Photocatalysis Using GaN Nanowires

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ARTICLE

ABSTRACT The photocatalytic activity of GaN nanowires was investigated for the use of GaN nanowires as photocatalysts in harsh environments. GaN nanowires with diameters of 20–50 nm and lengths of 4–6 μm were prepared by Ni catalyst-assisted metal—organic chemical vapor deposition. Comparisons of GaN nanowires with GaN submicron dot arrays and thin films showed that GaN nanowires exhibit much better photocatalytic activity, resulting from a high surface-to-volume ratio. In addition, GaN nanowires exhibited good ability to photodegrade organic dye at various pHs, even under strong acidity and alkalinity. The photocatalytic activity of GaN nanowires was also compared with that of ZnO and TiO_2 nanowires.

KEYWORDS: GaN · nanowire · photocatalysis

High photocatalytic activity and reusability are two major factors that should be considered for photocatalyst applications.[1,2] Regarding the first factor, semiconductor nanomaterials have attracted much attention as photocatalysts because their high surface-to-volume (S/V) ratio results in enhanced photocatalytic effect.[3] Among numerous nanomaterials, fine oxide powders such as TiO_2 and ZnO have received tremendous attention because these powders can be easily prepared using simple methods.[3,4] However, these photocatalyst powders are generally suspended in water, which limits their practical use because of the difficulty in collecting and recycling photocatalyst powders from a suspension.[5] This problem becomes more serious when nanometer-size ultrafine powders are used but can be solved by making a photocatalytic thin film adhered to a rigid substrate. In particular, a film with highly dense one-dimensional (1-D) nanostructure is a good candidate for photocatalytic applications because photocatalytic activity generally increases with the S/V ratio.[6] Many industrial processes require photocatalysts that work under harsh conditions such as low or high pH. Accordingly, it is very important to synthesize a substrate-supported nanostructured photocatalyst that is chemically stable under harsh conditions. Here, we propose GaN single crystalline nanowires as a photocatalyst that functions under a wide range of pHs.

GaN is a well-known wide bandgap semiconductor that has a fundamental bandgap energy of 3.4 eV at room temperature. Although GaN has been widely studied for light-emitting device applications, photocatalytic applications of GaN have rarely been reported.[7] Generally, electrons generated in semiconductors during light irradiation contribute to reductions whose potential positioned between the conduction and valence bands, and the bandgap of GaN possesses all the possible redox potentials shown below.[7] Among the redox reactions, reactions near conduction bands occur most frequently. Because the potential of the reaction generating OH^- at −0.83 eV is placed beneath the GaN conduction band, the OH^- radicals can be formed easily on the GaN surface and contribute to photocatalytic activity in aqueous solutions.

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)\ (-0.83\ eV)$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g)\ (0.00\ eV)$$

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)\ (0.40\ eV)$$

$$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)\ (0.68\ eV)$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O\ (1.23\ eV)$$

$$H_2O_2(l) + 2H^+(aq) + 2e^- \rightarrow 2H_2O\ (1.77\ eV)$$

$$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + 2H_2O\ (2.07\ eV)$$

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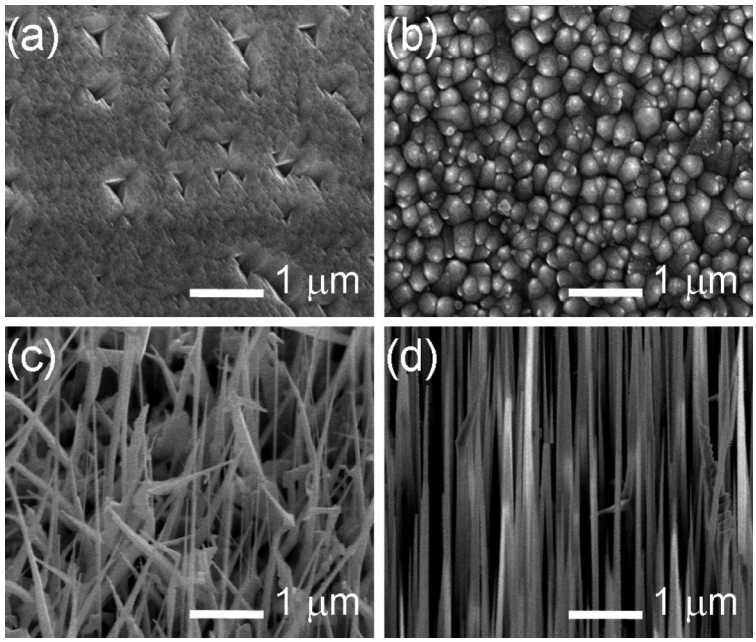

