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A Hybrid Electrochemical−Colorimetric Sensing Platform for Detection of Explosives

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Detection of trace explosives is a leading priority in security. In spite of significant advances made recently,[1–3] a portable device that can be reliably deployed in a field environment still faces formidable challenges. These challenges include low levels of explosives in most practical scenarios, multiple interferences from common household and personal care products, variable environmental conditions (e.g., temperature, humidity, and pollutants), and the need for low-cost and highly portable detection methods. Here, we present a novel hybrid electrochemical−colorimetric (EC−C) sensing platform to meet these challenges. The hybrid sensor is based on consorted operations of electrochemical reactions of trace explosives, colorimetric detection of the reaction products, and unique properties of the explosives in an ionic liquid (IL) (Figure 1). Unlike previous electrochemical detection methods, the electrochemical reactions in the present work are mainly used to generate reaction products (Figure 1A) which are detected with an optical imaging device (Figure 1B). This approach affords not only increased sensitivity but also selectivity as evident from the demonstrated null rate of false positives and low detection limits (Supporting Information, SI).

A basic version of the device is constituted of merely a microcontroller-based potentiostat, a typical webcam, a transparent substrate of indium tin oxide (ITO) printed electrodes, and a thin layer of ionic liquid (IL) covering it (Figure 1). Excellent selectivity is achieved by (1) controlling the electrode potential to induce the electrochemical reactions of the target analytes, (2) specific interactions between the reaction products and the supporting electrolyte (IL), and (3) distinct optical absorption patterns. In addition, the device hardware can be rather simple and compact, allowing the benefits of low cost and high portability.

One of the key elements of the hybrid sensing platform is the use of a thin layer of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6),[4–6] an IL with extraordinary properties (see SI for synthesis details). The BMIM-PF_6 coating provides (1) a medium that selectively preconcentrates explosives and quickly transports the analytes to the electrodes, (2) an electrolyte that is highly stable under ambient conditions for electrochemical reactions, and (3) a medium that promotes the formation of colored reduction products. We applied this hybrid sensing platform to detect nitroaromatic explosives and explosive signatures, including 2,4,6-trinitrotoluene (TNT), picric acid (PA), and 2,4-dinitrotoluene (DNT). This approach should also be applicable to other nitroexplosives.

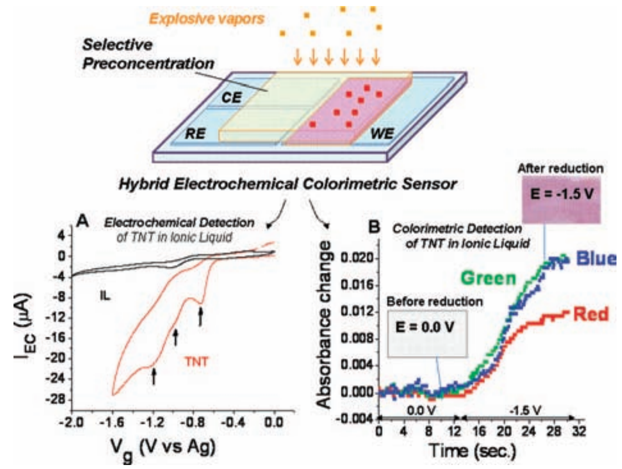

Figure 1. Hybrid electrochemical−colorimetric sensor with a thin layer of ionic liquid as a selective preconcentration medium. (A) Cyclic voltammograms of blank IL, BMIM-PF_6 (black line) and 2 ppm TNT in IL (red line) at 100 mV/s. Arrows indicate peak currents of TNT. (B) Color (absorbance) changes during the electrochemical reduction of TNT in BMIM-PF_6. The absorbance change for each color is defined as the logarithmic ratio of the intensity in a sensing area (working electrode) to the intensity in a reference area (reference electrode). Insets in part B show two images taken before (0.0 V) and after (−1.5 V) TNT reduction. The distinct color change provides a fingerprint for identification and quantification of the explosive.

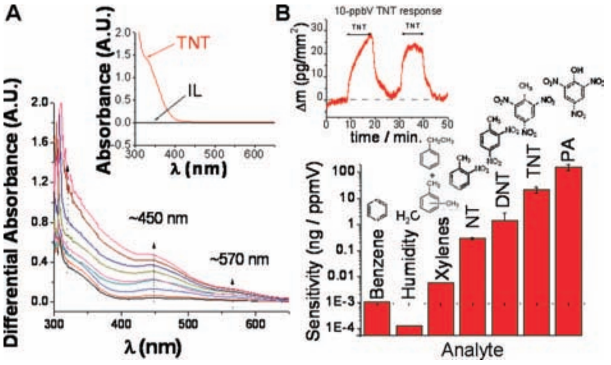

Figure 2. (A) Optical properties of the electrochemical reduction products of TNT in BMIM-PF_6, where the differential absorbance is the spectrum of the reduction products after subtraction of the spectrum before reduction. Inset: TNT spectrum in BMIM-PF_6 before the reduction (background due to BMIM-PF_6 absorption was corrected). (B) Comparison of preconcentration capacities of various analytes in BMIM-PF_6. Inset: Absorption/desorption kinetics of TNT vapor determined with a BMIM-PF_6-coated tuning fork sensor at room temperature (SI).

