Interface-Regulated Contact Electrification for Power-Free and Highly Selective Gas Sensing

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The detection of volatile organic compounds (VOCs) is critical in various applications, e.g., medical care, environmental monitoring, public security, agriculture, the food industry, etc., requiring high sensitivity, good selectivity, fast response/recovery, multivariate data treatment, anti-interferon, and wide tolerance of gas temperature. Herein, taking advantage of the interface inside the composite thin film of contact electrification-based sensors, a “fill two needs with one deed” strategy is successfully demonstrated and developed to selectively detect VOCs without a power source, which may shed a new light on VOCs’ sensing in the future sensor network.

1. Introduction

Artificial intelligence (AI), a kind of intelligence demonstrated by machines for achieving the natural intelligence of humans or other animals, is one of the top three cutting-edge technologies in the 21st century. Artificial olfaction, one of the sub-branches in AI, has received booming interests from both research and industry for recognizing the odors. As an important group of odors, volatile organic compounds (VOCs) are associated with much information in various applications, e.g., medical care, environment monitoring, public security, agriculture, food industry, etc. The “smelling” of VOCs requires a precise detection, discrimination, and recognition to make decisions relying on VOCs’ sensing. In addition, the continuous monitoring or detection in the sensor networks challenges and issues new requirements at a low power consumption or power-free technology for VOC sensors. Much effort has been undertaken to develop novel and feasible sensors with high performance, their so-called golden criteria, including high sensitivity, good selectivity, fast response/recovery, multivariate data treatment, anti-interferon, and wide tolerance of gas temperature, which are based on the various kinds of gas sensors, e.g., chemiresistors, field effect transistors, optical sensors, quartz crystal microbalance, surface acoustic waves, solid-state electrochemical sensors, etc. However, to our best knowledge, there is no sensor that can satisfy and meet all the golden criteria. Especially, for VOCs’ sensing, the strong interferon by humidity, the difficulty to discriminate between the VOCs with similar molecular structures, or the weaker affinity to the sensitive materials compared with inorganic gas hinder precise recognition. Modifying the surface with silane-coupling agent (SCA) containing a similar functional group to

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DOI: 10.1002/aisy.201900066
analyte has been demonstrated as an effective way to enhance the selectivity of VOCs’ sensing.\cite{11,16} Otherwise, most of those sensors need to be powered by a source meter with high accuracy. Recently, SCAs are reported to successfully regulate the process of donating and depriving the electrons in contact electrification, which has been applied to generate electricity for powering electronic devices.\cite{17} Fortunately, the process of donating and depriving electrons is also a critical factor for gas sensing.\cite{18} Possibly, a “fill two needs with one deed” strategy could be an effective way to detect the gas through taking advantage of the varied generated electricity, ascribing to the changed contact electrifications.\cite{19} However, how to design and fabricate the contact materials for achieving selectivity is still a challenge in this case.

In this study, interfaces between polyvinylidene difluoride (PVDF) and SCAs have been created through imbedding SCAs-modified silica nanoparticles (SNPs) inside PVDF polymer thin films. The electron accumulation/decay and maximum charge density in this interface have been demonstrated, greatly correlating with the output amplitudes of contact electrification-based energy harvesters. Considering the other side of the coin, the properties of this interface can be greatly regulated by the variation (molecular chain swell or shrinkage) when the functional group of SCA contacts VOCs, which means that the selective detection of VOCs has been achieved in this study. Although the concentrations of VOCs in this gas sensing are still not low (2500 ppm), this study, undoubtedly, sheds new light for power-free VOCs’ detection with high selectivity.

2. The Fabrication of the Contact Electrification-Based VOC Sensors

Figure 1a is the schema of the flow chart to fabricate contact electrification-based VOC sensors. First, the SNPs are synthesized using a modified Stöber method (the details are depicted in Section 6). The morphology of the SNPs has been characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in Figure 1b,c. The diameter of the monodispersed SNPs is ≈45 nm in good agreement with the results of diameter distribution (Figure S2a, Supporting Information) characterized by the dynamic light scattering (DLS) measurement. After the modification of SCAs, the surface polarizations of the mSNPs are varied and are shown in Figure S2b, Supporting Information. The zeta potentials are from ≈25 to ≈32 mV, which is regulated to accept electrons. The particle size changes from ≈45 to ≈90 nm, which ascribes the polarization change–induced particle aggregation in ethanol. 3-Aminopropyltriethoxysilane, dodecyltriethoxysilane, hexadecyltrimethoxysilane, phenyltrimethoxysilane, and diphenyl(dimethoxysilane)-modified SNPs are dispersed in dimethylformamide (DMF) homogeneously. PVDF is added to enhance the viscosity of dispersion until they are suitable for the spin-coating process. The PVDF-mSNPs composite thin film is spin coated on the Al electrode covered with the poly(methyl methacrylate (PMMA) plate being the electron-depriving

![Figure 1](image-url)
layer. The thickness of the PVDF–mSNPs composite thin film is \( \approx 5 \mu m \), as shown in Figure 1d. The other piece of the Al–PMMA plate is assembled with the PVDF–Al–PMMA plate face to face.

