

Research Article

Structure, Optical Properties, and Photocatalytic Activity towards H₂ Generation and CO₂ Reduction of GaN Nanowires via Vapor-Liquid-Solid Process

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High quality single crystalline GaN nanowires with large aspect ratio (>100) are synthesized on n-type Si (111) substrate via Au-catalyzed vapor-liquid-solid process. Morphology, crystal structure, and optical property of the as-synthesized GaN nanowires are characterized by means of X-ray diffraction, scanning/transmission electron microscopy, UV-vis diffuse reflection spectroscopy, and room temperature photoluminescence. The results indicate that the as-prepared GaN nanowires with a large aspect ratio are well crystallized in the hexagonal wurtzite structure, and a slight blue shift appears in both the absorption edge and emission peak probably due to the quantization effect. Photocatalytic H₂ evolution over the as-prepared GaN nanowires is performed with the incorporation of Pt or Rh as the cocatalyst, exhibiting greatly enhanced capability compared to the GaN powder tested under the same conditions. Moreover, photocatalytic CO₂ reduction over the GaN nanowires is also successfully realized using Pt or Rh as the cocatalyst, depending on which the products show a strong selectivity inherently related to the reductive electrons transferred by cocatalyst.

1. Introduction

In view of the globally concerned energy shortage and environment pollution issues, photocatalysis using semiconductor and solar energy has been regarded as an ideal green chemistry technology [1–3]. While TiO₂-based photocatalysts were most popularly studied in last four decades [4], a huge number of new semiconducting materials have also been developed for photocatalytic applications. For example, a direct III–V group semiconductor GaN has been attracting extensive attention due to the following facts [5–8]: the band structure of GaN can encompass several possible redox

potentials; in addition, the high stability of GaN makes it work well under various harsh conditions.

One-dimensional (1D) nanomaterials have been paid much attention in photocatalytic field owing to their advantageous properties compared to the particulate materials [9]. On one hand, the surface-to-volume ratio can be enhanced due to the large surface area exposed on the nanowires, which in turn can act as the active sites for physical and chemical processes. On the other hand, 1D nanostructures provide the possibility of guiding the charge carriers transport in restricted pathways by limiting the transport in the transverse direction. By modifying the nanostructures with cocatalysts

as the reactive sites, the charge carriers, especially electrons, are prone to accumulate at the reduction sites, thus enhancing the separation of the photogenerated electrons and holes [10]. For above reasons, a lot of researches have focused on photocatalytic water splitting over GaN nanowires and great progresses have been achieved in recent years [11, 12]. For the synthesis of substrate-supported GaN nanostructures, the plasma-assisted molecular beam epitaxy (MBE) [13] and metal-organic chemical vapor deposition (MOCVD) [14] are widely used. However, the high cost and low production efficiency have limited their practical application.

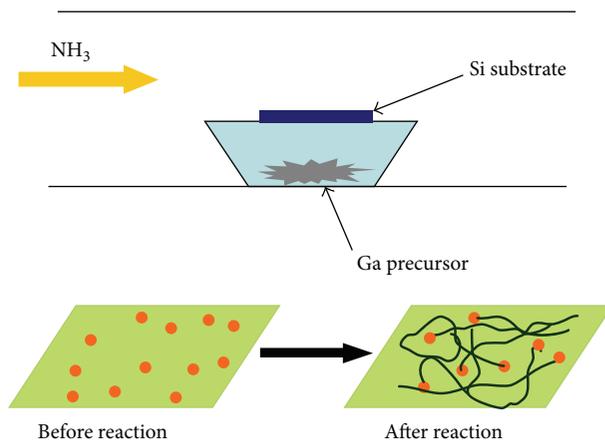
In this paper, we report a simple and cheap chemical vapor deposition (CVD) method to prepare GaN nanowires in a tube furnace at ambient pressure. The growth of GaN nanowires by Au-catalyzed CVD process is based on the vapor-liquid-solid (VLS) mechanism [15]. Photocatalytic activities of GaN nanowires for H_2 evolution and CO_2 reduction are performed and the effect of noble metal cocatalyst (e.g., Pt and Rh) on the photocatalytic activity is also clarified.

