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Fabrication and photocatalysis of ZnO nanotubes on transparent conductive graphene-based flexible substrates

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Zinc oxide (ZnO) is one of the most widely used benchmark standard photocatalysts in the field of environmental applications [1–3]. As a wide band-gap semiconductor oxide (E_g=3.37 eV) with large excitation binding energy (60 meV), zinc oxide becomes one of the most important functional materials with unique properties of optical transparency, electric conductivity and piezo electricity [4–10]. However, the large band gap and the massive recombination of photogenerated charge carriers, especially in its nanosize, limit the overall photocatalytic efficiency. Intensive studies have demonstrated new applications such as piezoelectric nanogenerators, self-powered piezotronic strain sensors and Schottky contact-based nanosensors using 1D ZnO nanotubes (NTs) [11–14]. Substantial effort has been devoted to the development of novel synthetic methodologies for 1D ZnO NTs [15–19]. Nevertheless, it is still a challenge to realize ZnO NTs arrays with controllable sizes and dimensions. Currently, large-scale low-cost controllable growth of well-aligned ZnO NTs on properly fitting substrates is desirable for these novel applications [20,21]. As the widely used high-temperature vapor-phase processes are expensive and energy-consuming, various solution-phase approaches to ZnO NTs have recently attracted extensive interest because of their low growth temperatures and potential for scale up. Among these reported approaches, the preparation methods remain complex and hard to perform.

Graphene as an emerging carbon material, its two-dimensional conjugated chemical structure leads to attractive properties such as optical transparency [22], high electro-conductivity [23], mechanical flexibility [24] and high thermal/chemical stability [25]. Such a synergistic combination of novel properties renders graphene a promising component for next-generation flexible electronics and optoelectronics. In this letter, we report a simple hydrothermal process for large-scale fabrication of single-crystal ZnO NTs on transparent conductive flexible graphene-coated polyethylene terephthalate (GPET) substrates. The whole process of ZnO NTs fabrication can be completed in an aqueous solution at low temperature. The corresponding mechanism is discussed and the improved photocatalytic efficiency of the ZnO NTs/GPET is investigated.

Large-scale single-crystalline ZnO NTs on GPET substrates were synthesized by the hydrothermal method. Prior to the synthesis of ZnO, the GPET substrates were cut and cleaned with acetone, methanol, and de-ionized (DI) water under ultrasonication. The substrates were purchased from Sigma-Aldrich Corporation. For the hydrothermal growth of ZnO, the aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine ($C_6H_{12}N_4$) aqueous solution of equal concentration were mixed together and kept under mild magnetic stirring for 30 min. The pH value of reaction solution was controlled around 11 with ammonia. Subsequently, the autoclaves were sealed and heated to a constant temperature of 90°C for 5–15 h. The products were thoroughly washed with distilled water to remove the residual salts before dried naturally in air.

The morphologies and composition of the sample were characterized by means of scanning electron microscopy (SEM, by JEOL JXA-8200 electron probe micro-analyzer) and X-ray diffraction (XRD, by Rigaku D/MAX-RA with

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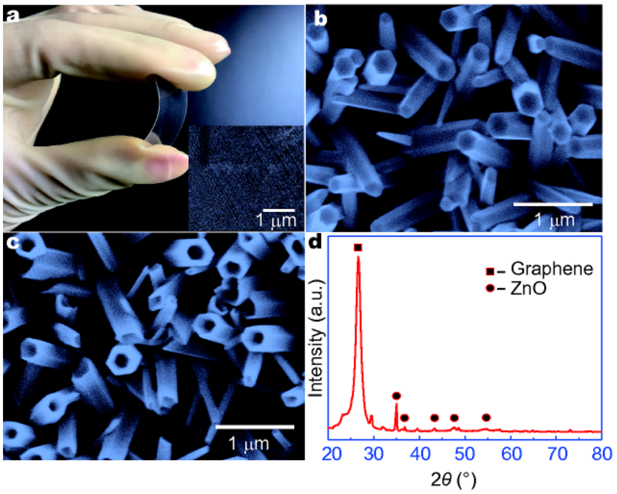

Figure 1 (a) Original image of the GPET substrate, inset is the SEM image of GPET. (b) SEM image of ZnO NRs grown on GPET for 5 h, (c) ZnO NTs grown on GPET substrate, (d) XRD spectra of the ZnO NTs.

