Contactless and Rapid Discrimination of Improvised Explosives Realized by Mn$^{2+}$ Doping Tailored ZnS Nanocrystals

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In order to sensitively, selectively, and rapidly detect the constituents relevant to improvised explosive devices (IEDs), the sensing properties of ZnS nanocrystals (NCs) are regulated by tailoring the doping level of Mn$^{2+}$. The responses of the sensors fabricated by ZnS NCs with different Mn-doping levels (Mn:ZnS) toward the constituents, such as sulphur powder and black powder, generally increases first and then decreases with the increase of the concentration of doped Mn$^{2+}$, and reaches the climate with an atomic ratio of 2.23% at room temperature. The sensory array based on eight sensors of Mn:ZnS NCs can realize the detection of two typical military explosives and six constituents relevant to IEDs within 7 s and can recover in 19 s. Furthermore, the fingerprinting of the constituents is achieved by pattern recognizing the inherent kinetics and thermodynamics of interaction between the sensory array and the constituents. Thus, a simple chemiresistive sensing strategy based on semiconductor NCs which can rapidly, supersensitively, and discriminatively detect the constituents relevant to IEDs is explored for the first time.

1. Introduction

In recent years, explosive-based terrorism has grown enormously because explosive-based weapons are simple, easy to deploy, and can cause enormous damage.[1] While military explosives, such as trinitrotoluene (TNT), dinitrotoluene (DNT), and its variants, are heavily regulated, the ease with which improvised explosive devices (IEDs) can release vapors or locally change the atmosphere environment around a sensor. However, up to now, there is no systematical report on chemiresistive gas sensors toward constituents relevant to IEDs detection, not to mention the discriminative identification upon the exact species. Nanocrystals (NCs) are superior sensing component due to the large specific surface area, abundant surface defects and reaction sites, as well as the easy manipulation of the charge depletion layer.[11] ZnS nanocrystals, as a representative II–VI semiconductor, has been the subject of intensive research in the fields of optical devices, bioimaging agents, and energy materials.[12] And the detection of military explosives, such as TNT and DNT, based on their fluorescence properties has also been reported.[4d,13] Nevertheless, their gas sensing properties as chemiresistive gas sensors have been largely ignored due to the low thermal stability.[12a] Most important of all, the chemiresistive sensors of pure ZnS nanomaterials always suffer from some disadvantages, such as systems in Madrid and London, several terrorist attacks in Indonesia, and the recent Boston marathon terrorist attacks. Not to mention the troubled Iraq and Afghanistan, where more than 70% of these injuries and deaths were caused by IEDs, including roadside bombs, explosive vehicles, and suicide bombers.[3] Although there are many studies concerning the detection of military explosives, including fluorescence-based chemosensing technology,[1b,4] nanostructure-based sensors,[5] etc., there have been considerably fewer investigations concerning the detection of the constituents relevant to IEDs, such as high performance liquid chromatography,[6] ion chromatography,[7] mass spectrometry,[8] and ion mobility spectrometry.[9] Although these methods can provide sensitivity and selectivity in general, they require sample preparation (e.g., swabbing and elution) and long analysis time approximately several minutes, and can be costly and complex to operate.[8,10] Furthermore, due to the wide variability of constituents contained in IEDs, the ability to detect broad classes of explosives with a single instrument is of great significance. Therefore, there is a pressing need for a complementary technique to detect the constituents relevant to IEDs, and possibly, also being contactless, rapid, and cheap.

Chemiresistive gas sensing method is promising in fulfilling these requirements since the constituents relevant to IEDs can release vapors or locally change the atmosphere environment around a sensor. However, up to now, there is no systematical report on chemiresistive gas sensors toward constituents relevant to IEDs detection, not to mention the discriminative identification upon the exact species. Nanocrystals (NCs) are superior sensing component due to the large specific surface area, abundant surface defects and reaction sites, as well as the easy manipulation of the charge depletion layer.[11] ZnS nanocrystals, as a representative II–VI semiconductor, has been the subject of intensive research in the fields of optical devices, bioimaging agents, and energy materials.[12] And the detection of military explosives, such as TNT and DNT, based on their fluorescence properties has also been reported.[4d,13] Nevertheless, their gas sensing properties as chemiresistive gas sensors have been largely ignored due to the low thermal stability.[12a] Most important of all, the chemiresistive sensors of pure ZnS nanomaterials always suffer from some disadvantages, such as...
the low response value, slow response or recovery process. These drawbacks limit the practical application of ZnS nanomaterials in the field of chemiresistive sensors. Therefore, it is necessary to explore some new strategies to revolutionize the sensing properties of ZnS to satisfy the rapid, sensitive, and discriminative detection toward vapors of the constituents relevant to IEDs.