2. Materials and Methods

2.1. Fabrication of GaN Nanowires. GaN nanowires were grown via a two-step process. Pieces of $2 \times 2 \text{ cm}^2$ n-type Si (111) substrates (Sinopharm Chemical Reagent Co., Ltd) were ultrasonically cleaned in acetone and alcohol for 30 min each before rinsing with deionized water. Using an ion sputtering coater (SCB-12, KYKY Technology Development Ltd., China), a very thin gold film was coated on the substrates to catalyze the GaN nanowires growth. The Ga precursor, Ga_2O_3 , was used as received without any further treatment.

As illustrated in Scheme 1, GaN nanowires were grown by means of chemical vapor deposition in a horizontal quartz tube furnace ($\Phi 60 \times 1000 \text{ mm}$, GSL-1200X, Hefei Kejing Materials Technology CO., LTD, China). The Si substrate was loaded into a polycrystalline alumina crucible, upright on the Ga source, and then the crucible was put into the middle of the quartz tube. Both the Ga precursor and the substrate were heated to 1000°C for 1 h and flowed with 60 mL/min NH_3 and then the reactor was naturally cooled down to the room temperature under flow of the carrier gas.

2.2. Materials Characterization. The morphology and microstructure of the as-synthesized sample were observed on a field-emission scanning electron microscope (FE-SEM; S4800, JOEL, Japan, operated at 5 kV) equipped with an EDAX (Genesis XM2) attachment and a high-resolution transmission electron microscope (HRTEM; JEM-2100F, JEOL, Japan). Crystal structure was measured on an X-ray diffractometer (XRD; Bruker D8, operated at 40 kV, 40 mA) using $Cu \text{ K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). UV-vis diffuse reflectance spectra were measured at room temperature in the range of 220–800 nm on a UV-vis spectrophotometer (UV-2700; Shimadzu, Japan) and converted to absorbance by the Kubelka-Munk method. Photoluminescence (PL) spectra were acquired on a spectrofluorometer (Fluorolog-3 system, Horiba Jobin Yvon) with an excitation wavelength of 320 nm.



SCHEME 1: CVD reaction setup and growth mechanism for GaN nanowires by the vapor-liquid-solid process.

2.3. Photocatalytic Performance. Photocatalytic water splitting was carried out in a quartz glass cell (220 mL) connected to a glass-closed gas circulation and evacuation system. A 300 W UV-enhanced Xenon lamp was used as the light source. To improve the photocatalytic activity, 0.5 wt% Rh and 0.5 wt% Pt were preloaded on the surface of GaN nanowires by the in situ photodeposition method: under light irradiation, an equivalent molar amount of Na_3RhCl_6 or H_2PtCl_6 in solution (50 mL water + 10 mL methanol) was reduced to metallic state and deposited onto catalyst surface, forming the Rh or Pt-loaded catalyst.

Before reaction, the cell containing the reactant solution was well evacuated and then $\sim 2.5 \text{ kPa}$ of argon gas was introduced as carrier gas. With increase of irradiation time, the gases evolved photocatalytically were mixed and circulated by an online electromagnetic circulation pump. The gases evolved were in situ analyzed with an online TCD gas chromatograph (Shimadzu GC-8AIT, argon carrier).

Photocatalytic CO_2 reduction was carried out in a quartz glass reactor, in which the GaN nanostructured film on the Si substrate with an area of $2 \times 1 \text{ cm}^2$ was placed, and 3 mL of deionized water was injected. The 300 W UV-enhanced Xe lamp was used as the light source. The reactor was connected to a closed gas circulation and evacuation system. After evacuating the online system, high purity of CO_2 was purged into the reactor until a pressure of 80 kPa was achieved. The products from CO_2 reduction were detected by an online gas chromatograph (GC-14B, Shimadzu).

