Hollow NiCo-LDH polyhedrons for 1-second level humidity detection and respiratory monitoring

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Keywords: Humidity sensor; Quartz crystal microbalance; NiCo-LDH; Respiration Monitoring

1. The Chemical Raw Materials

2-Methylimidazole, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)\ 2 \cdot 6H_2O$, methanol and ethanol were purchased from Macklin (Shanghai, China). All reagents and chemicals are of analytical grade and was used directly without further purification.

2. Synthesis of ZIF-67

0.249 g $Co(NO_3)_2 \cdot 6H_2O$ and 0.328 g 2-Methylimidazole were separately dissolved in 25 mL methanol. Then, the solution of 2-Methylimidazole was quickly added to the $Co(NO_3)_2 \cdot 6H_2O$ solution, which was stirred for 10 min and aged at room temperature for 48 h. Afterwards, the mixture was washed by centrifuging with methanol and dried at 60 °C, and then heated at 400 °C (2 °C min^{-1}) for 2 h under N_2.

3. Synthesis of hollow NiCo-LDH polyhedrons

For preparing hollow NiCo-LDH polyhedrons, 60 mg ZIF-67 and 180 mg $Ni(NO_3)\ 2 \cdot 6H_2O$ were dissolved in 15 mL ethanol separately, which were ultrasonic treated for 10 min. The mixture was hydrothermally reacted at 80°C for 6 h. Products were obtained by centrifugation and washing.

2. Characterization

The morphology of hollow NiCo-LDH polyhedrons was observed by scanning electron microscope (SEM, Germany ZEISS Sigma 300) and transmission electron microscopy (TEM, Japan JEOL JEM F200). Wide angle X-ray diffraction patterns of the materials were obtained on a Germany Bruker D2 Phaser diffractometer using Cu

KR radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K by using a surface area and porosity analyzer (Micromeritics ASAP 2020). The materials were degassed before the measurements. The BET method was used to extract the specific surface areas. FT-IR spectra of the sample was measured on an FTIR-8400s (Shimadzu) spectrometer in the transmission mode. Standard KBr technique was applied.

3. Fabrication and Test Methods of the QCM humidity Sensor

Prior to measurements, QCM sensors ultrasonic cleaning was successively carried out three times in acetone, ethanol and deionized water for 10 min, respectively. Then the sensors were dried at 40 °C for 30 min. After obtaining clean crystals chips, the corresponding frequency was recorded as the fundamental frequency. The as-prepared 20 mg/mL hollow NiCo-LDH polyhedrons dispersions were dropped on silver surface of the QCM chips. In order to evaluate the effect of the depositing amount of hollow NiCo-LDH polyhedrons on sensor performance, the sensors with 1, 2, and 3 μL of hollow NiCo-LDH polyhedrons deposited on the electrode of QCMs were fabricated. The corresponding sensors were labeled as LDH-1, LDH-2 and LDH-3. After drying at 40 °C for 40 min, hollow NiCo-LDH polyhedrons modified QCM humidity sensors were successfully made. Then, the frequencies of all sensors were recorded. The details were exhibited as in Table 1. The humidity-sensing experiments were performed at room temperature (298 K). In order to explore the capability of humidity detection, a man-made measure setup is sketched in Fig. S1. The sensor was exposed to relative humidity (RH) level of 11%, 33%, 52%, 75%, and 97% produced by the saturated

solution of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, and K_2SO_4, respectively. The superabsorbent P_2O_5 powder was used as a desiccant in a vessel to provide a relative dry atmosphere (ca. 0% RH) as the baseline environment [1]. The real-time resonant frequency of QCM transducer was recorded by a frequency counter. In order to know the deposition amount of hollow NiCo-LDH polyhedrons on the electrode of QCMs, the resonance frequencies values before and after films deposition were measured, which was shown in Table 1. The deposition mass of hollow NiCo-LDH polyhedrons on the electrode of QCMs were calculated according to the Sauerbrey equation.

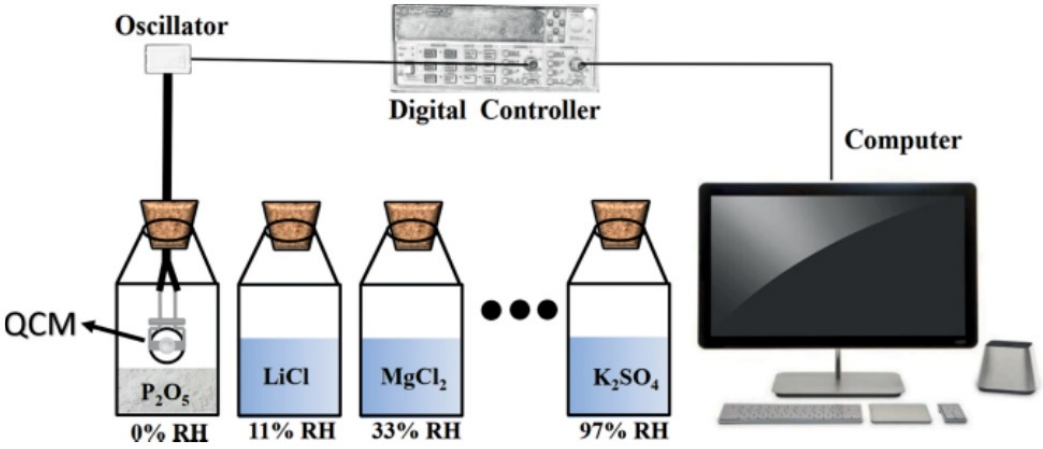

Fig. S1. The sketch diagram of humidity detection system.

References

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