Figure 1A is a cyclic voltammogram of TNT in BMIM-PF_6, which shows three irreversible reduction peaks as marked by arrows. We found that reduction processes produce distinctive red colored products (Figure 1B) with an absorption peak at ∼450 nm (Figure 2A) and a large extinction coefficient of 6060 M^{-1} cm^{-1}. The

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reduction products were identified to be azo and azoxy derivatives, using Fourier transform infrared spectroscopy (FTIR) and liquid chromatography/mass spectrometry (LC/MS) (SI). This identification is also supported by work on nitrosobenzene in acetonitrile.[7,8] No visible color changes have been found in the electrochemical reduction of TNT in aqueous solution, so the IL medium is essential to provide a stable environment for the reaction products with a distinct color for TNT. Electrochemical reaction products with distinctive colors can also be produced in the IL for other nitroaromatic explosives, such as PA and DNT (SI).

In addition to providing a desirable medium[4–6] to promote the formation of stable colored reaction products, the IL has an astonishing preconcentration capability for the explosives. Figure 2B shows the relative preconcentration capacities of BMIM-PF_6 toward different analyte vapors determined on a BMIM-PF_6-coated quartz crystal mass loading sensor (SI). The partition coefficients obtained from these measurements as well as from UV−visible quantification (SI) are as follows: 5.0×10^5 for TNT, 4.0×10^5 for DNT, 1.2×10^5 for nitrotoluene (NT), 2.9×10^3 for xylenes, 7.1×10^2 for benzene, 3.7×10^2 for water. The coefficient increases rapidly with the number of nitro groups in the aromatic structure. This effect may be related to a combination of several factors: (1) electron-withdrawing power of nitro groups, (2) electron-donating properties of the IL, due to deprotonated BMIM cations (acidic),[4] and (3) hydrophobic anions (PF_6^-).[4] According to the mass sensor measurements (Figure 2B), PA shows 6 times larger affinity than TNT, indicating that the hydroxyl group may promote hydrogen bond interactions with a BMIM cation and lead to the larger partition coefficient.

The high and selective preconcentration capability of BMIM-PF_6 for the explosives is partially responsible for the high sensitivity and selectivity of the hybrid sensor. The achieved detection limit is in the ppbV range (SI). However, based on the noise level ($\sim 10^{-4}$) of the webcam/LED and IL preconcentration factor, the estimated detection limit is a few tens of pptV. The detection limit can be further improved by using a more sophisticated optical[9] and more efficient electrochemical detection[10] system (SI).

We have also demonstrated highly selective detection of explosives with various common interferents with realistic concentrations such as large humidity changes (ΔRH = 21%), perfumes, mouth wash vapors, cleaners (all at ∼1% of saturation vapors), and high vapor pressure petroleum derivatives (84 ppmV). Figure 3A shows the relative color (Red (R), Green (G), Blue (B)) changes due to different explosives and as well as the interferents. Large color changes are detected only in the presence of the explosives, and no color changes are visible within the noise level for all the interferents, which demonstrate discriminative detection of nitroexplosives from common interferences. Furthermore, the data show distinct color patterns for different explosives, allowing us to identify different nitroexplosives. We note that additional discrimination can be achieved by (1) controlling the electrochemical potential because different analytes have different electrochemical activities (SI) and (2) following the kinetics of the color changes due to the different reaction mechanisms. We have determined the total color change on a sensing area normalized by the color change of a reference area as a function of analyte concentration and observed a quasi linear dependence (Figure 3B), which can be used for quantitative detection of explosives.

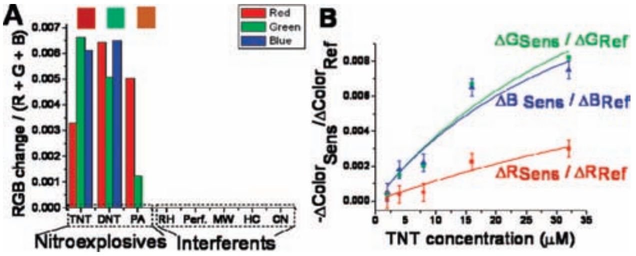

Figure 3. (A) RGB color changes due to reduction products of nitroexplosives: TNT, DNT, and PA and realistic concentrations of interferents: RH = RH change of 21%, Perf = mist (Coty, US), MW = mouth wash (Listerine), HC = hydrocarbons, hexane/toluene mixture, 42 ppmV e.a., CN: general cleaner (3M). The RGB signal changes were recorded after 2.5 min exposure at a potential of −2.0 V. The 3 blocks at the top represent the final colors of the 3 explosives after reduction. (B) RGB color changes on sensing (Sens) area normalized to the RGB color changes on reference (ref) area vs concentration of TNT in IL.

In summary, a highly selective, sensitive, and low-cost hybrid sensing platform is developed based on extraordinary properties of explosives in an ionic liquid (BMIM-PF_6) and an integrated electrochemical and colorimetric approach. High selectivity is achieved due to a selective preconcentration effect of BMIM-PF_6, distinct electrochemical activity, and RGB color patterns of the reaction products. High sensitivity is possible because of the large preconcentration factors and large optical extinction coefficient of reduced products. Using an inexpensive webcam we have achieved a detection limit of ppbV and demonstrated selective detection of explosives in the presence of common interferences (perfumes, mouth wash, cleaners, petroleum products, etc.).

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Supporting Information Available: Synthesis of IL, characterization of reduction products, and vapor phase detection. This material is available free of charge via the Internet at http://pubs.acs.org.

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