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One-dimensional isomeric and hierarchical TiO\textsubscript{2} nanostructures: novel air stable semiconducting building blocks†

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One-dimensional (1D) semiconducting nanostructures, as building blocks in fabricating electronic, biological/chemical sensors, optoelectronic, electrochemical, and electromechanical devices, attract immense interest. However, all those 1D semiconducting nanostructures are sensitive to both volatile organic compounds (VOFs) and relative humidity (RH), causing the instability of those devices operated in air (except in biological/chemical sensors). Herein, we demonstrated an effective route to not only stabilize 1D semiconducting nanostructures in air but also maintain their electrical properties by constructing 1D isomeric semiconducting nanorods on 1D semiconducting nanostructures to form 1D isomeric and hierarchical semiconducting nanostructures. 1D isomeric and hierarchical TiO\textsubscript{2} nanostructures (IHTNs) were chosen as a model, both excellent air stability and good electrical properties can be achieved. With such IHTNs as building blocks, a stable field-effect transistor has been realized.

One-dimensional (1D) semiconducting (inorganic,\textsuperscript{4} organic,\textsuperscript{5} inorganic/organic hybrids\textsuperscript{6}) nanostructures, as building blocks in fabricating diverse nanodevices, gain tremendous attention because they can provide good system to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction within the integrated devices.\textsuperscript{5–8} However, one of the challenges associated with the use of those 1D semiconducting nanostructures in practice is the electrical properties of all 1D semiconducting (inorganic, organic, inorganic/organic hybrids) nanostructures can be easily influenced by ambient gases such as volatile organic compounds (VOFs) and relative humidity (RH%), causing the serious air instability of the devices based on them (except in biological/chemical sensors).\textsuperscript{5–11} So rational design and construction of novel structures to both eliminate the influences from the ambient gases and maintain the electrical properties of 1D semiconducting nanostructures is very useful for the future science.\textsuperscript{12–14} Herein, we demonstrate an effective and general synthetic route to realize air stable 1D semiconducting nanostructures with 1D isomeric and hierarchical TiO\textsubscript{2} nanostructures (IHTNs: rutile TiO\textsubscript{2} nanorods standing on anatase TiO\textsubscript{2} nanofibers) as a model. The air stability and electrical properties of such 1D IHTNs have been evaluated by integrating them in chemiresistors and field-effect transistors (FETs), respectively.

1D TiO\textsubscript{2} nanostructures, as a typical sensing element, have been widely investigated in fabricating high-efficient chemical sensors for the detecting of VOFs and RH%.\textsuperscript{15–17} So construction of a 1D air stable semiconducting building block with 1D IHTNs as a model is typical of all 1D semiconducting nanostructures. Fig. 1(a) and (b) show the typical SEM images of the 1D anatase TiO\textsubscript{2} nanofibers and

![SEM images of (a) 1D anatase nanofibers and (b) 1D IHTNs (scale bar, 1 μm).](image)

(c) XRD patterns of as-prepared materials. (d) Weight fraction of rutile calculated in separate sample.

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1D IHTNs after the hydrothermal treatment, respectively. After the hydrothermal treatment, rutile TiO$_2$ nanorods with the average diameter of 40 nm and length of 400 nm can be detected on the anatase TiO$_2$ (av. 80 nm) nanofibers. Furthermore, it can be clearly seen that the continuity of the electrospun anatase nanofibers could be preserved after the hydrothermal treatment. The crystal structures of the rare anatase TiO$_2$ nanofibers and IHTNs were supported by XRD as shown in Fig. 1(c). Herein, the anatase (101) peak at 2\(\theta\) = 25.3° and the rutile (110) peak at 2\(\theta\) = 27.4° were chosen to calculate the weight fractions of rutile TiO$_2$ following the previous method (ESI†) as shown in Fig. 1(d).

To better evaluate the air stability and the electrical properties of such 1D IHTNs, a typical chemiresistor and FET based on both 1D TiO$_2$ nanofibers and 1D IHTNs have been established. All the procedures have been illustrated in Scheme S1 (ESI†). Fig. 2(a) and (b) show the air stabilities of the 1D TiO$_2$ nanofibers and 1D IHTNs against volatile organic compounds (VOFs: ethanol as model) and relative humidity (RH%), respectively. From Fig. 2(a), it can be clearly seen that the 1D electrospun TiO$_2$ nanofibers is ultra-sensitive to ethanol (1000 ppm) with the response \(R/R_0\) larger than 45 under the operate temperature of 320 °C. While 1D IHTNs exhibit inert against ethanol (1000 ppm) with the response less than 1.1 under the operate temperature of 320 °C, which is only one-fortieth of the 1D nanostructures, confirming the excellent stability of such 1D IHTNs. Similar phenomena can be also observed against relative humidity (RH%) as shown in Fig. 2(b). Increasing the RH%, the response (the variety of \(R/R_0\)) of the impedances) of the 1D electrospun TiO$_2$ nanofibers became larger and larger. As the RH% is 85%, the response of 1D electrospun TiO$_2$ nanofibers can reach 6.11, while the response of 1D IHTNs is less than 1.10. All those data mentioned above can directly prove the excellent air stability of 1D IHTNs, which can be applied in fabricating long-lived devices.

