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Microwave assisted rapid growth of $Mg(OH)_2$ nanosheet networks for ethanol chemical sensor application

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ABSTRACT

This paper reports a facile microwave-assisted synthesis of magnesium hydroxide ($Mg(OH)_2$) nanosheet networks and their utilization for the fabrication of efficient ethanol chemical sensor. The synthesized nanosheets networks were characterized in terms of their morphological, structural and optical properties using various analysis techniques such as field emission scanning electron microscopy (FESEM), X-ray diffraction pattern (XRD), Fourier transform infrared (FTIR) and UV–Vis spectroscopy. The detailed morphological and structural investigations reveal that the synthesized ($Mg(OH)_2$) products are nanosheet networks, grown in high density, and possessing hexagonal crystal structure. The optical band gap of as-synthesized $Mg(OH)_2$ nanosheet networks was examined by UV–Vis absorption spectrum, and found to be 5.76 eV. The synthesized nanosheet networks were used as supporting matrices for the fabrication of *I–V* technique based efficient ethanol chemical sensor. The fabricated ethanol sensor based on nanosheet networks exhibits good sensitivity ($\sim$3.991 $\mu A\,cm^{-2}\,mM^{-1}$) and lower detection limit (5 μM), with linearity ($R = 0.9925$) in short response time (10.0 s). This work demonstrate that the simply synthesized $Mg(OH)_2$ nanosheet networks can effectively be used for the fabrication of efficient ethanol chemical sensors.

1. Introduction

Water pollution caused by hazardous chemicals creates severe adverse effects to the environment, and therefore, whenever the effluent contaminated by such pollutants is released in the environment, it spreads aesthetic pollution and effectively disturbed the ecosystem [1–5]. Among various hazardous chemicals, ethanol, a volatile colorless liquid is one which possesses high corrosive nature and can easily miscible with water and many other organic solvents. In addition to this, it is one of the commonly used solvents in the industries; hence its release into the environment could contaminate the groundwater and surface water which could associate with serious medical illnesses such as cancer, stroke, hypertension, cardiovascular problems, liver cirrhosis, and brain damage. Therefore, due to high-toxic nature and various medical illnesses, it is highly desirable to develop a reliable and sensitive sensor which can allow a convenient and rapid determination of ethanol. For the effective detection of various hazardous chemicals, variety of methods have been developed and reported in the literature [6,8]. Among various detection techniques, the electrochemical method presents itself as a reliable, sensitive, effective and low-cost analytical technique [9]. In the electrochemical technique, various materials were used to modify the electrode for the effective detection of target chemicals. Recently, the utilization of nanomaterials for the modification of electrodes has received a considerable attention due to their exotic and interesting properties.

Among various nanostructured materials, the magnesium hydroxide $Mg(OH)_2$ has attracted much attentions due to its environmental friendly, nontoxic, noncorrosive and thermally stable behavior [2,7]. $Mg(OH)_2$ is used in variety of applications such as smoke letting, desulphurization, flame retardant composite, wood pulp bleaching, water treatment, food stuff, and so on [10–13].

This paper reports a facile microwave-assisted synthesis of $Mg(OH)_2$ nanosheet networks and their efficient utilization for the fabrication of ethanol chemical sensor. The synthesized materials were characterized in terms of their morphological, structural and

