



Nickel-metal organic framework/MWCNT composite electrode for non-enzymatic urea detection



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ABSTRACT

A porous composite catalyst based on nickel-metal organic framework (Ni-MOF) and multiwalled carbon nanotubes (MWCNTs) was synthesized for non-enzymatic urea detection. The Ni-MOF was characterized by Fourier transform infrared spectroscopy, X-ray photo electron spectroscopy and X-ray diffraction techniques. The morphology and the structure of the Ni-MOF were studied using scanning electron microscopy and transmission electron microscopy. The Ni-MOF/MWCNTs coated indium tin oxide glass was used as a novel electrochemical sensor for urea detection. The Ni-MOF/MWCNT electrode showed a very high sensitivity of $685 \mu\text{A} \text{mM}^{-1} \text{cm}^{-2}$, low detection limit of $3 \mu\text{M}$ and a response time of 10 s. Moreover, the sensor showed remarkable stability with no loss in activity after 30 days of storage under ambient conditions. Overall, the novel hybrid inorganic–organic material showed notable potential for designing of micro-scale point of care diagnostic devices for urea sensing applications.

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1. Introduction

Urea is a metabolic product of nitrogen containing compounds and its level has been an important parameter in assessing kidney and liver functioning by examining human excreta or blood samples [1–3]. Besides, industrial waste water also contributes urea to the environment contaminating ground water and aquatic system [4,5]. Currently, urea biosensors based on electrochemical enzymatic reaction have been most widely used due to the specific binding capabilities and catalytic activity of enzymes. However, a high cost of enzymes and limited lifetime of the sensors are the major drawbacks [6–9]. In contrast, non-enzymatic biosensors comprising metals and metal oxides are considered to be a potential substitute for the enzymatic biosensors because of their high sensitivity and stability.

Nickel oxide has been widely applied as a catalyst for the electro-oxidation of urea [10,11]. The electro-catalytic performance of the nickel-based catalysts has been further improved by synthesizing various nano-structures such as nanoparticles, nanorods, nanowires, and three-dimensional networks [12–15]. In addition, supporting materials such as carbon nanotubes [16], graphene [17], and cellulose fibers [18], have been employed to provide a high

surface area with good mechanical integrity and to enhance electron and mass transfer.

As a new class of electrochemically functional materials, metal-organic frameworks (MOFs) have generated considerable amount of interest because of their excellent structural properties [19,20]. MOFs consist of metal ion coordinated to organic ligands forming a three dimensional structure with large surface area, highly tunable porosity, and open metal sites. The MOFs were reported to be efficient catalysts in wide range of oxidation-reduction reactions [21,22], due to the presence of metal complex in a porous skeleton. For instances, Cu-MOFs have been examined in the electro-oxidation of glucose [23] and H_2O_2 [24]. However, using single-phase MOFs are marred by a low electrical conductivity and weak mechanical stability [25]. Thus, to overcome these potential drawbacks, MOFs have been composited with carbon based nanostructures (such as graphene and carbon nanotubes) [26].

In the present investigation, a novel electrode employing Ni-MOF/multiwalled carbon nanotube (MWCNT) composite was prepared for the non-enzymatic detection of urea. The structural, morphological, and electrochemical properties of the Ni-MOF and Ni-MOF/MWCNT composites were investigated. The prepared electrode exhibited an excellent sensitivity for urea detection.

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2. Experimental

2.1. Materials

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), *N,N*-dimethylformamide (DMF), benzene-1,3,5-tricarboxylic acid (H_3BTC , 98%wt), and urea ($\text{CO}(\text{NH}_2)_2$) were obtained from Sigma-Aldrich. Multiwalled carbon nanotubes (MWCNTs) (>95% wt, 10–15 nm diameter) was procured from Bioneer (USA). All others chemicals used in the present investigation were of analytical reagent grade.

2.2. Synthesis of Ni-MOF and electrode preparation

Ni-MOF, $[\text{Ni}_3(\text{BTC})_2]$, was prepared by a modified solvothermal method based on a report published elsewhere [27]. Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in methanol was mixed with an aliquot of H_3BTC and stirred for 1 h at room temperature. It was then autoclaved at 150 °C for 24 h. After the completion of the reaction, the product was centrifuged and washed repeatedly with methanol. Finally, Ni-MOF powder was dried in a vacuum oven at 60 °C for 24 h.

For the electrode preparation, Ni-MOF powder was added into MWCNT dispersion in DMF in the ratio of 1:2 (MWCNT/Ni-MOF, w/w), followed by sonication for 30 min. Then, the Ni-MOF/MWCNT dispersion was dropped on an indium tin oxide (ITO) glass, which was then dried in a vacuum oven at 60 °C to get a uniform layer of Ni-MOF/MWCNT with an active area of 0.25 cm².

2.3. Analysis

The chemical states of the samples were analyzed by using a Fourier transform infrared (FTIR) spectrophotometer (Vertex 70,

Bruker, Germany) and an X-ray photoelectron spectrophotometer (XPS, K-alpha, Thermo VG, U.K.) with a monochromated Al X-ray source (AlK α line: 1486.6 eV). The crystal structure of the sample was analyzed by an X-ray diffractometer (XRD, Rigaku DMAX 2200, Japan) at a scan rate of 5°/min using K-alpha radiation ($\lambda = 1.506 \text{ \AA}$). The morphology and the structure of the samples were studied by a scanning electron microscope (SEM, Hitachi S-4700, Japan) and transmission electron microscope (TEM, Tecnai G2 F30 S-Twin, USA).