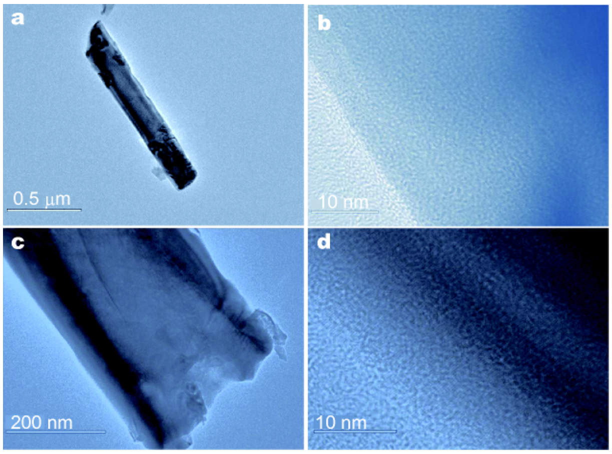

Figure 2 (a) TEM image of a single ZnO NR, (b) HRTEM image taken from the single ZnO NR, (c) TEM image of a ZnO NT, (d) HRTEM image taken from the ZnO NT.

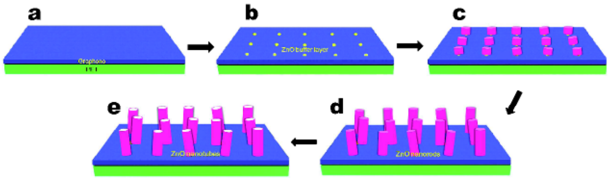

Figure 3 Schematic diagram for the growth mechanism of ZnO NTs.

Cu Kα radiation). The reactive yellow-15 (RY15) solution was irradiated by Hg lamp at 500 W for the photocatalytic characteristics.

The photograph of the GPET substrate is shown in Fig. 1a. The SEM image of ZnO fabricated on GPET flexible substrate for 5 h is shown in Fig. 1b. The whole substrate surface was successfully covered with uniform and dense arrays of hexagonal ZnO nanorods (NRs). The micrograph demonstrates that the ZnO NRs are fine-grained and contain, therefore, developed grain boundaries and free surfaces [26]. After being etched in ammonia water with the pH value of reaction solution controlled around 11, a shallow pit was formed in the center part of the tip of the NRs. With increasing etching time, the depth of the pit gradually increased. Furthermore, ZnO NTs (Fig. 1c) were observed when the etching time increased to 15 h. This illustrates that the ZnO NTs can be synthesized with a simple one-step approach, and the formation of the ZnO NTs is the result of the evolution of NRs under hydrothermal reaction condition. Analyzed from the XRD patterns (Fig. 1d), the peaks can be indexed to wurtzite hexagonal ZnO. In addition, the weak peaks at 26.6° are assigned to the graphene.

Fig. 2 shows transmission electron microscopy (TEM) images of a single ZnO NR (Fig. 2a, b) and ZnO NT (Fig. 2c, d) grown on flexible GPET substrates. The HRTEM in Fig. 2d shows that the interplanar spacing of ZnO NTs is about 0.26 nm, which corresponds to the ZnO (002) crystal plane, and the growth direction for ZnO NTs is the [0001] orientation [27].

The formation mechanism of the ZnO NTs is shown schematically in Fig. 3a–e. Initially, ZnO seed layer was spin-coated on a bare flexible GPET substrate (Fig. 3b). Subsequently, zinc nitrate hexahydrate and $C_6H_{12}N_4$ were used for the growth of ZnO NRs (Fig. 3c). The NRs were completely converted into the NTs by the following transition mechanisms. Generally, the growth habits of ZnO always directly dictate the final shape of the crystal, which in turn is greatly influenced by its growth conditions.

The formation of ZnO NRs or NTs is suggested to be closely associated with OH^- ligands [28,29]. On the gentle reaction condition, tiny ZnO particles are deposited on the GPET substrate in the early stage. Then the particles function as crystal nuclei for the subsequent growth of the ZnO NRs. During the etching process, ZnO NTs may be formed *via* the following procedure:

$$C_6H_{12}N_4 + 6H_2O \rightleftharpoons 6HCHO + 4NH_3 \cdot H_2O, \quad (1)$$

$$Zn^{2+} + NH_3 \cdot H_2O \rightleftharpoons Zn(NH_3)_4^{2+} \quad (2)$$

$$Zn(NH_3)_4^{2+} + OH^- \rightleftharpoons ZnO + NH_3 \cdot H_2O. \quad (3)$$

Presumably the precursor $Zn(NH_3)_4{}^{2+}$ reacts with OH^- to form ZnO, which is deposited on GPET substrate.

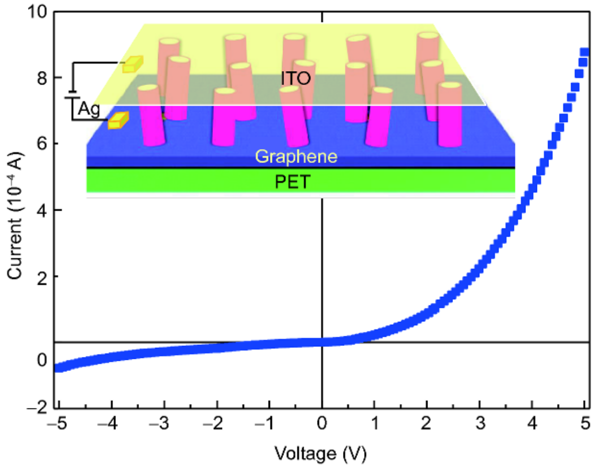

Figure 4 I–V characteristics of ZnO NTs on GPET. Inset is the schematic diagram of device structure.