In this work, the tailoring of the sensing properties of ZnS NCs is realized by the doping of Mn\(^{2+}\), which manipulates the surface states significantly. Thus, a chemiresistive sensing scheme to sensitively and rapidly detect the vapors of the constituents relevant to IEDs at room temperature by employing the sensory array of Mn:ZnS NCs is demonstrated. The differential identification between explosives is achieved by pattern recognizing the naturally inherent interaction, both kinetically and thermodynamically, between the sensory array and the target analytes. As a result, a unique explosives fingerprinting database can be created, enabling to fast and reliably identify individual chemical agent from similar chemical entities.

2. Results and Discussion

2.1. Tailoring of ZnS NCs by Mn\(^{2+}\) Doping

The morphology and size of the Mn:ZnS NCs were characterized by transmission electron microscope (TEM). As demonstrated in Figure 1a–h, the average sizes of the pure ZnS and Mn:ZnS NCs are about 3–6 nm. The phase of the pure ZnS and Mn:ZnS NCs are confirmed by X-ray diffraction (XRD) to be zinc blende structure (Figure 1i). The diffraction peaks located at 28.7°, 48.1°, and 56.4° correspond well with the (111), (220), and (311) planes of zinc blende ZnS (JCPDS no.77-2100). In all the 8 samples, no other peak was observed, which indicates the formation of pure phase ZnS NCs. Moreover, the broadening of the XRD peaks shows the formation of nanosized particles. Based on the most intense peak corresponding with the (111) plane, the particle sizes can be calculated with the Debye-Scherrer formula, and all of the particle sizes are in the range of 2.4–3.6 nm (Table S1, Supporting Information), which

![Figure 1. TEM images of Mn:ZnS NCs with a) 0%, b) 1%, c) 1.6%, d) 2%, e) 5%, f) 10%, g) 14% and h) 20% Mn\(^{2+}\); i) XRD spectra of Mn:ZnS NCs dried at 40 °C; j) Content of Mn element in Mn:ZnS NCs according to EDS test.]
is consistent with the TEM observation. XRD patterns of the Mn:ZnS NCs annealed at 100 °C in air for 24 h shows no phase transition (Figure S1, Supporting Information), indicating the good thermal stability and the sensors based on Mn:ZnS NCs can work stably below 100 °C. The content of Mn element in ZnS NCs was determined by energy dispersive spectroscopy (EDS) and increases significantly with the increase of the ratio of Mn/Zn in the precursor, achieving 0.296%, 0.435%, 1.0%, 2.23%, 5.24%, 5.47%, and 6.61% (Figure 1j), respectively, and the color of Mn:ZnS NCs turns from white to pale pink (Figure S2, Supporting Information).

To further confirm that Mn $^{2+}$ was effectively doped in ZnS NCs, X-ray photoelectron spectroscopy (XPS) was used to determine the valence state of Zn, S, and Mn atoms in the ZnS host (Figure S3, Supporting Information). The presence of Mn in the doped NCs is evidenced by the Mn 2p spectra in the range of 630–670 eV (Figure 2a). The observed intensity of Mn 2p is weak in the doped NCs due to the little amount of Mn. The noticed peaks around 641.7 and 655.6 eV in the doped NCs can be attributed to the Mn 2p3/2 and 2p1/2, which forms a sharp contrast with the pure ZnS NCs. This observation clearly indicates the presence of Mn$^{2+}$ in the ZnS NCs and they could act as substitutes for Zn atoms or as interstitial one. The sharp orange emission around 600 nm in the Mn:ZnS NCs can be attributed to the $^{4}T_1-^{6}A_1$ transition of the Mn$^{2+}$ impurity (Figure 2b). It is observed that the intensity of this emission peak increases dramatically when the doping amount of Mn$^{2+}$ increases from 0% to 2%, and it decreases with a further increase of the doping amount from 5% to 20%. This phenomenon can be explained by the quenching effect resulted from the high concentration of the doped Mn$^{2+}$ which further demonstrates the successful doping of Mn$^{2+}$.