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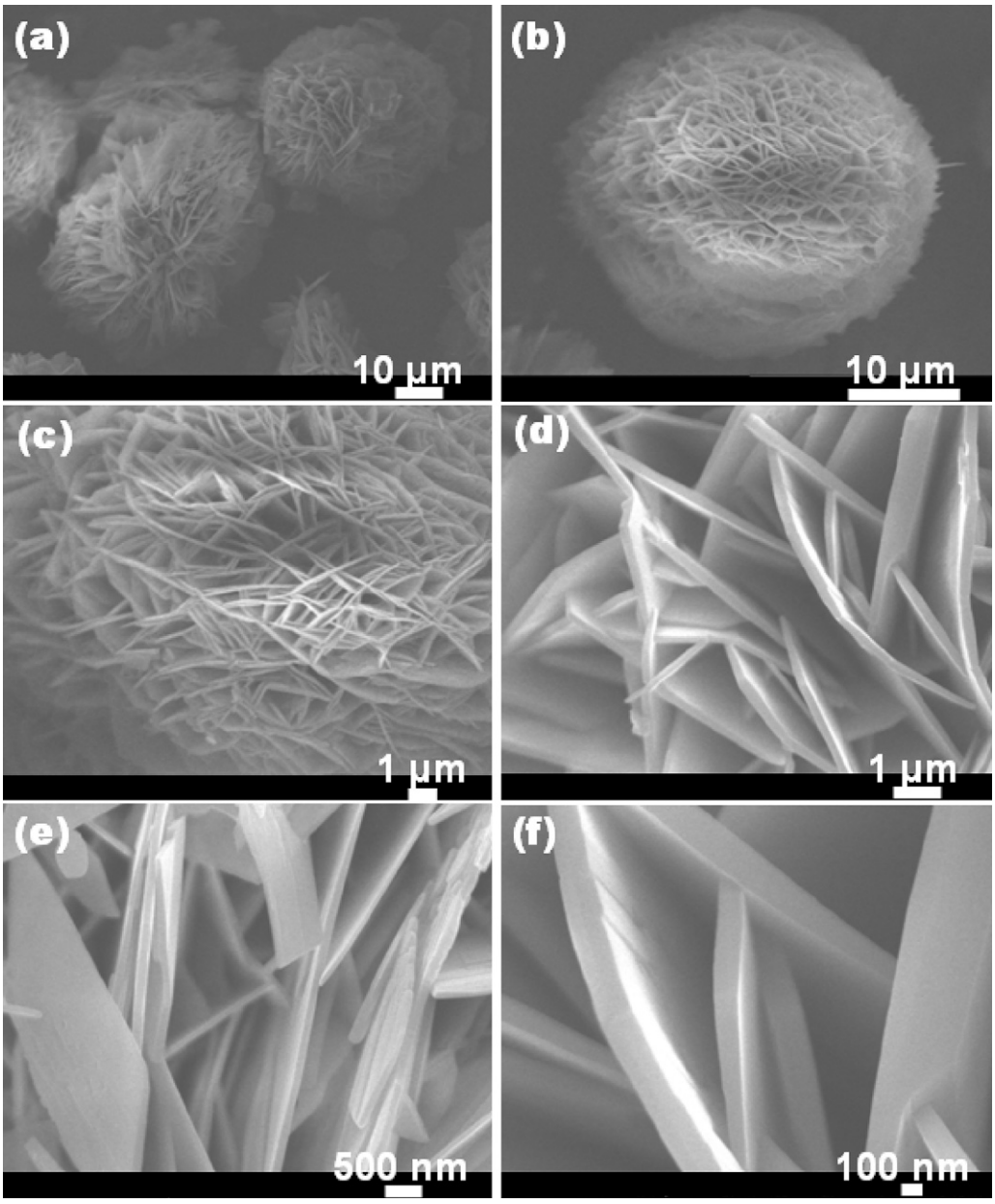

Fig. 1. Typical (a and b) low-magnification and high-resolution (c–f) FESEM images of as-synthesized $Mg(OH)_2$ nanosheet networks via facile microwave process.

optical properties. The fabricated ethanol sensor exhibited a very high sensitivity and low detection limit.

2. Experimental

2.1. Synthesis of $Mg(OH)_2$ nanosheet networks

Large-scale synthesis of $Mg(OH)_2$ nanosheet networks was done via microwave process using magnesium chloride, urea and NaOH. All the chemicals were obtained from Sigma–Aldrich and used as received without further purification. In a typical reaction process, 1 g $MgCl_2{\cdot}6H_2O$ was dissolved in 50 ml distilled water (DW) under continuous stirring followed by the drop-wise addition of 1.8 g urea solution, made in 50 ml DW. Consequently, few drops of NaOH was also added in the solution to maintain the pH 10. The resultant solution was then transferred to a hydrothermal Teflon cell and kept in the microwave oven at 220 °C (microwave power = 1000 W). The temperature was raised up to 220 °C in 10 min and reaction was completed in 30 min. After terminating the reaction, the hydrothermal cell was cooled down at room temperature and finally white precipitate was obtained which was washed with DW, ethanol and acetone sequentially and dried at room-temperature. The as-synthesized products were characterized in terms of their structural, optical and sensing properties.