Along with the extended reaction time, ZnO can dissolve according to Equation 3 as the equilibrium moves to the left due to the etching effect of ZnO in ammonia aqueous solution to result in ZnO NTs (Fig. 3e). It is known that the wurtzite ZnO crystal has two polar planes. The nonpolar planes parallel to the c axis are the most stable ones and have a lower surface energy. Furthermore, the etching rate of the polar (001) plane (the top plane of ZnO NRs) is faster than that of the nonpolar planes (the lateral planes of NRs). The etching prefers to take place in the metastable area of the defect-rich initial parts of the NRs, and subsequently NTs are formed.

The I–V characteristic of ZnO NTs on GPET is illustrated in Fig. 4. Inset is the schematic diagram of the diode. For generating electric charges by pushing and separating processes, the electrodes were set apart from each other by inserting the spacer, and the conductive wires were contacted, as shown in Fig. 4. When the bias is applied to 5 V, the current reaches 0.9 mA, while the reverse leakage current is almost 0.1 mA at −5 V.

Fig. 5a shows the decrease in concentration of RY15 with time when the reaction is photocatalyzed, seen from the time-dependent degradation ratio (C/C_0) where C is the concentration of RY15 solution at the irradiation time t, C_0 is the initial concentration. After 120 min illumination, the degradation of RY15 in a direct photolysis process without any photocatalyst is about 93% for reference. The C/C_0 for the ZnO NTs/GPET is about 57%, while the value for the ZnO NRs/GPET is 78%, indicating the degradation ratio of the latter (~22%) is significantly lower than that for ZnO NTs (~43%). The specific areas of ZnO NTs are likely higher than that of ZnO NRs, which might play a role in the increased photocatalytic performance.

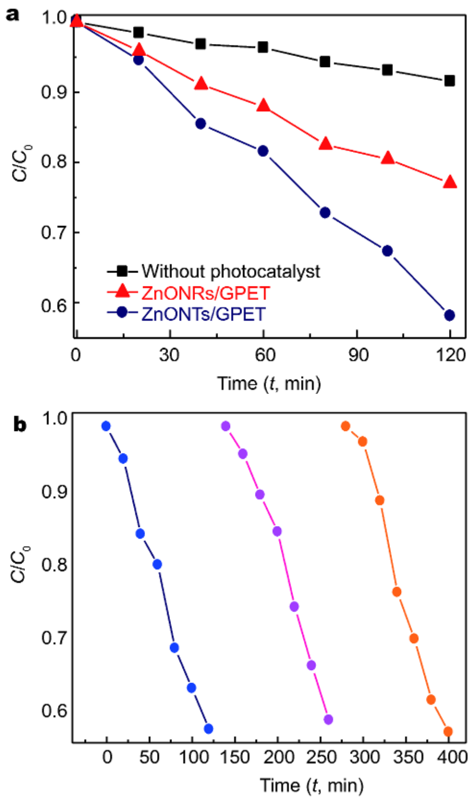

Figure 5 (a) Photocatalytic decomposition of RY15 solution with ZnO NRs, ZnO NTs and without photocatalyst for reference, (b) the principle of photocatalytic process with ZnO NTs.

The stability of the ZnO NTs photocatalyst was also tested by proposing the recycling test. Evidently, after three cycles of photocatalytic degradation, no significant loss of activity has been observed (Fig. 5b). The tubular shape of the product with large specific area is favorable for realizing high adsorption capacity to improve oxidation (reduction) reaction. Thereby, the ZnO NTs/GPET can promote the photocatalytic reaction.

In summary, oriented ZnO NTs have been fabricated on GPET flexible substrates *via* the hydrothermal method. The NTs are formed by a selective etching of NRs on the (001) planes with the fastest rate of etching along the (001) direction. The ZnO/GPET has been realized with good rectifying behaviour. The high photocatalytic performance of ZnO NTs/GPET shows promising applications for photocatalytic devices.

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Author contributions Yu Q designed and engineered the samples; Lin R, Jiang L and Wan J performed the characterization; Yu Q wrote the paper with support from Chen C. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

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透明导电石墨烯柔性衬底上ZnO纳米管的制备及其光催化性能研究

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摘要 本论文以水热法在透明导电石墨烯柔性衬底(GPET)上生长氧化锌(ZnO)纳米管阵列，发现其纳米管形成机理为选择性地沿(001)面生长, ZnO/GPET异质结具有较好的整流特性. 光催化测试表明, ZnO/GPET复合结构可提高光催化性能, 并具有良好的循环性. 此方法可在柔性衬底上稳定生长ZnO纳米管, 并可应用于相关光电器件及光催化领域中.