2.2. Diverse, Sensitive, and Rapid Response toward Constituents Relevant to IEDs

The corresponding explosive vapor sensors were fabricated by coating Mn:ZnS NCs on the interdigitated electrodes and grouped into a sensory array (Figure 3a). To evaluate the influence of the doping level of Mn$^{2+}$ on the responses to DNT, TNT, and the constituents relevant to IEDs, including urea, urea fertilizer (UF), SP, PP, black powder (BP), and PN, three successive cycles were tested (Figure 3b, and Figures S4–11, Supporting Information). From the resistance change behavior, for example, toward TNT, it is clearly shown that with the immersing of the sensor into TNT vapor, the resistance decreases rapidly, and with the immersing of the sensor into air, the resistance increases fast and can recover to the initial value, indicating the good repeatability of the sensor. It is clearly shown that, on one hand, the responses of different sensors to the same constituent change obviously with the varying of the doped Mn$^{2+}$ concentration, and on the other hand, the responses of the same sensor to different constituents change remarkably, which provides the basis for sensory array-based discriminative detection. One should note that, the sensing responses for all the sensors generally increase with the increase of the doped Mn$^{2+}$ concentration in the range of 0%–5% and decrease with the further increasing of Mn$^{2+}$ concentration in the range of 5%–20%. For example, with the increase of the doping level of Mn$^{2+}$, the responses of the resulting sensors to TNT vapor achieve 21%, 25.7%, 28.9%, 36.9%, 46.9%, 36.5%, 29.3%, and 27.3%, respectively, and to PP vapor achieve 21.2%, 26.4%, 35.6%, 35.8%, 57.8%, 39.6%, 22.7%, and 30.8%, respectively. This nearly strict changing trend with the increase of the Mn$^{2+}$ doping level clearly indicates that the Mn$^{2+}$ concentration has an obvious tailoring effect on the sensing performance of ZnS NCs.

To gain a comprehensive understanding of the overall sensing performance of the sensory array, the sensing responses, response times and recovery times are statistically analyzed in Figure 4. All the sensors response well to urea and the responses are higher than 98% (Figure 4a), probably due to its well-known high hygroscopicity characteristic.
responses of the sensor based on pure ZnS NCs to DNT, TNT, UF, SP, PP, BP, and PN are just 18.3%, 21%, 20.8%, 20.9%, 21.2%, 4.3%, and 6.4%, respectively. However, upon incorporation of only 2.23% Mn^{2+} (corresponding to 5% Mn^{2+} in the precursor), the responses to DNT, TNT, UF, SP, PP, BP, and PN are remarkably improved by about 148%, 123%, 183%, 211%, 173%, 588%, and 330%, respectively. Although the responses generally decrease with the increase of the doping level of Mn^{2+} in the range of 5%–20%, the responses of the sensor based on ZnS NCs with 20% Mn^{2+} to the constituents (except urea) are larger than those of the sensor based on pure ZnS NCs. It should be noted that the room-temperature saturated vapor pressures of all these analytes are extremely low, such as 9 ppb for TNT, 411 ppb for DNT, 2 ppb for SP, 9 ppt for urea, and those for the PP, PN, and BP may be even lower (Table S2, Supporting Information). According to the responses of the sensor from ZnS NCs with 5% Mn^{2+}, the estimated limits of detection (defined as LOD = 3 S_D/m, where m is the slope of the linear part of the calibration curve and S_D = 0.1 is the standard deviation of noise in the response curve) for DNT and urea are determined to be 2.5 ppb and 0.05 ppt, respectively (Figure S12, Supporting Information). These results further demonstrate that Mn^{2+} doping can be an effective strategy to improve the sensing properties of ZnS NCs, and the resulting sensor can achieve supersensitive detection toward explosive vapors.

The most important characteristics of trace explosive sensors also include real-time operation. To facilitate continuous operation, the sensors should be readily reversible at room temperature and have fast response and recovery processes for efficient operation. As shown in Figure 4b,c, TNT takes the longest time to be detected (7 s) and urea takes the longest time to be recovered (19 s) in this sensory array at room temperature. And generally, the response time to almost all the tested constituents relevant to IEDs for this sensory array is less than 6 s, and the recovery time is less than 10 s. The above results clearly indicate that the present tailoring strategy has an obvious advantage in boosting

**Figure 4.** a) Sensing responses, b) response times, c) recovery times of the sensory array based on Mn:ZnS NCs over three peaks for eight kinds of constituents.
the sensor response and shortening the response time over the previously reported methods to fabricate the component sensor in a sensory array, which usually adopt chemical modification to discriminate different analytes,[14,10] thus, representing a facile, effective, and reliable strategy to acquire a quality sensory array.