2.2. Characterizations of $Mg(OH)_2$ nanosheet networks

The morphologies of synthesized $Mg(OH)_2$ nanosheet networks were examined by FESEM (JEOL-JSM-7600F) while the crystallinity and crystal phases were characterized by X-ray diffraction (XRD; PANanalytical Xpert Pro.) pattern measured with Cu Kα Radiation (λ = 1.54178 Å) in the range of 10–70°. The chemical composition of as-prepared $Mg(OH)_2$ nanosheet networks was examined by Fourier transform infrared (FTIR; Perkin Elmer-FTIR Spectrum-100) spectroscopy in the range of 450–4000 cm^{-1} and the optical property was characterized by UV–Visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) at room-temperature.

2.3. Fabrication and characterization of ethanol chemical sensor using $Mg(OH)_2$ nanosheet networks modified GC electrode

For fabricating the ethanol chemical-sensor, the as-synthesized $Mg(OH)_2$ nanosheet networks were coated on glassy carbon electrode (GCE, surface area 0.0316 cm^2) surface and the modified GCE was used as working electrode for evaluating the ethanol sensor performance. For modifying the electrode, a slurry of $Mg(OH)_2$ nanosheet networks was finely coated on GCE and kept in an oven at 60 °C for 3–5 h. For measuring the sensor performance, a very simple *I–V* (current–voltage technique) technique based two electrode system was used in which the $Mg(OH)_2$ modified nanosheet networks was used as working electrode and Pd wire as a

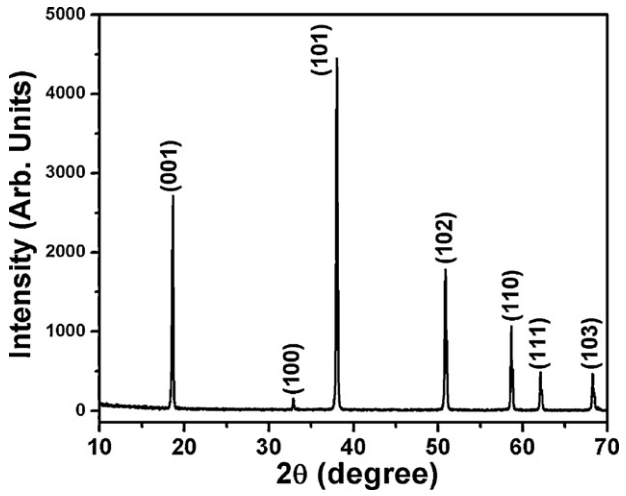

Fig. 2. XRD pattern of as-synthesized $Mg(OH)_2$ nanosheet networks via facile microwave process.

counter electrode. The current response was measured from 0 to 1.0 V while the time delaying and response time were 1.0 s and 10.0 s, respectively. For all the measurements, the amount of 0.1 M phosphate buffer solution (PBS) was kept constant as 10.0 ml. Electrometer was used as a current–voltage source for *I–V* measurement in simple two electrode system. A wide concentration range of ethanol (10 μM–1.0 M) was used for all the experiments. The sensitivity is calculated from the ratio of voltage and current of the calibration plot by considering the active sensor surface area.

3. Results and discussion

3.1. Morphological, structural and optical properties of as-synthesized $Mg(OH)_2$ nanosheet networks

Fig. 1 exhibits the typical FESEM images and demonstrates the general morphologies of as-synthesized $Mg(OH)_2$ products. Fig. 1(a) and (b) exhibit the low-magnification FESEM images of as-synthesized products and reveal that spherical ball-shaped morphologies are grown in very highly density. The typical sizes of the spherical shaped morphologies are in the range of 30 ± 3 μm. The high-resolution FESEM images clearly exhibit that the synthesized spherical ball-shaped morphologies are made by the accumulation of hundreds of thin nanosheets which are penetrating in each other in such a special fashion that they made network-like morphologies (Fig. 1(c)). The thicknesses of nanosheets are in the range of $\sim 95 \pm 10$ nm which several micrometers in length. Moreover, the nanosheets show clean and smooth surfaces and sharp edges throughout their dimensions (Fig. 1(d) and (f)).