Figure 1. Plan-view scanning electron microscopy (SEM) images of (a) GaN thin films and (b) GaN submicron dot arrays and 45°-tilted view SEM images of GaN nanowires with (c) a low density of 3.3 × 10^8/cm^2 and (d) a high density of 6.3 × 10^8/cm^2.

Compared with the well-known photocatalysts TiO_2 and ZnO, GaN shows excellent chemical stability in both acidic and basic solutions, which makes it very useful in many industrial processes in which pollutant degradation under extreme pH conditions is required. We investigated the photocatalytic activity of GaN nanowires under various pHs and compared it to the photocatalytic activity of TiO_2 and ZnO nanowires.

RESULTS AND DISCUSSION

Photocatalytic Activity of GaN Thin Films and Nanowires. Figure 1 shows the scanning electron microscopy (SEM) images of GaN materials prepared for photocatalytic application. GaN thin films, submicron dot arrays, and nanowires were synthesized using metal−organic chemical vapor deposition (MOCVD) methods. In Figure 1a, the SEM image of the GaN thin film shows planar surface morphology with submicron pits. The root-mean-square (rms) roughness of the film surfaces measured on a 15 × 15 μm area, using atomic force microscopy (AFM), was 25 nm. Figure 1b shows the morphology of GaN submicron dot arrays with an average diameter of 400 ± 200 nm and a number density of 10^9 dots/cm^2. The rms roughness of GaN submicron dot arrays measured by AFM was 96 nm, which was much higher than that of GaN films. The diameters and lengths of GaN nanowires were 20–50 nm and 4–6 μm, respectively (Figure 1c and d). The number density of GaN nanowires varied from 10^7 to 10^9 wires/cm^2 depending on the growth conditions. Although GaN nanowires have a number density similar to that of GaN dots, the nanowire structure yields a much larger surface area than do GaN thin films and submicron dot arrays because of the high S/V ratio of GaN nanowires.

The photocatalytic activity of GaN thin films, submicron dot arrays, and nanowires was compared by measuring the amount of dye solution that was photodegraded by the GaN materials under ultraviolet (UV) light. Figure 2 shows the absorption spectra of the dye solutions that were photodegraded by GaN thin films, submicron dot arrays, and nanowires. After 10 h of UV irradiation, 55% of organic dye was degraded by GaN nanowires, whereas GaN films and submicron dot arrays only degraded 29% and 45% of organic dye, respectively (Table 1). The high photocatalytic activity of GaN nanowires presumably results from their high S/V ratio.

To confirm the effect of GaN nanowire surface area on photocatalytic activity, the relationship between nanowire number density and photocatalytic activity was also investigated. For this experiment, GaN nanowires were grown under the same growth conditions, except for the thickness of the Ni catalyst layer, which is a key parameter in determining nanowire density. By increasing the thickness of the Ni layer from 0.5 to 4 nm, the number density of GaN nanowires increased from 1.6 × 10^8/cm^2 to 6.6 × 10^8/cm^2. Figure 3 shows the absorption spectra of the dye solution photode-

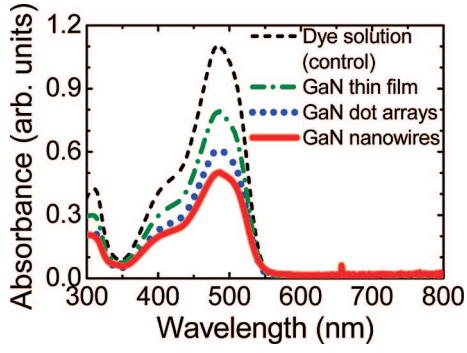

Figure 2. Absorption spectra of organic dye solution photodegraded by GaN thin films, submicron dot arrays, and nanowires.

