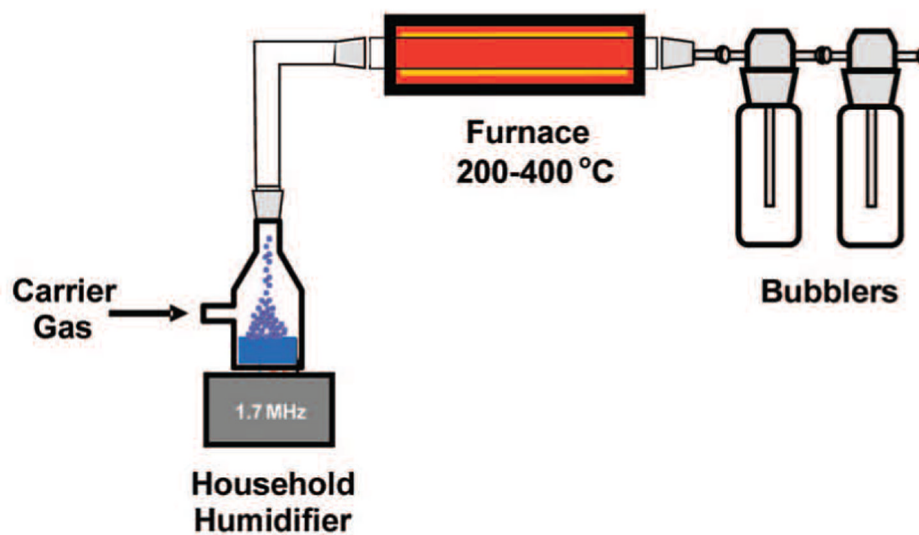
Figure 1.
Ultrasonic spray rig for aerosol–gel synthesis of chemoresponsive pigments.
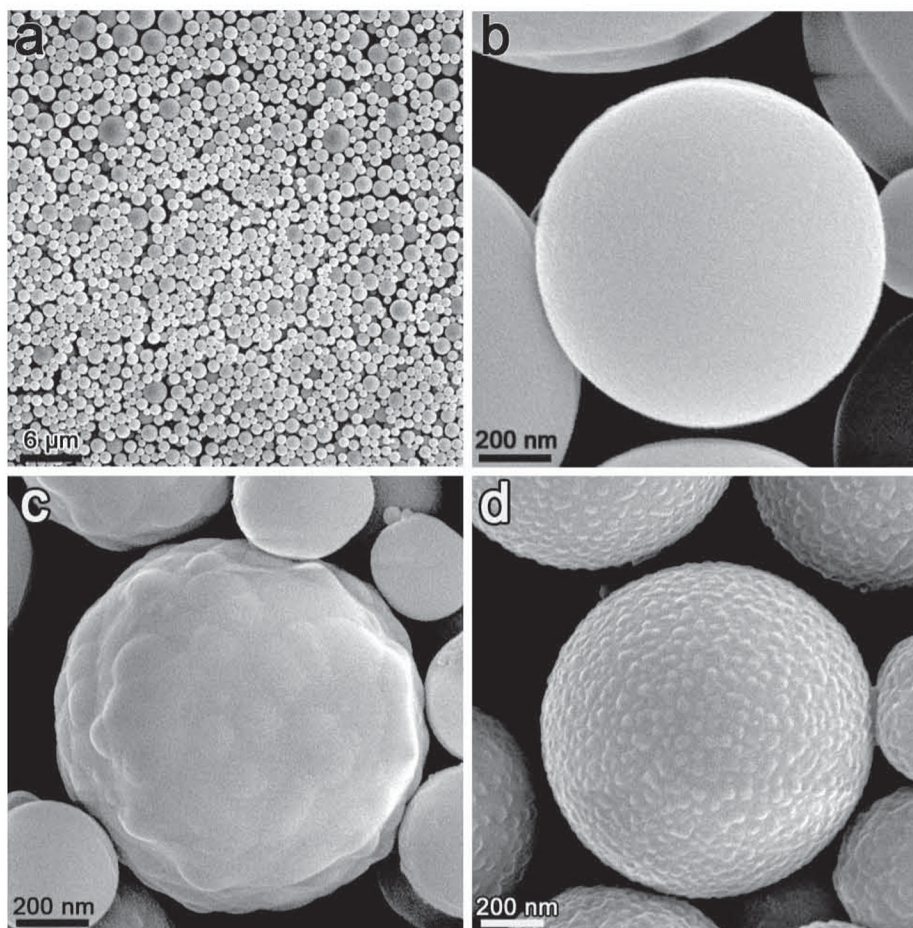
Figure 2.