To examine the crystallinity and crystal phases of as-synthesized $Mg(OH)_2$ nanosheet networks, the synthesized product was examined by X-ray diffraction and result is shown in Fig. 2. All the observed reflections in the pattern are well matched with the hexagonal brucite structure [space group $P3m1$] of $Mg(OH)_2$ with calculated lattice constants of $a = 3.147$ Å and $c = 4.769$ Å. The obtained results are well matched with the reported data (JCPDS 7-239). Importantly, the sharp and strong intensity reflections confirm the well-crystalline nature of as-synthesized $Mg(OH)_2$ nanosheet networks. Except $Mg(OH)_2$, no other reflection related to any impurity was observed in the pattern which confirms the pure phase of as-synthesized $Mg(OH)_2$.

To determine the chemical compositions of as-synthesized $Mg(OH)_2$ nanosheet networks, Fourier transform infrared (FTIR) spectroscopy was done in the range of 450–4000 cm^{-1}. Fig. 3(a) exhibits the typical FTIR spectrum of as-synthesized nanosheet networks which exhibit various well-defined distinct peaks. The appearance of two peaks at 465 cm^{-1} and 555 cm^{-1} in the

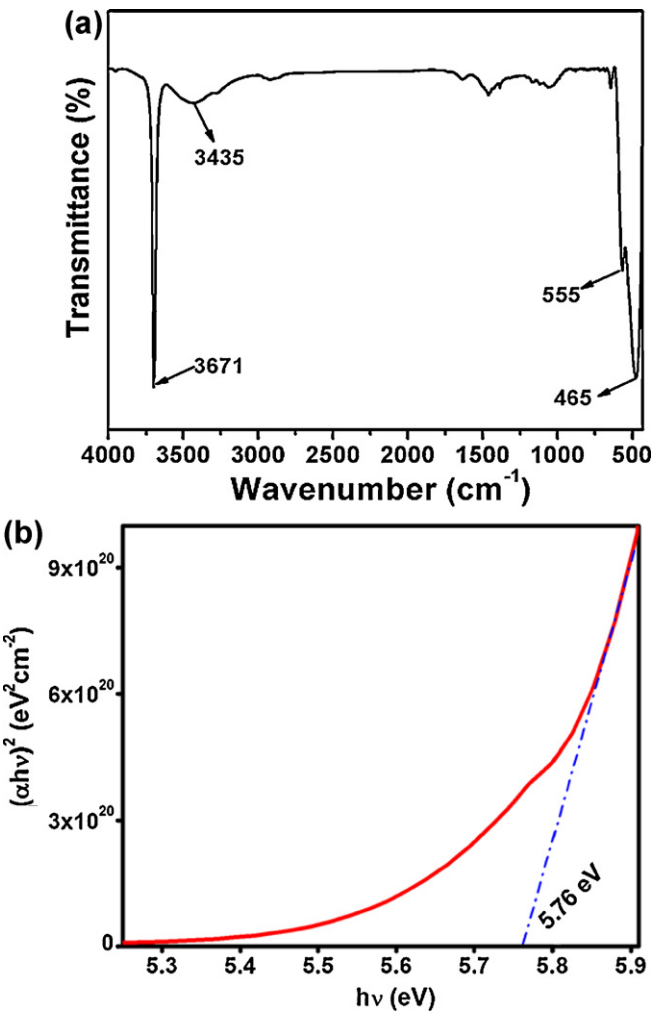

Fig. 3. (a) FTIR spectrum and (b) $(\alpha h\nu)^2$ vs. photon energy plot for as-synthesized $Mg(OH)_2$ nanosheet networks via facile microwave process.

spectrum are due to the in-plane deformation vibration of water (δ_{OH}) and stretching vibration of Mg–OH (ν_{Mg-OH}), respectively [14]. In addition to this, the presence of a broad peak at 3435 cm^{-1} is originated due to the stretching mode of hydrogen bound hydroxyl group while the appearance of a sharp peak at 3671 cm^{-1} is related to stretching vibrational mode (ν_{OH}) of non-hydrogen bonded hydroxyl groups [14].