The comparison of the performance of the Mn:ZnS NCs-based sensors and other recently reported chemiresistive sensors toward the detection of explosives vapors can be found in Table 1. It is clearly shown that the present Mn:ZnS (5% Mn\textsuperscript{2+}) NCs-based sensor belongs to the best TNT and DNT sensors since the responses toward them are 46.9% and 45.4%, respectively. What is more, the response times for TNT and DNT are 4 and 3 s, respectively, which is remarkably superior to all of the other sensors.[9d,e,19–21] More importantly, the sensor based on Mn:ZnS NCs with 5% Mn\textsuperscript{2+} can also detect rapidly and sensitively six constituents relevant to IEDs. The response values of urea, PP, PN, BP, and SP, and UF are up to 99.4%, 57.8%, 27.5%, 29.6%, 64.9%, and 58.8%, respectively, and their response times and the recovery times are within 4 and 14 s. This comparison further confirms that the present tailoring of ZnS NCs by Mn\textsuperscript{2+} doping could be a very promising strategy to put the ZnS NCs-based explosive sensors into practical application.

It is known that the sensing properties of chemiresistive sensors is dominated by the depth of charge depletion layer (\(w\)), which can be classically expressed while the semiconductor grains are adsorbed by gas molecules:[10]

\[ w = L_0 \left(2\beta V_s\right)^{1/2} \]

where \(L_0\) is the Debye length, \(V_s\) is the surface potential barrier, and \(\beta = e/kT\), where \(e\), \(k\), and \(T\) are the electron charge, Boltzmann constant, and the absolute temperature, respectively. While, \(V_s\) can be expressed as the following equation:

\[ V_s = \frac{-eN_i^2}{2\varepsilon_0\varepsilon_dN_d} \]

where \(N_i\) is the surface density of the adsorbed oxygen ions (O\textsuperscript{2–}, O\textsuperscript{−} or O\textsuperscript{2+}), \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon\) is the dielectric constant, and \(N_d\) is the charge carrier density. Apparently, the value of \(V_s\) depends on the density of the adsorbed oxygen ions and the dopant concentration, which will influence \(w\) and finally the sensitivity. Therefore, the tailored responses with the increase of Mn\textsuperscript{2+} concentration can be attributed to the dynamic competition between the enhanced oxygen molecule adsorption and the increasing carrier density in ZnS NCs resulting from Mn\textsuperscript{2+} doping.

The loosely bound oxygen on the surface of the ZnS NCs can be investigated by the symmetric O 1s peak located at the binding energy of 532.1 eV (Figure 5a).[15] It is worth noting that the ratio of O 1s to S 2p for Mn:ZnS NCs doubled at least compared with that of the pure ZnS (inset in Figure 5a). This result indicates that the active sites on the surface of Mn:ZnS NCs are remarkably increased due to the introduction of Mn\textsuperscript{2+}, and thus, help to attract more oxygen molecules on the surface, which is of vital importance to increase \(w\) and improve the gas sensing performance.

The change of the charge carrier density in the Mn:ZnS NCs is highly related to the local environment of the doped Mn\textsuperscript{2+}.

As evidenced by the electron paramagnetic resonance (EPR) spectra (Figure 5b), with a low doping level of Mn\textsuperscript{2+} (1%–2%), the hyperfine structure of cubic Mn:ZnS lattice arises due to substitutionally doped isolated Mn\textsuperscript{2+}.[16] However, with a further increase of the doping level of Mn\textsuperscript{2+} (5%, 10%, 14%, and 20%), a broad spectrum appears with the gradual decrease of the hyperfine structure, indicating the existence of weak dipole–dipole interaction and strong exchange coupling interaction between Mn\textsuperscript{2+} with intermediate and high doping levels, respectively.[16] Thus, the carrier density in the Mn:ZnS NCs increases gradually, leading to the decrease of \(w\), which is not beneficial for the improvement of the sensing performance.