The basic electrical properties of both 1D electrospun TiO$_2$ nanofibers and 1D IHTNs were tested by integrating in a FET as shown in Scheme S1 (ESI†). Fig. 3(a) shows basic electrical properties without applying the gate voltages \(V_{gs}\) indicating the favorable electrical properties retained after the hydrothermal treatment. Fig. 3(b) and (c) present the source-drain current versus source-drain voltage \(I_{ds}-V_{ds}\) output curves of anatase nanofibers coated with rutile nanorods obtained under different \(V_{gs}\). The increase of the source-drain currents with increasing gate voltages in output curves shows a general gating effect of n-type conductivity. Typical scanning electron microscopy (SEM) images of these FET devices are shown in the insets. The device fabricated from 1D IHTNs has a saturated mobility of approximate 0.5 cm$^2$ V$^{-1}$ s$^{-1}$. Furthermore, much higher field-effect mobility of 1.7 cm$^2$ V$^{-1}$ s$^{-1}$ can be also achieved by simply introducing Au nanoparticles into the TiO$_2$ nanofibers during electrospinning as shown in Fig. 3(d).

It has been well proven that FET-based chemiresistors can exhibit improved sensing performances in contrast to normal chemiresistors owing to the easy shift of the threshold voltages within the FET can be observed by adsorption of target molecules. To further confirm the air stability of the 1D IHTNs-based FET, the FET device was stored under ambient condition for two months with the \(V_{gs}\) and \(V_{ds}\) of 20 V and 40 V, respectively. Only slight changes [the variation \(I_{ds}/I_{ds,0}\) is less than 10%] in \(I_{ds}\) can be found as shown in Fig. 4. From the criteria discussed above, it can be clearly proven that the air stability of our 1D IHTNs-based FET surpass all the previous FETs reported in the literature. Such excellent air stability could be explained by the unique structures of as-prepared 1D IHTNs. Firstly, the continuity of the 1D semiconducting nanofibers within the 1D IHTNs ensures the good electric properties along the fiber direction. Secondly, 1D isomeric semiconducting nanorods, standing on 1D semiconducting nanofibers, can act as the protecting shell, which can effectively adsorb the environmental gases prior to those gases react with the 1D semiconducting nanofibers owing to their much larger surface area and

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**Fig. 2** (a) The ultra-sensitivity to ethanol of 1D anatase nanofibers while 1D IHTNs are inert. (b) The ultra-sensitivity to RH% of 1D anatase nanofibers while 1D IHTNs are inert.

**Fig. 3** (a) The electrical properties of 1D anatase TiO$_2$ nanofibers and 1D IHTNs without apply the \(V_{gs}\). (b) Output curves of a 1D anatase nanofiber FET. (c) Output curves of a 1D IHTN FET. (d) Output curves of a 1D isomeric and hierarchical Au-TiO$_2$ nanostructures (rutile nanorods stand on Au–TiO$_2$ composite nanofibers) FET. The inset shows SEM images of separate sample bridging the source-drain electrodes. Scale bar is 200 \(\mu m\).

**Fig. 4** Time stability of a 1D IHTNs FET over a period of 2 months.
same ingredients. Thirdly, the changed electric properties of those isomeric semiconducting nanorods, caused by the environmental target molecules, do not affect the basic electric properties of the 1D semiconducting nanofibers because they are not formed an integrated circuit within the whole devices (chemiresistors and FETs). Thus, a novel 1D air stable semiconducting nanostructure with both good electrical properties and excellent air stability based on 1D isomeric and hierarchical TiO₂ nanostructures can be realized.

We have demonstrated the construction of isomeric rutile TiO₂ nanorods standing on 1D anatase TiO₂ nanofibers to form a novel 1D semiconducting building block with both good electrical properties and super air stability via an electrospinning and hydrothermal method. Although we only explored the air stabilities of 1D isomeric and hierarchical semiconducting nanostructures with a TiO₂ model material, our method could be extendible to other 1D isomeric and hierarchical semiconducting nanostructures. For this reason, this novel 1D isomeric and hierarchical semiconducting nanostructure offers an exciting pathway and general guidance towards the realization of novel 1D air stable building block for long-lived devices, including photodetectors, FETs, and so on.

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Notes and references

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