3. Interface-Dominated Contact Electrification

There are interfaces with a large area between the mSNPs and PVDF inside the composite thin film (Figure 2a). The output amplitude of the contact electrification-based sensor contains three stages including electron accumulation (Figure 2b), saturation (Figure 2c), and decay. The electrons are deprived from the counter Al electrode and accumulated inside the composite thin film until the charge density is saturated, which is strongly correlated with the current amplitude. As shown in the inset of Figure 2d, the current versus different accumulated times are plotted to present the ability of depriving and accumulating electrons in various composite thin films. All fitted lines in the inset of Figure 2d are then differentiated as shown in Figure 2d, from which the different accumulating speeds can be clearly seen. All fitted functions are listed in Table 1. Therefore, the process of electron accumulation and decay is related to the different SCAs.

Figure 3a, a 3D plot for evaluating the performance of the contact electrification-based sensors, shows that the density of current amplitude (\( J_{\text{max}} \)), the time to reach 90% of the maximum density of output amplitude (\( t_{90} \)), and the time to decay to the 1/e of the maximum density of output amplitude (\( \tau \)) are dramatically regulated when mSNPs are imbedded into PVDF. The enhanced \( J_{\text{max}} \) of the different kinds of mSNPs-based composite thin films ranges from 1.04 to 3.98 \( \mu A/cm^2 \), which is much higher than the \( J_{\text{max}} \) of pure PVDF (0.13 \( \mu A/cm^2 \)). As shown in Figure 3b, therefore, it is obvious that the different functional groups on the mSNP surface greatly influence \( J_{\text{max}} \) (phenyl group > dodecyl group > diphenyl group > 3-aminopropyl group > hexadecyl group). In addition, \( t_{90} \) and \( \tau \) vary with the interfaces inside the composite thin film of sensors (Figure 3c). The capacitance of electrons in the composite determines the accumulating capacitance which dominates \( J_{\text{max}} \). The \( t_{90} \) are

![Figure 2](image-url)

**Figure 2.** a) The schema of the interface inside the composite thin film of mSNPs and PVDF. b) The current signal including the process of accumulation and saturation. c) The saturated current signal. d) The current accumulation using different mSNPs (inset) and their differentiation of the fitting plots. e) The current decay using different mSNPs (inset) and their differentiation of the fitting plots.
125, 202, 206, 248, and 275 s for the hexadecyl group, 3-aminopropyl group, dodecyl group, diphenyl group, and phenyl group, respectively (Figure 3c). When the contact electrification process stops, the accumulated electrons start decaying, meanwhile, leading to the decrease of output current ($J$). The $\tau$ are 160, 180, 463, 566, and 643 s for the diphenyl group, hexadecyl group, 3-aminopropyl group, dodecyl group, and phenyl group, respectively (Figure 3c). The decaying speeds are diphenyl group $>$ hexadecyl group $>$ 3-aminopropyl group $>$ dodecyl group $>$ phenyl group, respectively.

The critical point of the contact electrification-based gas sensor is how to influence the process including electron depriving, storage, and decaying. As shown in Figure 3, the $t_{90}$, $\tau$, and $J_{\text{max}}$ apparently change comparing with the PVDF without mSNPs. The variation trends, viz., the sequence of the functional group rather than other factors. Therefore, the output amplitudes of contact electrification-based sensors are functional group dominated.

### 4. The Sensing Performance Toward Volatile Organic Compounds

In the VOCs’ sensing, we use the output voltages as the sensing signals because the voltages are in the levels of hundreds of volts, which is easier to measure compared with the amplitude of current. All data are extract in the positive voltage amplitude as shown in Figure 4a including accumulation, baseline, exposure, and recovery. The response is defined as

$$\text{Response}(\%) = \left( \frac{V_{\text{exposure}} - V_{\text{baseline}}}{V_{\text{baseline}}} \right) \times 100\%$$  \hspace{1cm} (1)$$

Five kinds of sensors made with different mSNPs-imbedded composite thin films are used to detect the VOCs. The sensors should be working after the electrons are saturated to eliminate the influence from the change of charge density. When the VOCs contact the composite thin film, they permeate into the film and interact with the molecular chain of SCAs. This interaction makes the molecular chains swell or shrink to further change the property of the interfaces, which determines the output variation of the contact electrification-based sensor. All responses of sensors versus VOCs are presented in Figure 4b,c. When we group the responses of the same sensor, the responses are different toward different VOCs as shown in Figure 4b.
The 3-aminopropyltriethoxysilane, dodecyltriethoxysilane, hexadecyltrimethoxysilane, phenyltrimethoxysilane, and diphenylidimethoxysilane modifications on SNPs imbedded in the PVDF generate selective signals toward formaldehyde, triethylamine, ethanol, formaldehyde, and triethylamine, respectively. On the other hand, the multiple responses of five sensors can provide fingerprint for the tested VOCs, which is the best method for achieving pattern recognition for VOCs (Figure 4c). Furthermore, a principle component analysis (PCA) was utilized to analyze the sensing responses of five different sensors (Figure 5). The PCA plot shows that formaldehyde, ethanol, and triethylamine can be 100% classified from each other by forming well-separated clusters. Even toluene and hexane, both nonpolar molecular structures with only one carbon atom difference, can...
be classified as well. These results suggest that the sensor arrays have an ability to achieve the discrimination of formaldehyde, ethanol, triethylamine, toluene, acetone, and hexane.