To examine the optical properties of as-synthesized $Mg(OH)_2$ nanosheet networks, UV–Vis spectrum was recorded at room-temperature. For UV–Vis measurements, the synthesized products were ultrasonically dispersed in water and 1 ml of this solution was used for analysis. Fig. 3(b) exhibits the typical UV–Vis spectrum of synthesized $Mg(OH)_2$ nanosheet networks. The optical band gap of nanosheet networks was determined by Tauc's formula which exhibits the relationship between absorption coefficient and the incident photon energy of semiconductors. The Tauc's equation is as follows:

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

where α is the absorption coefficient, A is constant, and n is equal to 1/2 for a direct transition semiconductor and 2 for indirect transition semiconductor. According to the equation, the calculated optical band gap for as-synthesized nanosheet networks was found ~5.76 eV which is consistent with the reported literature [15].

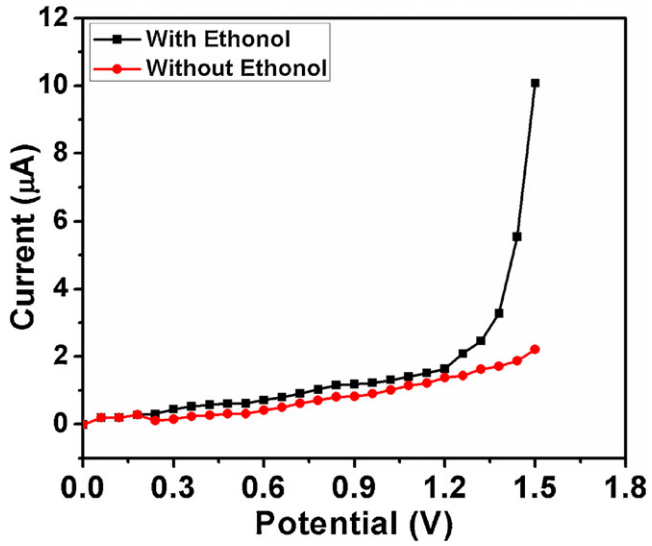

Fig. 4. Typical *I–V* response of $Mg(OH)_2$ nanosheet networks modified glassy carbon electrode (GCE) in 10 ml, 0.1 M PBS solution: (■) with 10 μM ethanol and (●) without the presence of ethanol.

3.2. Performance of fabricated ethanol chemical sensor based on $Mg(OH)_2$ nanosheet networks modified GC electrode

The ethanol chemical sensor performance of as-synthesized $Mg(OH)_2$ nanosheet networks was evaluated by simple *I–V* technique using two electrode system in which nanosheet networks modified electrode was used as working electrode and Pd wire as a counter electrode [2,7–9]. Fig. 4 exhibits the typical *I–V* electrical response of the fabricated ethanol chemical sensor based on $Mg(OH)_2$ nanosheet networks modified GCE in the absence and the presence of 10 μM ethanol in 10.0 ml of PBS solution. A significant increase in the current was observed when small amount (50 μL) of ethanol was added into 0.1 M phosphate buffer solution (pH 7.0). However, no significant increase in the current was observed in the *I–V* response of modified electrode measured without ethanol. This clearly exhibits that the synthesized $Mg(OH)_2$ nanosheet networks exhibits good electrocatalytic and fast electron exchange properties which leads a rapid increase in the current as observed in the presence of ethanol. This phenomenon clearly reflects that the synthesized nanosheets are highly active towards ethanol sensing [2].

For detailed sensing behavior of $Mg(OH)_2$ nanosheet networks towards ethanol, the electrical response of modified GCE was examined at various ethanol concentrations and results are shown in Fig. 5(a). A wide concentration range of ethanol (10 μM–1.0 M) into 0.1 M PBS solution (pH 7.0) was used for these experiments. As can be seen from the obtained electrical responses that with increasing the concentration of ethanol, the observed current was increased which reflects that the conductivity of modified electrode was enhanced due to increasing the concentrations of sensing ions. Fig. 5(b) exhibits the typical calibration curve, plotted from the wide range of ethanol concentrations. As can be seen in the calibration curve that the response current increases with increasing the concentration of ethanol and finally at high-ethanol concentration, the current reaches almost at a saturated value which may be due to the unavailability of free $Mg(OH)_2$ nanosheet networks sites for C_2H_5OH adsorption. The sensitivity of the fabricated chemical sensor was estimated from the slope of the current vs. concentration from the calibration plot shown in Fig. 5(b). The fabricated ethanol sensor based on $Mg(OH)_2$ nanosheet networks exhibits good and reproducible sensitivity of 3.991 $\mu A\,cm^{-2}\,mM^{-1}$ and detection limit of 5 μM with correlation coefficient (R) of