SEM micrographs of nanoporous silica microspheres that have BCG entrapped within them (BCG–SiO_2) synthesized at (a and b) 200 °C, (c) 300 °C, and (d) 400 °C.
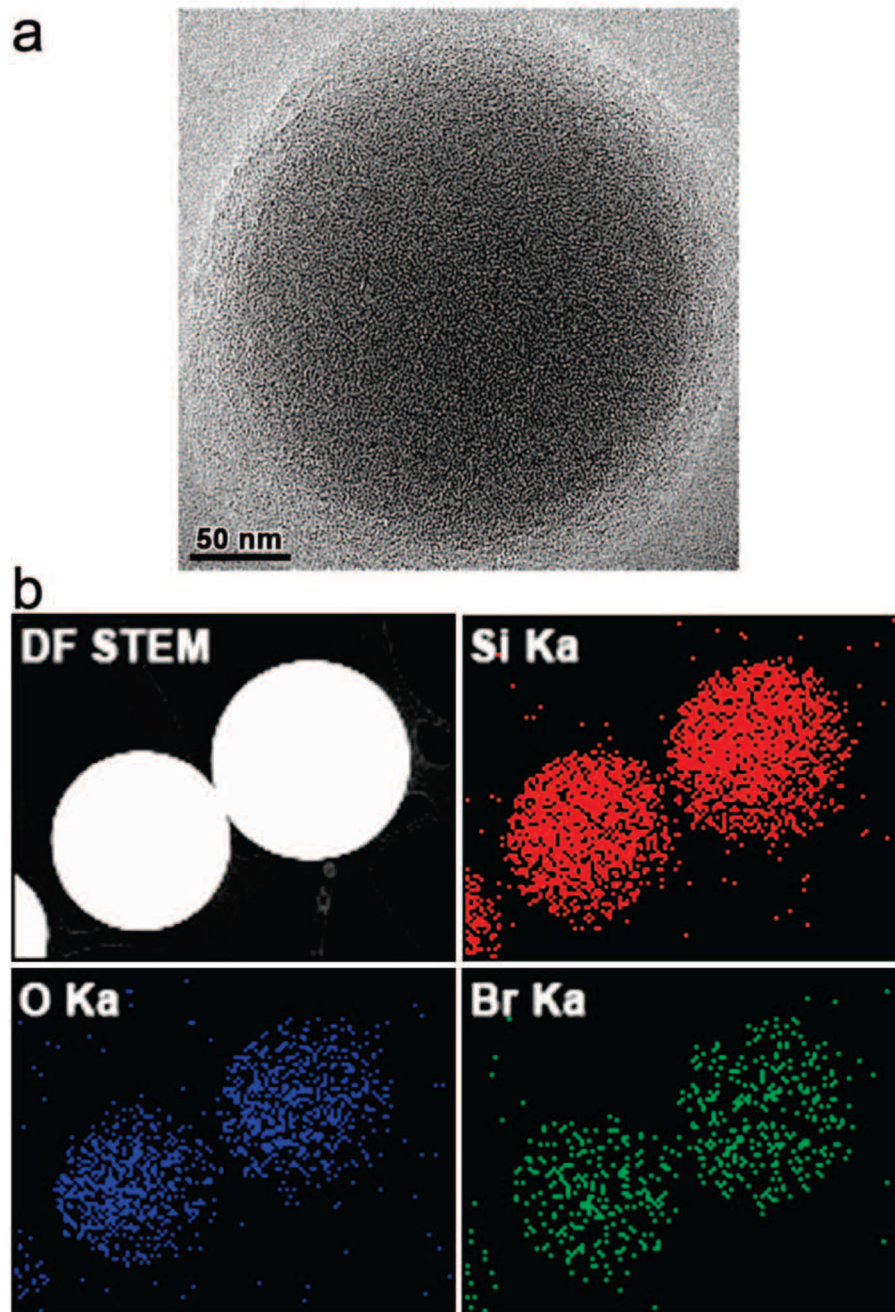
Figure 3.