The electrochemical measurements of the electrodes were performed at ambient conditions using a potentiostat-galvanostat (VSP, BioLogic-Science Instruments, France). A conventional three-electrode system with platinum wire and Ag/AgCl (3 M NaCl) as the counter and reference electrodes, respectively, was used for the measurements.

3. Results and discussion

3.1. Morphology and structural studies

The SEM images of the prepared Ni-MOF particles are shown in Fig. 1. The Ni-MOF particles appeared to be spherical (Fig. 1a) with an average diameter of 1.2 μm . The microspheres were conglomeration of individual Ni-MOF nanoparticles coalesced together to form a spherical superstructures, which were highly porous, as shown in a magnified surface view of the individual particle (Fig. 1b, c & d). Fig. 1c shows the SEM image of Ni-MOF/MWCNT composite; the Ni-MOF microsphere was covered with MWCNT. Further, the single point EDX mapping (Fig. 1d) of the Ni-MOF particle revealed the existence of Ni, C, and O, as the building block elements in the individual particle. The average pore size of the prepared Ni-MOF particles was found to be 8.1–8.5 nm as calculated from Barrett-Joyner-Halenda (BJH) pore size distribution curve (Suppl.

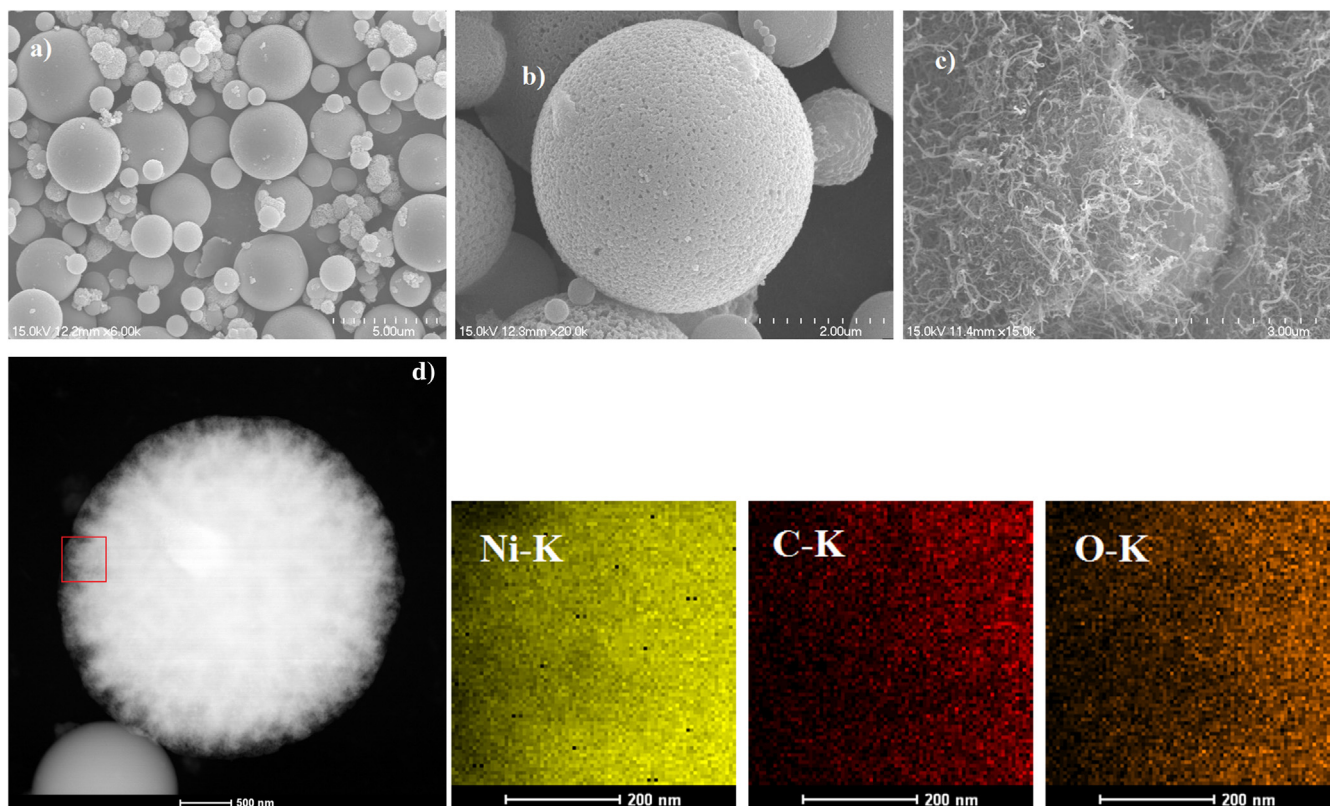


Fig. 1. SEM images of (a) Ni-MOF powder, (b) enlarged Ni-MOF particle, (c) composite of Ni-MOF/MWCNT, (d) STEM image of single Ni-MOF particle; and the corresponding elemental mapping of the nickel, carbon, and oxygen elements.

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