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Application of ZnO–Imine Nanocomposites for Optical Detection of Metal Ions in Water

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Summary:

This work presents a study of nanocomposites based on organic imine-type ligands and ZnO tetrapods, and their application as sensors for photochemical detection of metal ions. Structural and electronic properties of the obtained nanocomposite were investigated by SEM, XRD, DLS, photoluminescence, and diffuse reflectance spectroscopy. A hydrophilic sensor platform was developed to detect metal cations in water. The selectivity of the nanocomposite was significantly improved compared to the pure ligand. Main sensor parameters, such as limit of detection and sensor response time, were calculated.

Keywords: ZnO tetrapod, imines, photochemical sensors, detection of metal ions, water pollution.

Introduction

The detection of metal ions in water is important in various fields such as agriculture, medicine, biology, and environmental protection[1]. Many accurate methods exist for deter-mining ion concentrations in aqueous media, but most are expensive, time-consuming, and require laboratory conditions. Thus, the industry seeks low-cost, portable, and sufficiently accurate optical sensors for metal ions that can operate in real-world conditions.

Schiff bases, imines, salens, and related organic ligands show promise due to their room-temperature photoluminescence and chelation abilities. These ligands are easily modifiable for industrial applications but have limitations: they typically work only in solution, undergo photobleaching, and some are not selective[2].

To overcome these challenges, attaching the chelating ligand to a nanostructured template is proposed. This work presents nanocomposites based on ZnO tetrapods and a symmetric imine ligand.

Experimental

In this research, we used commercially produced ZnO tetrapods (**ZnO**) and the imine ligand (**L1**), whose chemical structure is shown in Fig. 1. First, 5 mg of **L1** were dissolved in 15 mL of ethanol (99.8%), followed by the addition of 50 mg of **ZnO**. The mixture was stirred at room temperature for 72 hours. The resulting solids were filtered, washed with ethanol, and freeze-dried.

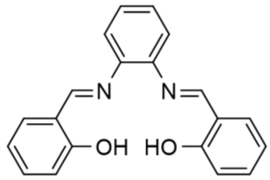

*Fig. 1. Chemical structure of **L1***

The structural properties of the ZnO-L1 nanostructures were investigated using XRD, SEM, FTIR, diffuse reflectance (300–800 nm), and photoluminescence (350–800 nm). Contact angle measurements were conducted to assess the chip's suitability for aqueous environments.

For sensor testing, samples were transferred to glass substrates. To enhance wettability and prevent sample washout, a protective hydrophilic layer was applied using a nafion dispersion solution (an ionomer and perfluorinated copolymer). The samples were coated with Nafion and dried overnight at 70°C to stabilize the polymer.

Results

The formation of the **ZnO-L1** composite was confirmed by XRD and FTIR analysis. XRD indicates that the ligand is amorphous on the ZnO surface, with no crystal planes from **L1**. FTIR confirmed the presence of **L1**-specific chemical bonds between 1750 and 700 cm^{-1}(**Fig. 3**).

The contact angle of the composite was 150°, indicating near-superhydrophobicity. The contact angle of the Nafion-coated **ZnO-L1** samples (**ZnO-L1-Naf**) was 70°, indicating hydrophilicity.

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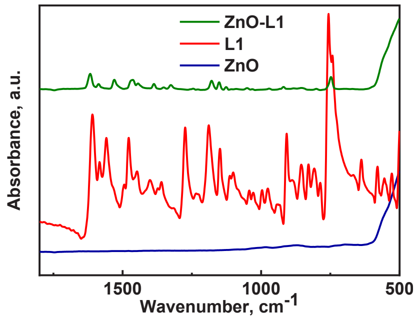

*Fig. 3. FTIR spectra of **ZnO-L1** composite, **L1, ZnO***

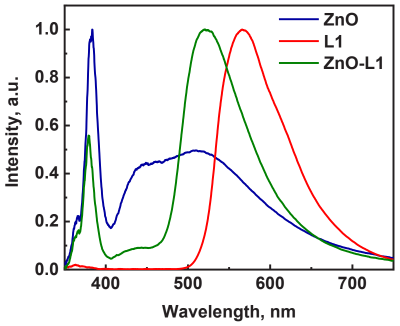

*Fig.4. PL spectra of **ZnO, L1, ZnO-L1***

The PL spectrum of the composite shows a strong emission peak at 520 nm, corresponding to L1, with a 40 nm blue shift (**Fig. 4**).

Sensitivity and selectivity were evaluated using steady-state and time-resolved PL measurements. As an example, the changing of **ZnO-L1-Naf** PL after interaction with Cd^{2+} ions are shown in **Fig.5**

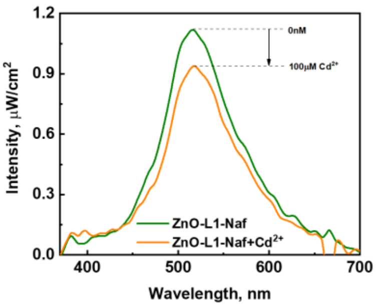

*Figure 5. PL spectra of **ZnO-L1-Naf** before and and after interaction with Cd^{2+} ions*

A rapid selectivity test was performed with 100 µM metal ion water solutions.

Sensor signal was evaluated using equation (1):

$$S = \left| 1 - \frac{I(C_n)}{I_0} \right| \times 100\% \quad (1)$$

Results for L1 and **ZnO-L1-Naf** samples are shown in **Fig. 6**. While L1 responded strongly to most ions, the **ZnO-L1-Naf** composite demonstrated improved selectivity with a comparable sensing response.

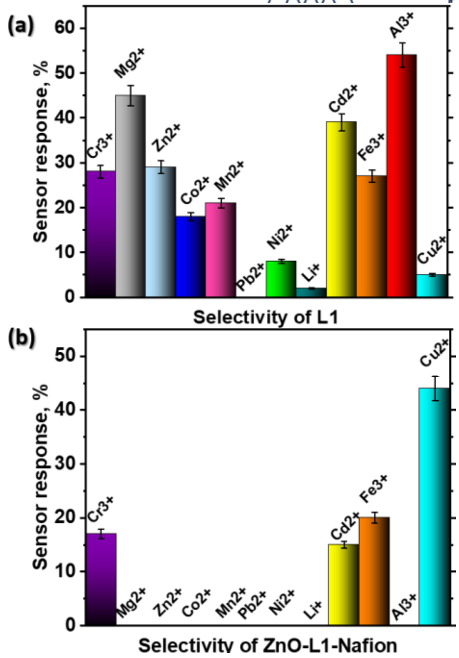

*Fig.6. Selectivity test of **L1(a), ZnO-L1-Naf (b)***

Conclusions

ZnO and **L1**-based composites have been successfully obtained. The hydrophilicity problem was addressed by incorporating Nafion ionomer. It is well established that perfluorinated copolymers possess a negative surface charge, which enhances the interaction of the chip with metal cations. The establishment of an innovative sensor platform for metal ion detection in water, based on ZnO and imine ligand composite, was achieved. Sensing layer can be further modified to improve the selectivity of sensor. Nevertheless, chips, based on metal oxides and chelating ligands composites, covered with ionomer layer are emerging as novel sensors with potential to implement optical detection of metal ions in aqueous media.

References

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