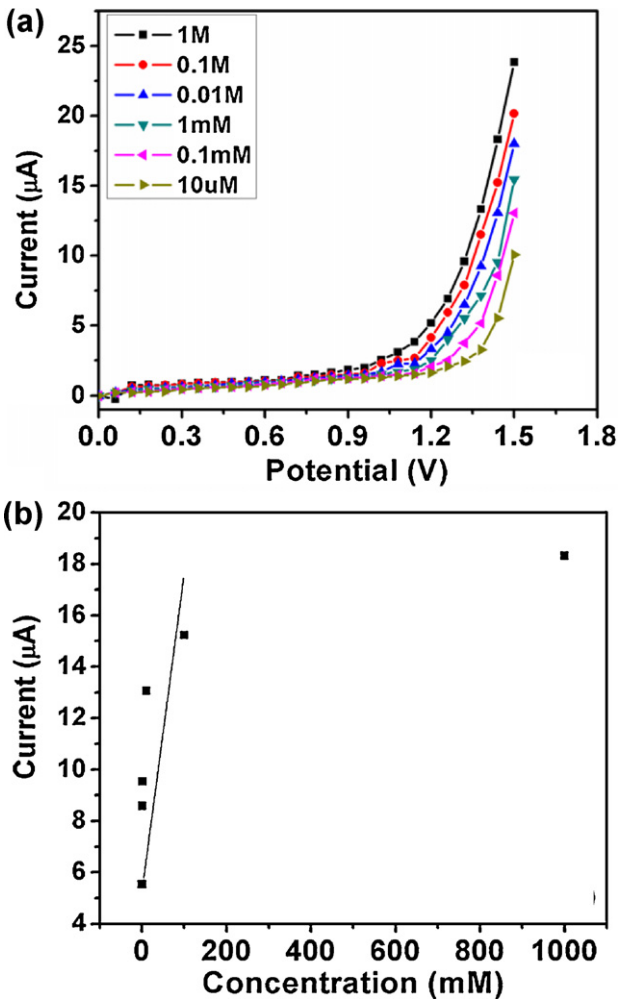

Fig. 5. (a) Typical *I–V* response of $Mg(OH)_2$ nanosheet networks modified GCE towards various concentrations (from 10 μM to 1.0 M) of ethanol into 10 ml, 0.1 M PBS solution (pH 7) and (b) calibration curve.

0.9925 in short response time (10.0 s). The good sensitivity of the electrode can be attributed to the excellent adsorption ability and high electrocatalytic activity of the $Mg(OH)_2$ nanosheet networks.

The fabricated $Mg(OH)_2$ nanosheet networks based ethanol chemical sensor exhibits good stability for over 3 weeks and no significant changes in current response was observed for approximately 20 days. After 20 days, the response of sensor was gradually reduced which may be due to the weak interaction between modified electrode surface and target analyte. The obtained observations clearly reflect that simply synthesized $Mg(OH)_2$ nanomaterials can be used as efficient electron mediators for the fabrication of effective chemical sensors.

4. Conclusion

In summary, $Mg(OH)_2$ nanosheet networks were synthesized in large quantity via facile microwave process and efficiently utilized for the fabrication of efficient ethanol chemical sensor. By detailed morphological, structural and optical characterizations, it was confirmed that the synthesized products are grown in high-density, possessing hexagonal phase and exhibiting the optical band gap of ~5.76 eV. The fabricated ethanol sensor based on nanosheet networks exhibits good sensitivity (~3.991 $\mu A\,cm^{-2}\,mM^{-1}$) and lower detection limit (5 μM), with linearity (R = 0.9925) in short response time (10.0 s).

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