3. Results and Discussion

GaN nanowires grown on Si substrates are seemingly yellowish. By tuning the important growth parameters such as the starting materials, growth temperature, and the rate of NH_3 flow, a variety of GaN nanowires with different morphologies can be selectively prepared. Shown in Figure 1(a) is a typical FE-SEM image of GaN nanowires with lengths from several tens to hundreds micrometers and quite uniform diameter of *ca.* 80 nm in average. Apparently, the aspect ratio of

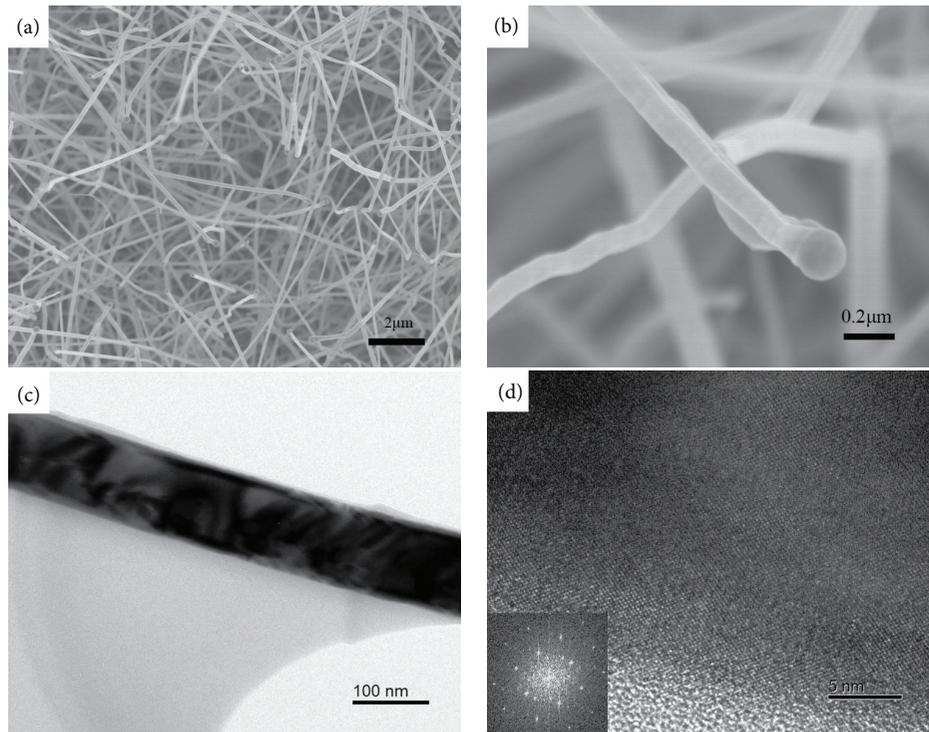


FIGURE 1: (a) Low magnification SEM image; (b) high magnification SEM image of the GaN nanowires synthesized via a vapor-liquid-solid process; (c) conventional low magnification TEM image; and (d) HRTEM image of a GaN nanowire (inset: FFT diffraction pattern of the corresponding HRTEM).

the as-grown GaN nanowires is extremely large (>100). Close examination reveals that over 95% of the products are nanowires, of which the side surface is smooth and straight. From the enlarged SEM image (Figure 1(b)) we can see clearly the droplet of Au nanoparticles on the apex of each nanowire, indicating the vapor-liquid-solid (VLS) mechanism for growth of GaN nanowires.

Figure 1(c) shows a typical TEM image, from which the smooth side surface can be clearly seen. Shown in Figure 1(d) are the HRTEM image and its corresponding fast Fourier transform (FFT) pattern (inset). No defects were observed from the HRTEM image, confirming the good crystallinity of the GaN nanowires, whereas the regular FFT patterns reveal the single crystalline nature of the nanowires.