Compared with that of Zn–S (2.34 Å), the ionic bond length of Mn–S (2.43 Å) is longer due to the larger radius of Mn\textsuperscript{2+} (0.83 Å) than that of Zn\textsuperscript{2+} (0.74 Å). Thus, it is easier for the adsorbed oxygen molecules to attract electrons from the conduction band of Mn:ZnS NCs (Figure 5c i), which is beneficial to increase \(w\) and obtain a higher response. Therefore, with the increase of the doping level, the barrier height (\(eV_s\)) at the NC–NC junction gets higher and \(w\) becomes larger (Figure 5c ii,iii), which enhances the sensing response.[34] However, \(w\) becomes smaller with the increase of the carrier density resulted from doping since \(w\) is inversely proportional to the square root of the electron density in n-type semiconductor (Figure 5c iv). When the doping level of Mn\textsuperscript{2+} is low (0%–5%), the enhanced oxygen molecule adsorption dominates the sensing response. However, when the doping level of Mn\textsuperscript{2+} is high (10%–20%), the remarkably increased carrier density plays a more significant role in the regulation of \(w\). While a maximum response is obtained with a doping level of 5%, which possesses the ideal oxygen molecule adsorption and appropriate carrier density. It should be pointed out that the response process of the gas sensor is very complicated, which is affected by many factors, including the vapor of the analyte, decomposition products, the humidity change caused by the analyte and the floating tiny clusters of the analyte (Table S2, Supporting Information), that is why the responses toward SP, BP, and PN are not strictly in line with the changing trend.

In order to evaluate the practical sensing performance of the sensory array at room temperature, firecrackers (FC) containing BP and matches containing SP and PN were chosen as suspectable IEDs. As shown in Figure 6a,b, the changing trends of the sensory array to FC and matches are similar to the phenomenon illustrated in Figure 3b, and the maximum responses to FC and matches are also obtained for the sensor with 5% Mn\textsuperscript{2+} doping. This result further demonstrates that Mn\textsuperscript{2+} doping can effectively tailor the sensing performance of ZnS NCs, and the resulting sensory array can also be applied to detect IEDs, such as FC and matches. The longest response time and recovery time of the eight sensors, to FC and matches, are only 13 and 11 s (Figure 6c,d), respectively, illustrating the fast response and recovery characteristics toward IEDs.

2.3. Discriminative Detection of Explosive Species

An obvious advantage of a sensory array compared to an individual sensor is that it can realize discriminative identification toward unknown analytes, based on certain mathematical
In the present study, the sensing response and the response time inherent to the interaction between any explosive chemical species and the sensor were chosen as the thermodynamic and kinetic parameters, respectively. For each species, its eight pairs of sensing responses and response times from the sensory array were used to calculate the ratio of sensing response to response time. Thus, the obtained eight parameters in each measurement represent the fingerprint of the species. In this case, each explosive is expected to exhibit a distinctive pattern.

Table 1. Comparison of different chemiresistive gas-phase explosive sensors and the present Mn:ZnS NCs-based sensors.

<table>
<thead>
<tr>
<th>Sensing materials</th>
<th>Analyte concentration</th>
<th>Response [%]</th>
<th>Response time</th>
<th>Recovery time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titania(B) nanowires</td>
<td>TNT 9 ppb</td>
<td>47</td>
<td>≈5 s</td>
<td>≈6 s</td>
<td>[19]</td>
</tr>
<tr>
<td>Organic nanoribbons</td>
<td>DNT 100 ppb</td>
<td>40</td>
<td>&lt;5 s</td>
<td>&gt;100 s</td>
<td>[20]</td>
</tr>
<tr>
<td>ZnO nanowire</td>
<td>TNT 60 ppb</td>
<td>20</td>
<td>&gt;10 min</td>
<td>–</td>
<td>[5e]</td>
</tr>
<tr>
<td>SWNT</td>
<td>TNT 8 ppb</td>
<td>8</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>GaN/TiO2 NWNC hybrids</td>
<td>TNT 100 ppb</td>
<td>10</td>
<td>30</td>
<td>–</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>DNT 100 ppb</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni–ZnO</td>
<td>TNT 9.1 ppb</td>
<td>45.5</td>
<td>≈4.3 s</td>
<td>≈4 s</td>
<td>[5d]</td>
</tr>
<tr>
<td>Fe–ZnO</td>
<td>DNT 411 ppb</td>
<td>38.9</td>
<td>≈5.3 s</td>
<td>=6.3 s</td>
<td>–</td>
</tr>
<tr>
<td>Fe–ZnO</td>
<td>Urea</td>
<td>99.9</td>
<td>≈6 s</td>
<td>≈30 s</td>
<td>–</td>
</tr>
<tr>
<td>Mn:ZnS NCs with 5% Mn2+</td>
<td>TNT 9.1 ppb</td>
<td>46.9</td>
<td>≈4 s</td>
<td>≈6 s</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>DNT 411 ppb</td>
<td>45.4</td>
<td>≈3 s</td>
<td>≈5 s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Urea</td>
<td>99.4</td>
<td>≈1 s</td>
<td>≈14 s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td>57.8</td>
<td>≈4 s</td>
<td>≈6 s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>PN</td>
<td>27.5</td>
<td>≈2 s</td>
<td>≈5 s</td>
<td>–</td>
</tr>
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<td>≈4 s</td>
<td>≈5 s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>UF</td>
<td>58.8</td>
<td>≈4 s</td>
<td>≈6 s</td>
<td>–</td>
</tr>
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</table>