The proposed sensing mechanism is that the functional groups of SCAs are sensitive and selective to the VOCs with different affinities. The swelling and shrinkage of the alkyl chain in the interface (Figure 3a) are regulated by the contact between the SCAs and VOCs, ascribing to the interface property change, which further determines the different responses as shown in Figure 4b,c. Herein, it is worthy to note that all the responses of triethylamine are positive which might be caused by the strong polarity of the N atom for depriving electrons rather than the molecular change. Triethylamine leads to the composite thin film, which can deprive and store more electrons from the counter Al electrode, which in turn provides all responses with positive values. However, the working mechanisms of all non-polar and moderate polar VOCs are caused by the change of molecule chains. Actually, the real interaction between the SCAs and the VOCs needs to be further studied by in situ detection technologies, e.g., in situ Fourier transform infrared spectroscopy (FTIR), in situ X-ray photoelectron spectrometer (XPS), etc., which are valuable to study further in the future.

5. Conclusions

In summary, a new “fill two needs with one deed” strategy, i.e., interface-regulated contact electrification, is developed to selectively detect VOCs integrating with the output of contact electrification-based VOC sensors. The various SCA-modified SNPs are applied to create different interfaces inside the PVDF film to form the composite thin films. The properties of these interfaces (electron accumulation/decay and maximum charge density) are demonstrated to influence gas sensing greatly, which vary (molecular chain swell or shrinkage) when the functional group of SCA contacts VOCs. The selective detections and the discrimination of VOCs have been achieved at the concentrations of 2500 ppm. This work, undoubtedly, sheds new light for power-free VOCs’ detection with high selectivity.

6. Experimental Section

Deionized water (DI water), tetraethyl orthosilicate (TEOS), ethanol, ammonia solution, triethylamine, DMF, PVDF, 3-aminopropyltrimethoxysilane, hexadecyltrimethoxysilane, diphenyl(dimethoxysilane, phenyltrimethoxysilane, and triethoxysbutylsilane were in analytical purity and used without further purification. First, 480 mL ethanol, 10 mL ammonia solution, and 40 mL DI water were mixed together under mechanical stirring at 1000 rpm and heated up to 40 °C. Then, 8 mL TEOS was injected in to the solution at a feeding rate of 6 mL h⁻¹ using a syringe pump. The reaction took 6 h, and the as-prepared SNPs were collected, washed by centrifugation and further washed with ethanol three times at least. After that, the SNPs were dried in a vacuum oven at 30 °C overnight to remove all the residual ethanol. The synthesized SNPs were characterized by the SEM and the TEM.

As shown in Figure 1a, the SNPs (0.3 g) were dispersed in 50 mL ethanol under sonication. The 4 mL dispersion was transferred into a bottle and mixed with 4 mL SCA ethanol solution (0.016 μmol L⁻¹). The mixture was stirred strongly for 12 h. And then, 0.4 mL DI water and 0.4 mL triethylamine were added and reacted with SNP dispersion for 6 h. The products were collected, washed by centrifugation, and again washed with ethanol three times at least to remove all residual SCAs. After that, modified SNPs (m-silica or mSNPs) were dried in a vacuum oven at 30 °C overnight to remove all the residual ethanol. After that, m-silica were dispersed in DMF (wt% = 5%), whose viscosity was enhanced by adding and dissolving PVDF (W_{PVDF}:W_{DMF} = 1:6) for 24 h. The viscous dispersion was spin coated on the PMMA, covered by an Al foil at 500 rpm for 3 min, which was assembled with another PMMA, covered by a foil to be a contact electri"
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was funded by the Thousand Youth Talents Plan of Shaanxi Province. Fundamental research funds were acquired from the central universities (Grant No. JX181309), the National Natural Science Foundation of China (51603161, 51702250), and the Natural Science Foundation of Shaanxi province (2018M6045, 2018M1046, 2017Q0593, 2018JQ0205). Research funding was received from Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration (SHUES2019A02). The authors thank associate professor Nuanyang Cui and Dr. Long Gu for helping to construct the measurement system.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

contact electrification, interfaces and surfaces, gas sensors, silica nanoparticles, volatile organic compounds

Received: July 4, 2019
Revised: July 25, 2019
Published online: August 14, 2019