(a) TEM image and (b) STEM-EDS elemental mapping analysis of BCG–SiO$_2$, showing a uniform distribution of BCG molecules throughout the silica microspheres.
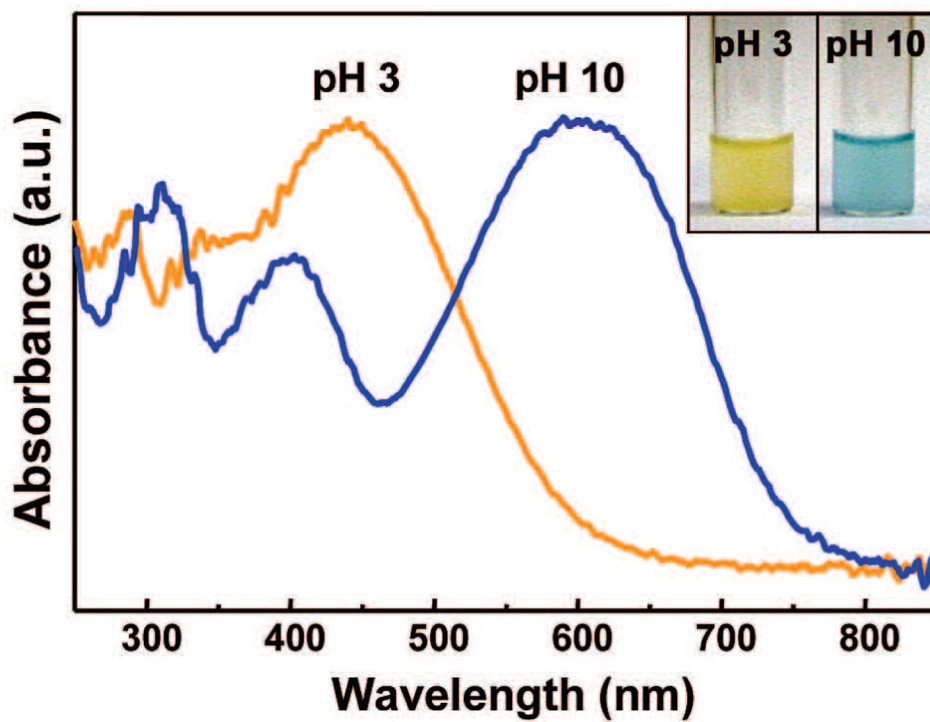
Figure 4.
Diffuse reflectance UV–vis spectra of BCG–SiO$_2$ washed with acidic and basic solutions; inset: photograph of BCG–SiO$_2$ suspended in different pH buffer solutions.