Figure 5. a) XPS spectra of O 1s for Mn:ZnS NCs, the inset is the ratio of O 1s to S 2p according to their peak areas; b) EPR spectra of Mn:ZnS NCs at 298 K, the inset is the EPR spectra of pure ZnS NCs; c) Structural and band models showing the role of Mn2+ doping, (i) surface adsorption illustration, (ii) pure ZnS, ZnS with (iii) intermediate, and (iv) high Mn2+ doping concentration.
of interaction. It is found that each species get its unique fingerprint pattern (Figure 7), for example, although DNT and TNT are nitroaromatic explosives with similar molecular structure, there is a big difference between their fingerprint patterns (Figure 7a). The fingerprint patterns for PN and PP are also different from each other even they are both potassium salts (Figure 7b). The fingerprint patterns for FC and matches are also different from those of their main component, BP and SP (Figure 7c,d), which could be caused by the additives in matches and FC. Similarly, the fingerprint patterns for urea and UF are also obviously different although the principal component is the same, the reason can be attributed to that there are additives, such as paraffin wax, in UF to control the release of the fertilizer (Figure 7e), indicating that the present sensory array is ultrasensitive to tiny changes in the atmosphere. Thus, the sensory array based on Mn:ZnS NCs achieves the recognizable detection of TNT, DNT, urea, UF, BP, PP, SP, FC, matches, and PN. This recognizable detection capability could be ascribed to

Figure 6. a) Response curves, b) sensing response, c) response time, and d) recovery time of the sensory array to vapors of FC and matches at room temperature.

Figure 7. Fingerprint patterns by combining kinetics and thermodynamics of ten constituents according to the ratio of response value to response time. a) TNT and DNT, b) PN and PP, c) FC and BP, d) SP and Match, and e) urea and UF.
3. Conclusions

In summary, the sensing properties of ZnS NCs were tailored effectively by Mn\textsuperscript{2+} doping and the resultant chemiresistive sensors were applied to detect the vapors of the constituents (SP, PP, BP, urea, UF, PN, FC, and match) relevant to IEDs as well as DNT and TNT at room temperature. Compared with that of the pure ZnS NCs-based sensor, the sensing responses of the sensor based on the Mn:ZnS NCs are remarkably improved upon incorporation of Mn\textsuperscript{2+}, typically, with a Mn\textsuperscript{2+} concentration of only 2.23%, the responses to DNT, TNT, UF, SP, PP, BP, and PN are promoted by about 148%, 123%, 183%, 211%, 16%, 88%, and 330%, respectively. The underlying tailoring mechanism can be attributed to the dynamic competition between the enhanced oxygen molecule adsorption and the increasing carrier density in ZnS NCs resulting from Mn\textsuperscript{2+} doping. The sensory array assembled with 8 Mn:ZnS NCs-based sensors could realize fingerprint patterning of different constituents by combining the kinetics and thermodynamics naturally inherent between the sensory array and the target analytes within 7 s. Thus, the present tailoring strategy represents a facile, effective and reliable method to acquire a quality sensory array and opens up a new way to rapidly, sensitively and contactlessly recognize the constituents relevant to IEDs, making the on-the-spot detection of IEDs possible.

