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Highly Sensitive and Stable Humidity Nanosensors Based on LiCl Doped TiO$_2$ Electrospun Nanofibers

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Design and fabrication of chemical sensors has become one of the most active research fields due to their diverse practical and potential applications.[1] To improve the sensing characteristics, a general route is to make chemical sensors at the nanoscale, taking advantage of the large surface areas of nanoscale structures.[2] Chemical nanosensors based on one-dimensional (1D) carbon,[3] silicon,[4] and ceramic[5] nanostructures are of particular interest because of their high surface to volume ratio and special physical and chemical properties.[6] Among the chemical nanosensors, the humidity nanosensor is very important for their practical applications in environment monitoring, industrial process control, and our daily life.[1a,c,7] Many humidity nanosensors based on 1D nanostructure have been successfully obtained. However, the sensing characteristics (e.g., response, recovery, reproducibility, stability, and linearity) still need to be improved.

TiO$_2$ is an important ceramic material with a variety of applications in environmental cleaning and protection, photocatalysis, sensors, and solar cells.[8] These excellent properties make TiO$_2$ a good candidate in fabricating humidity nanosensors. On the other hand, LiCl has been often used in fabricating humidity sensors.[9] In this communication, we report a new type of humidity nanosensors based on LiCl-doped TiO$_2$ electrospun nanofibers using the electrospinning technique[10] and calcination. The as-prepared humidity sensor exhibits excellent sensing characteristics, including ultrafast response time (≤ 3 s) and recovery time (≤ 7 s) for measuring relative humidity (RH) in a wide range of 11−95% in air at room temperature (25 °C) with the impendence changing from 10^7 to 10^4 Ω. In addition, the nanosensor has good reproducibility, linearity, and stability.

Thus, a solution of tetrabutyltitanate, LiCl, and poly(vinyl pyrrolidone) (PVP) in acetic acid and ethanol was electrospun into nanofibers followed by calcination to remove PVP and to afford LiCl-doped TiO$_2$ nanofibers as the humidity sensors. The experimental details (Scheme S1) and schematic steps (Scheme S2) are given in Supporting Information. Figure 1 shows the SEM images of the electrospun TiO$_2$ nanofibers containing different amounts of LiCl, indicating a large scale of product uniformity with the fiber diameters ranging from 150 to 260 nm. The corresponding XRD patterns (inset in Figure 1d) demonstrate that the structure of TiO$_2$ changes from pure anatase to a mixture of anatase and rutile and to pure rutile as the amount of LiCl is increased. This result reveals that the addition of LiCl can change the structures of TiO$_2$ nanofibers upon calcination.

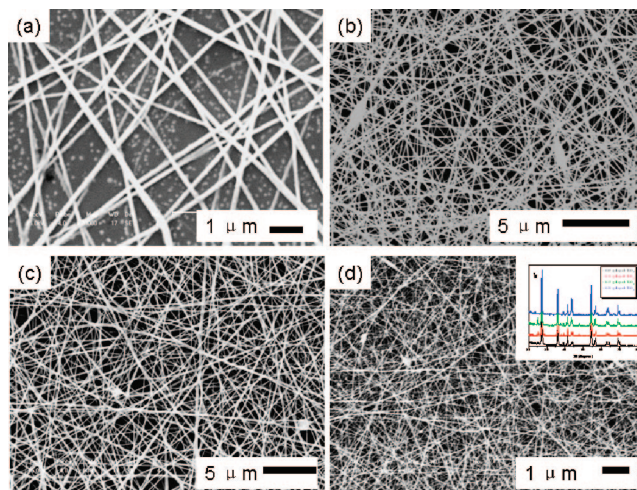The impedance of the nanosensor has been measured at different frequencies at 25 °C. The results, as shown in Figure

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Figure 1. SEM images of the TiO$_2$ nanofibers containing different contents of LiCl. The contents of (a), (b), (c), and (d) are 12.5, 22.2, 30.0, and 36.4%, respectively. The inset in (d) is XRD patterns of the products.
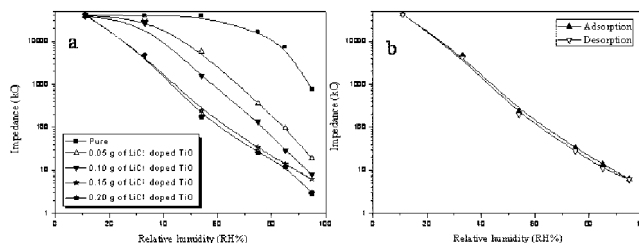

Figure 2. (a) The dependence of impedance on the RH for TiO$_2$ nanofibers containing different contents of LiCl. (b) The humidity hysteresis characteristics of the as-prepared humidity nanosensors containing 30.0% LiCl. The AC voltage and the frequency are 1 V and 100 Hz, respectively.