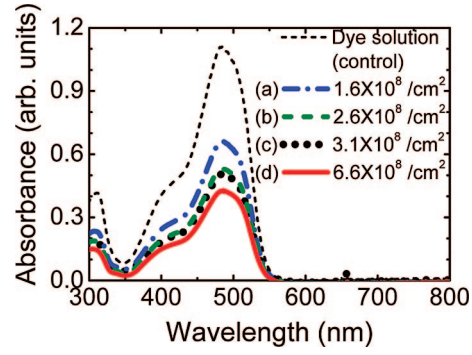

Figure 3. Absorption spectra of organic dye solution photodegraded by GaN nanowires with densities of (a) 1.6 × 10^8/cm^2, (b) 2.6 × 10^8/cm^2, (c) 3.1 × 10^8/cm^2, and (d) 6.6 × 10^8/cm^2.

graded by GaN nanowires with number densities of 1.6, 2.6, 3.1, and 6.6 $\times$ 10^8/cm^2. The amount of organic dye degraded by GaN nanowires increased from 41% to 62% with increasing nanowire density from 1.6 $\times$ 10^8/cm^2 to 6.6 $\times$ 10^8/cm^2 (Table 2), presumably resulting from the larger surface area of the denser nanowires.

In general, crystal defects near photocatalyst surfaces reduce photocatalytic activity because the defective states trap carriers generated by light absorption.[1] Because crystallinity affects photocatalytic activity, the crystallinity and structural defects of GaN nanowires were investigated using transmission electron microscopy (TEM). A low-magnification TEM image of a single nanowire showed neither kinks nor other branches that may cause defects (Figure 4a). High-resolution TEM (HRTEM) was used to explore any atomic-scale structural defects. Highly ordered crystal lattices were observed, and no dislocations or stacking faults were found (Figure 4b). In addition, the selected area electron diffraction (SAED) pattern of the GaN nanowire exhibited regular spot arrays (Figure 4c), indicating that the GaN nanowire was single crystalline. Single crystalline nanomaterials generate electron–hole pairs with longer lifetimes because the crystal defects act as recombination sites. Most photocatalytic reactions occur within a few nanoseconds (typically between a few hundred picoseconds and tens of nanoseconds). The lifetime of excitons was previously estimated to be a few nanoseconds using time-resolved photoluminescence spectroscopy.[11] This long lifetime of electron–hole pairs can lead to many photocatalytic reactions.

pH-Dependent Photocatalytic Activity of GaN Nanowires. Nanostructure photocatalysts fixed on a substrate and with good photocatalytic activity under strong acidic or basic conditions would be very useful for many industrial processes. Figure 5 shows the photocatalytic activity of GaN nanowires in acidic and basic solutions. The amounts of photodegraded dye in acidic solutions with pH of 1.8, 3.4, and 4.7 were 85, 92, and 88%, respectively, whereas the amount in pH 7 solution was 53%. This indicates that the photocatalytic activity of GaN nanowires is more effective under acidic than neutral conditions. However, in strong acidic or mild basic solutions such as pH 1 or 10, the photocatalytic activity was reduced to 39 and 40%, respectively, which was 75% less activity than observed at neutral pH. The strong dependence of photocatalytic activity on pH may result from differences in the space charge layer of the solutions. These differences may cause an energy band shift at the surface of the GaN and a subsequent change in redox potential related to the photocatalytic reaction.[8]

In addition to photocatalytic activity, the reusability of a photocatalyst must be considered for many photocatalyst applications because many oxide photocatalysts are dissolved or degraded in acidic or basic solutions. After photocatalytic reaction under such harsh conditions, we investigated the change in surface morphology of GaN nanowires using SEM. Figures 6a and b are SEM images of GaN nanowires before and after photodegradation at pH 2.3 for 10 h, respectively. GaN nanowires exhibited no significant changes in surface morphology, even after reaction under extreme pH of 0.9 or 12 for a few days. Furthermore, after photocatalytic reaction under

TABLE 1. Photocatalytic Activity of GaN Thin Films, Submicron Dot Arrays, and Nanowires

sample #	Sample description	rms surface roughness[a] [nm]	absorbance at 486 nm (arbitrary unit)	amount of dye photodegraded (%)
control	dye solution	—	1.1	0
133P	GaN thin film	25	0.79	29
132P	GaN submicron dot arrays	96	0.61	45
135P	GaN nanowires	—	0.50	55

[a]The root-mean-square (rms) surface roughness was determined by atomic force microscopy measured on a 15 $\times$ 15 μm area.