Figure 2 shows the XRD pattern of GaN nanowires grown on the Si substrates. All peaks except those from Si substrate ($2\theta = 28.6^\circ$) and Au catalyst ($2\theta = 38.5^\circ$) can be precisely indexed as the wurtzite GaN structure (JCPDS card, number 74-0243). The refined crystal parameters $a = b = 3.189 \text{ \AA}$ and $c = 5.166 \text{ \AA}$ are in good agreement with previously reported standard values, implying the good crystallinity of as-grown GaN nanowires. In fact, the sharp diffraction peak shown in the XRD pattern (see Figure 2) also confirms that the GaN nanowires are well crystallized. It should be noted that no characteristic peaks corresponding to impurities such as GaON [16] and the starting materials were present in the XRD patterns, further demonstrating the high purity of the GaN nanowires.

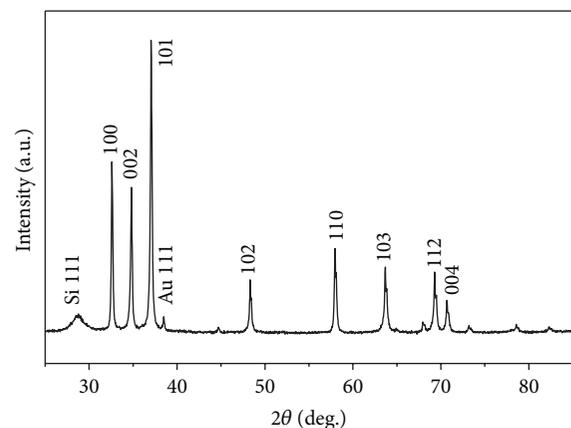


FIGURE 2: XRD pattern and indices of the GaN nanowires grown on Si substrate by Au-catalyzed vapor-liquid-solid reaction. All peaks except those from Si ($2\theta = 28.6^\circ$) and Au ($2\theta = 38.5^\circ$) can be indexed as the wurtzite GaN structure.

UV-vis diffuse reflectance spectrum (DRS) and room temperature photoluminescence (PL) spectrum of the as-prepared GaN nanowires were measured and the results are shown in Figure 3. From the UV-vis DRS spectrum, we can see a steep absorption edge located at *ca.* 355 nm, which is slightly shorter than that of the bulk GaN [17], probably due to the quantum confinement effect in nanomaterials. It should be pointed out that, in addition to the main absorption edge,

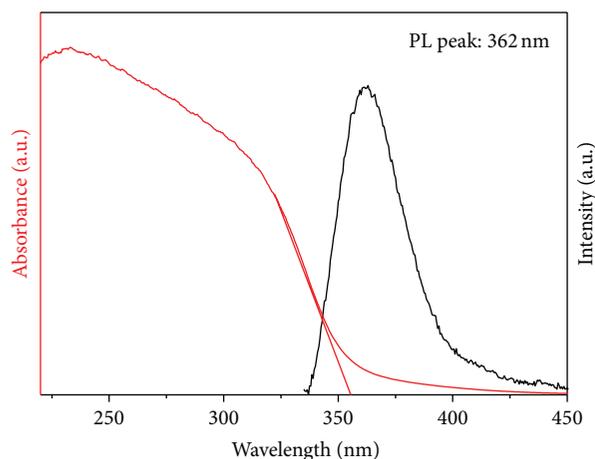


FIGURE 3: UV-visible diffuse reflectance spectrum (red) and room temperature photoluminescence spectrum (black) of the as-grown GaN nanowires on Si substrate.

the long tail can also be observed in visible region. Highly likely, the long absorption tail resulted from the Si substrate and/or the possible plasmonic effect of Au nanoparticles.

The room temperature photoluminescence (PL) is usually adopted to get the radiation-emission-related information such as the crystal defects and impurity levels in semiconductors. As shown in Figure 3, the emission peak centered at 362 nm in the PL spectrum is in good consistency with the standard peak [18] position of wurtzite GaN. Moreover, the sharp and smooth PL peak indicate the high crystalline quality of the as-prepared GaN nanowires.