S1 in Supporting Information, indicate that the high humidity sensitivity and good linearity in the entire RH range were obtained in the low frequency region of 20−100 Hz. At higher frequencies, the dielectric phenomenon did not appear because the adsorbed water molecules could not be polarized. Therefore, we kept the operation AC voltage and frequency at 1 V and 100 Hz, respectively, in the following experiments.

The dependence of impedance on the RH for TiO$_2$ nanofibers containing different amounts of LiCl is shown in Figure 2a. Compared to the pure TiO$_2$ nanofibers, LiCl-doped TiO$_2$ nanofibers exhibited greatly improved sensitivity. In the same time, by keeping the RH range of 11–95%, the humidity nanosensor containing 30.0% LiCl shows the best linearity with the impedance varying more than 3 orders of magnitude
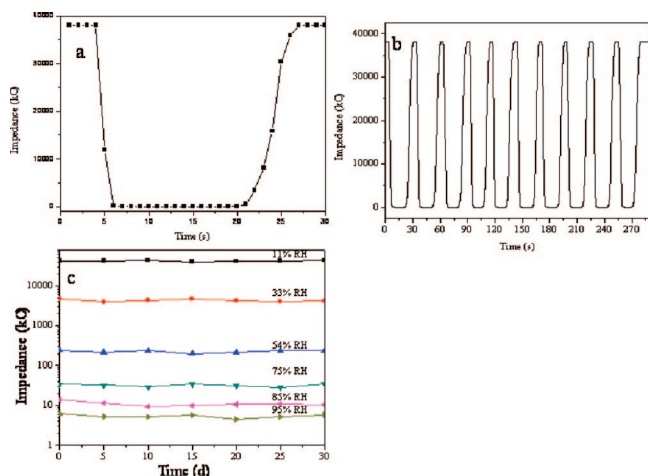
Figure 3. Response and recovery characteristic curves based on the product containing 30.0% LiCl-doped TiO$_2$ nanofibers for 1 cycle (a) and 10 cycles (b). (c) Stability of the sensor after exposing in air for 30 days.

($10^7 - 10^4$ Ω). Figure 2b shows the humidity hysteresis characteristic of the as-prepared humidity nanosensors (30.0% LiCl). The lines for adsorption and desorption processes are very close to the maximum humidity hysteresis being less than 2.5% RH under 65% RH for our nanosensors.

The response and recovery behavior is an important characteristic for evaluating the performance of humidity sensors. Figure 3a,b shows the response and recovery characteristic curves based on the product containing 30.0% LiCl-doped TiO$_2$ nanofibers for 1 cycle and 10 cycles with the RH changing from 11 to 95%. When the humidity was increased from 11 to 95%, the response time for our sensor was less than 3 s. When the RH was decreased from 95 to 11%, the recovery time was less than 7 s. Such an ultrafast response and recovery behavior could be explained by the structures of 1D TiO$_2$ nanofibers. The large surface of the nanofiber makes the absorption of water molecules on the surface of our sensors easy. The 1D structure of the fibers can facilitate fast mass transfer of the water molecules to and from the interaction region as well as improve the rate for charge carriers to transverse the barriers induced by molecular recognition along the fibers.[11] Additionally, comparing with 2D nanoscale films, the interfacial areas between the active sensing region of the nanofibers and the underlying substrate is greatly reduced. Those advantages lead to significant gain in the sensing signal and good stability.[12] From the curves for 10 cycles, the highest and lowest impedance values varied little, suggesting that the as-prepared humidity nanosensors have good reproducibility. (More descriptions on basic humidity sensing principles are given in Figure S2 in Supporting Information.) To test the stability, the sensor containing 30.0% LiCl was exposed in air for 30 days followed by measuring impedances at various RHs. As shown in Figure 3c, there were almost no changes in the impedances, which directly confirms the good stability of our sensors. From the criteria as discussed above, our humidity nanosensors based on LiCl-doped TiO$_2$ nanofibers *surpass* all the previous humidity sensors reported in the literature.[3–5]

In summary, we reported a highly sensitive and stable humidity nanosensor based on LiCl-doped TiO$_2$ nanofibers through electrospinning and calcination techniques. The sensor exhibited excellent characteristics (ultrafast response and recovery behavior, good reproducibility, linearity, and stability), which are of great importance in humidity detection and control. Moreover, our method provides a useful platform to design and construct highly effective humidity nanodetectors.

Supporting Information Available: Experimental details, schematic steps for product, impedance dependence of RH at various frequencies, improving properties of LiCl, and the humidity sensing principles based on our products. This material is available free of charge via the Internet at http://pubs.acs.org.

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