4. Experimental Section

Chemicals and Reagents: Zinc acetate (Zn(CH\textsubscript{3}COOH)\textsubscript{2}•2H\textsubscript{2}O), manganese acetate (Mn(CH\textsubscript{3}COOH)\textsubscript{2}•4H\textsubscript{2}O), sodium sulfide (Na\textsubscript{2}S•9H\textsubscript{2}O), urea, potassium permanganate (PP), potassium nitrate (PN), and sulphur powder (SP) are analytical grade and used as received. 2,4-Dinitrotoluene (DNT) was purchased from Sigma-Aldrich. Black powder was self-made by blending SP, PN, and graphite powder with a molar ratio of 1:2:3. TNT was obtained from the National Security Department of China, and recrystallized with ethanol before use. UF, FC, and PP were purchased from Sigma-Aldrich. TNT and DNT used in the present study are highly explosive and should be handled only in small quantities.

Synthesis of Mn:ZnS NCs: 50 mmol of Zn(CH\textsubscript{3}COOH)\textsubscript{2}•2H\textsubscript{2}O was first dissolved in 50 mL of deionized water with stirring. After that, different amount of Mn(CH\textsubscript{3}COOH)\textsubscript{2}•4H\textsubscript{2}O (0.5, 0.8, 2.5, 5, 7, and 10 mmol) was added with stirring and followed with ultrasonication for 10 min at room temperature. Then, 10 mL aqueous solution containing 50 mmol Na\textsubscript{2}S•9H\textsubscript{2}O was dropwised added into the reaction system, and the mixture was vigorously stirred for 5 h at room temperature. The resulting Mn:ZnS NCs were centrifuged and washed thoroughly with deionized water and absolute ethanol, and finally dried in oven at 40 °C for 1 h.

Characterization: XRD measurement was conducted using powder XRD (Bruker D8 Advance, with Cu-K\textsubscript{α} radiation operating at 40 kV and 40 mA, scanning from 2θ = 20° to 80°). TEM (FEI Tecnai G2 F20 S-TWIN) and EDS and XPS (Thermo Scientific Escalab 250) were used to quantitatively evaluate the composition of the element in Mn:ZnS NCs. The content of Mn element in ZnS NCs was defined as the atomic ratio of Mn/(Mn+Zn) measured. EPR spectra were recorded on a Bruker Elexys E500 spectrometer by applying an X-band (9.43 GHz, 1.5 mW) microwave with sweeping magnetic field at room temperature in cells that can be connected to a conventional high-vacuum apparatus (residual pressure <10^{-4} mbar).

Gas Sensing Performance Evaluation: Initially, Mn:ZnS NCs were mixed with deionized water in a weight ratio of 100:25 and ground in a mortar for 15 min to form a paste. The paste was then coated on a ceramic substrate by a thin brush to form a sensing film on which silver paste was recrystallized with ethanol before use. The sensing film and ceramic substrate were attached to a self-made sensor by silver paste to form the sensing electrode. The film was dried in air at 40 °C for 24 h. The sensors were aged at 4 V in air for about 24 h to ensure the good stability since this procedure can greatly reduce the defects of the film. The sample was dried naturally in air overnight. The sensors were aged at 4 V in air for about 24 h to ensure the good stability since this procedure can greatly reduce the defects and improve the grain boundary contact. The room temperature (25 ± 3 °C) saturated explosive vapor was obtained by putting solid explosive powder at the bottom of a conical flask (250 mL) and sealed for 48 h. For gas sensing test, the sensor was inserted into the saturated vapor of an explosive. After the sensor resistance reached a new constant value, the sensor was then inserted into a same size conical flask full of air to recover. The electric signal of the sensor was measured by a Keithley 2636B SourceMeter. The relative sensor response in resistance is defined as, Response = -ΔR/R\textsubscript{a} = -(R\textsubscript{s} - R\textsubscript{a})/R\textsubscript{a} × 100%, where R\textsubscript{s} and R\textsubscript{a} are the electrical resistances of the sensor in air and in explosive vapor. The response time is defined as the period in which the sensor resistance reaches 90% of the response value upon exposure to the explosive vapor, while the recovery time is defined as the period in which the sensor resistance changes to 10% of the response value after the explosive vapor is removed.

Figure 8. Schematic diagram of discriminative detection of the constituents relevant to IEDs.
Supporting Information

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

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