Previous study has shown that GaN is a promising candidate to split water into H_2 since its conduction band edge of GaN is more negative than the H^+/H_2 reduction potential [19]. For the as-prepared GaN nanowires, photocatalytic H_2 evolution was performed in presence of methanol (50 mL H_2O , 10 mL CH_3OH) as the hole scavenger. In this reaction, 0.5 wt% Pt was in situ photodeposited as cocatalyst on the surface of GaN nanowires. As a comparison, GaN powders were also prepared by CVD method for photocatalytic H_2 evolution under the same conditions as mentioned above. Figure 4 shows the time courses of H_2 evolution on 0.5 wt% Pt/GaN-NWs and 0.5 wt% Pt/GaN-powder, respectively. With increase of irradiation time, H_2 evolution increased almost linearly. The rate of H_2 evolution over 5 h reaction with 0.5 wt% Pt/GaN-NWs was $6582 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, while that with 0.5 wt% Pt/GaN-powder was only about $25 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. Clearly, the 1-D GaN nanowires are much more advantageous over the GaN powders for photocatalytic H_2 evolution.

It is well known that the cocatalysts play a significant role in photocatalytic water splitting [20]. The interfacial charge transfer from the flat band of GaN to the Fermi level of Pt can drive the water splitting more efficiently [21]. In this work, we also investigated the effect of another metal cocatalyst Rh, which has been proven to promote H_2 evolution in the Rh/ Cr_2O_3 core-shell structure. As shown in Figure 5, when the same amount of Pt and Rh was loaded, respectively, on the surface of as-prepared GaN nanowires with the same

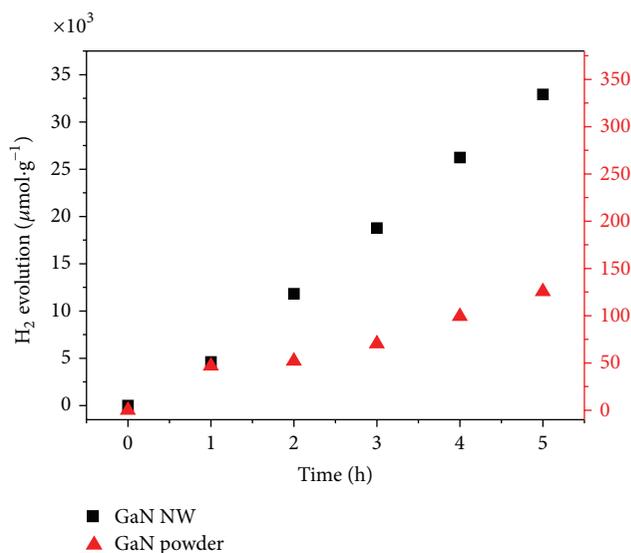


FIGURE 4: Photocatalytic H_2 generation over the 0.5 wt% Pt-loaded GaN nanowires and 0.5 wt% Pt-loaded GaN powder under a 300 W UV-enhanced Xenon lamp irradiation.

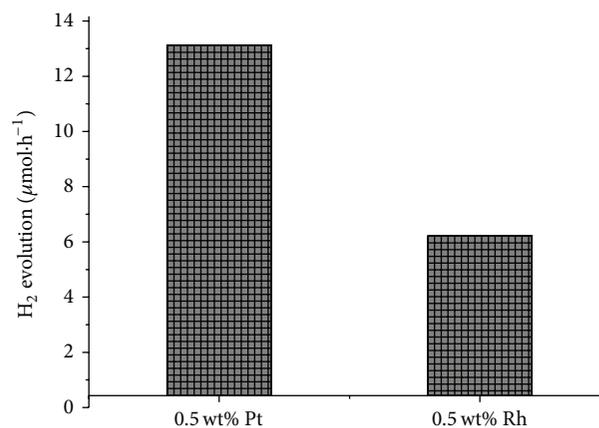


FIGURE 5: Photocatalytic H_2 generation from aqueous methanol solution over 0.5 wt% Pt/GaN-NWs and 0.5 wt% Rh/GaN-NWs under UV-enhanced irradiation. Reaction time: 1 h.

irradiation area ($\sim 2 \times 1 \text{ cm}^2$), an obvious difference was found in H_2 generation under the same conditions: Pt was a more effective cocatalyst than Rh for H_2 evolution. It should be pointed out that the structural stability of GaN nanowires has been confirmed since no difference was detected on the XRD patterns of the samples before and after the photocatalytic reaction.