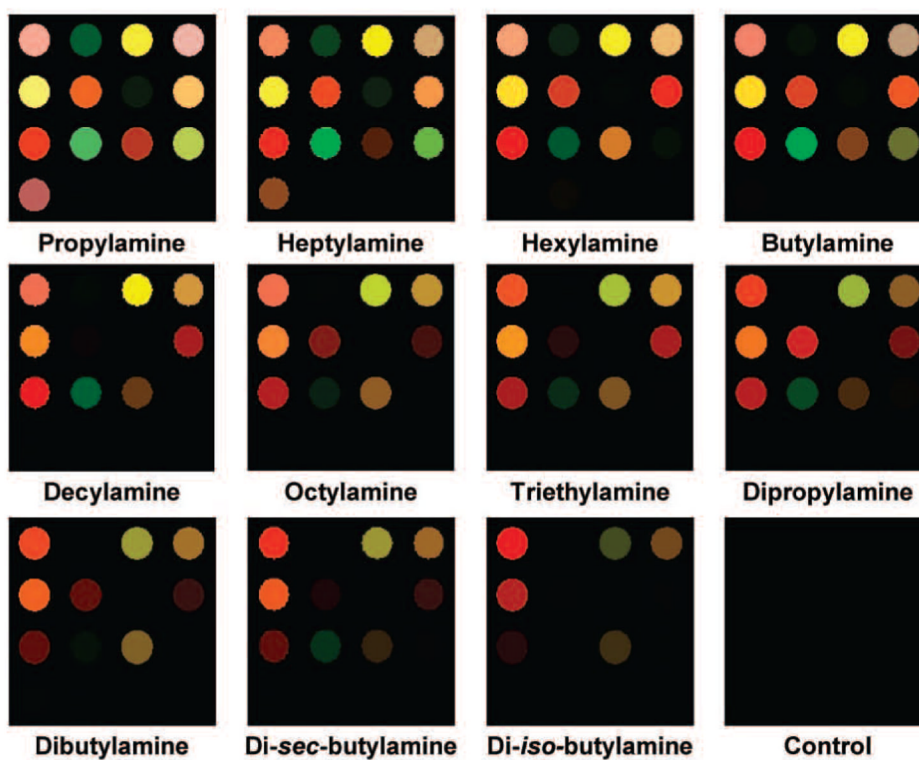
Figure 5.
color change profiles of 11 structurally similar aliphatic amines after equilibration. For purposes of display, the color range of these difference maps are expanded from 6 to 8 bits per color (i.e., RGB range of 4–67 expanded to 0–255). The full digital data are provided in Supporting Information, Table S1.
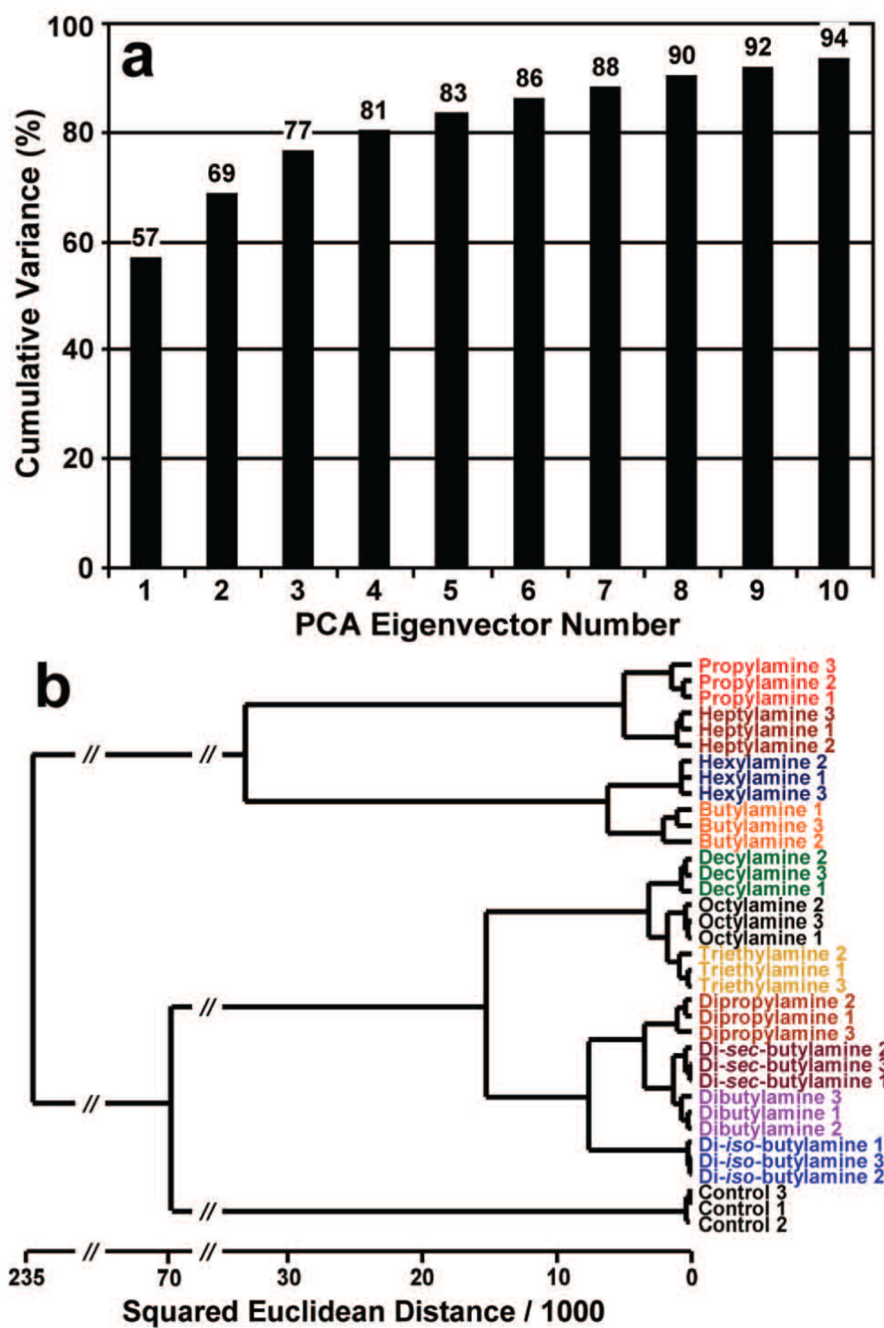
Figure 6.
(a) PCA and (b) HCA for 11 structurally similar aliphatic amines using Ward's method. No misclassifications were observed among the 36 trials. All experiments were run in triplicate. After the amine name, the trial number is given.
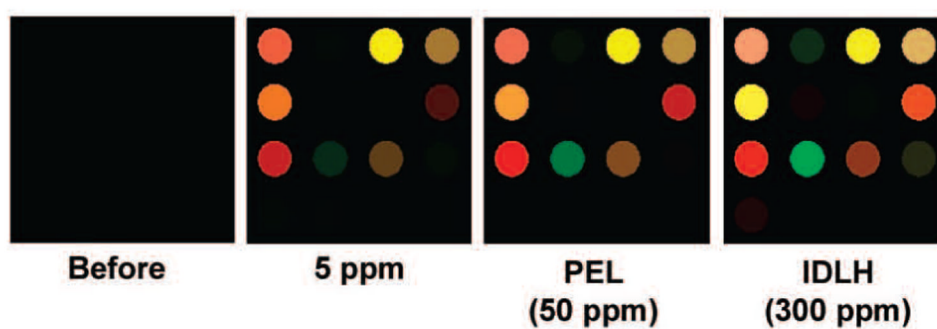
Before   **5 ppm**   **PEL (50 ppm)**   **IDLH (300 ppm)**

Figure 7.
Difference maps of pigment-based arrays after 2 min NH_3 exposure. For purposes of display, the color range of these difference maps are expanded from 6 to 8 bits per color (i.e.. RGB range of 4–67 expanded to 0–255). The full digital data and an HCA are provided in the Supporting Information, Table S2 and Figure S2.

Table 1

List of the Colorants in the Nanoporous Sol–Gel Pigments of the Colorimetric Sensor Array[a]

bromo-cresol green	methyl red	chloro-phenol red	bromo-phenol red
bromo-cresol purple	alizarin	bromo-thymol blue	bromo-xylenol blue
nitrazine yellow	phenol red	brilliant yellow	cresol red
m-cresol purple	thymol blue	Reichardt's dye	Reichardt's dye#3

[a] common names of the indicators are given. Reichardt's dye(4-(2,4,6-triphenyl-1-pyridinio)phenolate)and Reichardt's dye #3 (2,6-dichloro-4-(2,4,6-triohenyl-1-pyridinio)phenolate)are standard solvatochromic indicators.