TABLE 2. Photocatalytic Activity of GaN Nanowires with Various Number Densities

sample #	nanowire density (cm^2)	absorbance at 486 nm (arbitrary unit)	amount of dye decomposed (%)
control (dye solution)	—	1.1	0
140P	1.6 $\times$ 10^8	0.66	41
141P	2.6 $\times$ 10^8	0.58	52
138P	3.1 $\times$ 10^8	0.51	55
139P	6.6 $\times$ 10^8	0.43	62

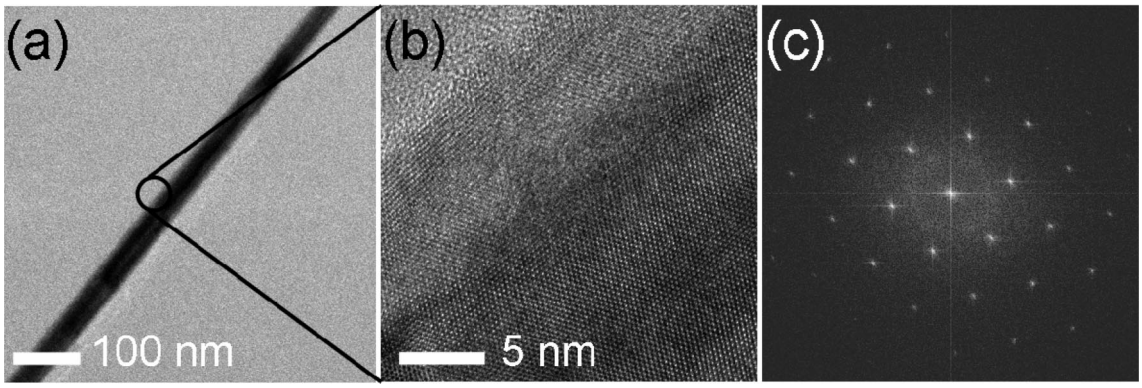

Figure 4. (a) Low- and (b) high-magnification transmission electron microscopy (TEM) images of a GaN nanowire. (c) Selective area electron diffraction pattern of a GaN nanowire.

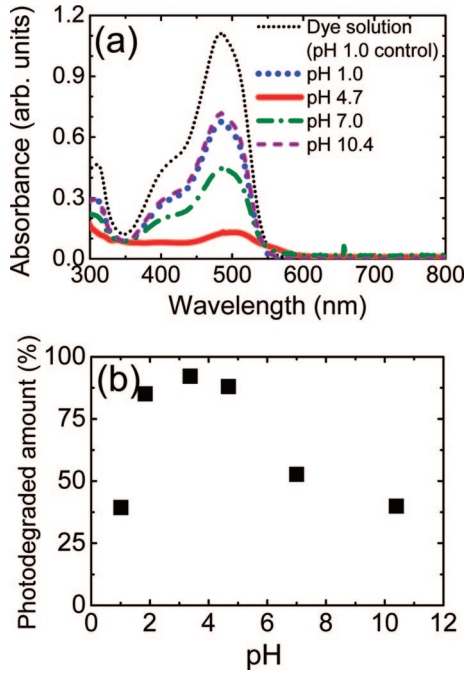

Figure 5. (a) Absorption spectra of organic dye solution photodegraded by GaN nanowires under various pHs. (b) Amount of organic dye photodegraded by GaN nanowires under various pHs.

UV light and strong acidic or basic conditions in the range of pH 0.9–12 for a few days, GaN nanowires did not exhibit any significant morphological changes in their number density, diameter, or length.