The photocatalytic reduction of atmospheric CO_2 into hydrocarbon fuels is also one of the main targets for conversion of solar energy into chemical energy [22]. Herein, CO_2 reduction on Rh/GaN-NWs and on Pt/GaN-NWs was also conducted. Figure 6 shows the production of CH_4 and CO under UV-enhanced Xe lamp irradiation for 13.5 h. It was found that CH_4 and CO were the main products of CO_2 conversion, and the cocatalyst played a significant role in the selectivity of products. For Pt-loaded GaN nanowires,

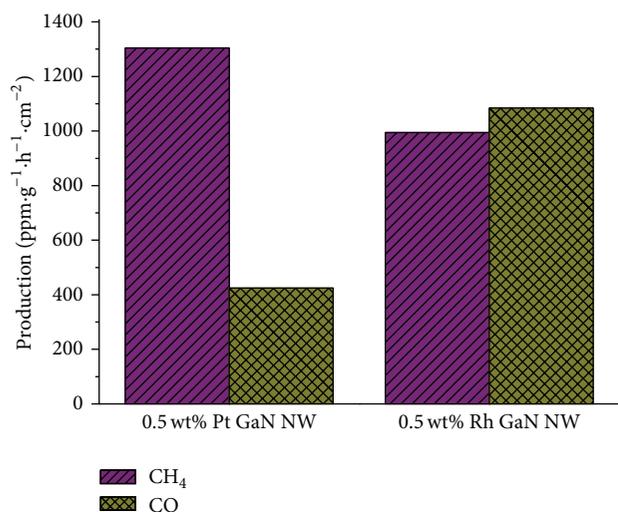


FIGURE 6: Photocatalytic CO₂ reduction tests over 0.5 wt% Pt/GaN NWs and 0.5 wt% Rh/GaN NWs under UV-enhanced irradiation.

CH₄ was the main product with an average conversion rate of 1304.8 ppm·h⁻¹·g⁻¹·cm⁻², which was in a strong contrast to an average rate of 424.8 ppm·h⁻¹·g⁻¹·cm⁻² for CO. For Rh-loaded GaN nanowires, both CO and CH₄ were the main products with a rate of 1084.6 ppm·h⁻¹·g⁻¹·cm⁻² and 994 ppm·h⁻¹·g⁻¹·cm⁻², respectively. The abovementioned results implied that the cocatalysts played a crucial role in the final product of photoreduction reaction. The photocatalytic CO₂ reduction involves a series of multielectrons reaction. Carbon monoxide (CO) is the most common product in photoreduction reactions since this step only needs two electrons and protons and single electron transfer to CO₂ occurs at -0.53V_{NHE}. However, to reform CH₄ with CO₂, six more electrons and same amounts of protons are required with the redox potential at -0.24V_{NHE} [23]. The noble metal, Pt, with larger work function and lower Fermi level than Rh, facilitates trapping the generated electrons more readily from the conduction band of GaN [20, 24]. Therefore, higher photocatalytic conversion of CO₂ to CH₄ is observed when loaded with Pt.

4. Conclusion

High quality single crystalline GaN nanowires are successfully synthesized through a vapor-liquid-solid process. Compared to the powder GaN samples also prepared by CVD method, GaN nanowires show significantly enhanced photocatalytic activities both for H₂ evolution from water splitting and for CO₂ reduction. Two noble metals Pt and Rh were photodeposited on the surface of GaN nanowires as cocatalysts in above reactions. It has been found that, for H₂ evolution, Pt/GaN nanowires show a higher photocatalytic activity than Rh/GaN nanowires, whereas, for CO₂ reduction, the cocatalyst plays an important role in controlling the multielectron reaction, that is, the final product selectivity: Pt/GaN was beneficial to reduce CO₂ to CH₄ while Rh/GaN produced nearly equal amount of CO and CH₄.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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