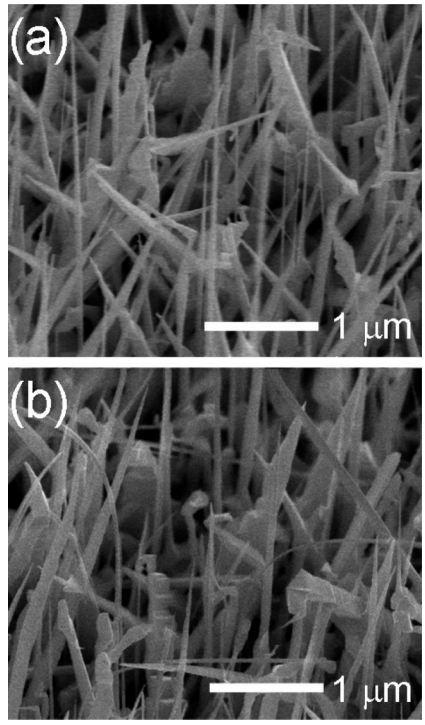

Figure 6. Field emission scanning electron microscopy (FE-SEM) images of GaN nanowires (a) before the photocatalytic reaction and (b) after the reaction at pH 2.3 for 10 h. The SEM images show no significant differences in nanowire morphology before and after the photocatalytic reaction.

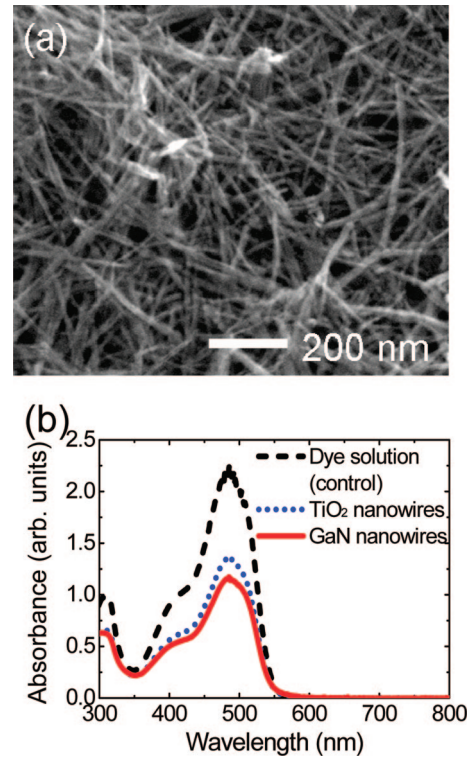

Figure 7. (a) FE-SEM image of TiO_2 nanowires grown using a hydrothermal method and (b) absorption spectra of organic dye solution photodegraded by GaN and TiO_2 nanowires.

Comparison of the Photocatalytic Activity of GaN Nanowires with that of TiO_2 and ZnO. The photocatalytic activity of GaN nanowires was compared to that of TiO_2 nanowires because TiO_2 is a well-known photocatalytic material. TiO_2 nanowires were grown on Ti substrates using a hydrothermal method.[9] Figure 7a shows a SEM image of TiO_2 nanowires with diameters of 10–20 nm and a nanowire number density of $10^{10}/cm^2$. Because the number density of TiO_2 nanowires was an order of magnitude higher than that of GaN nanowires, the surface area for TiO_2 nanowires was also an order of magnitude higher.

We measured the absorption spectra of dye solutions photodegraded by GaN and TiO_2 nanowires (Figure 7b). GaN nanowires exhibited 49% photodegradation of organic dye, whereas TiO_2 nanowires photodegraded only 40% of the dye. Even though the surface area of the GaN nanowires was an order of magnitude lower than that of the TiO_2 nanowires, the photocatalytic activity of GaN nanowires was slightly higher. This result strongly suggests that the photocatalytic activity of GaN nanowires is much higher than that of TiO_2 nanowires.

The photocatalytic activity of GaN nanowires was also compared to that of ZnO nanowires because ZnO and GaN have the same crystal structure and a similar electronic band structure, and ZnO is another well-known photocatalyst. ZnO nanowires (Figure 8a) were prepared by catalyst-free MOCVD,[6,10] and typical diam-

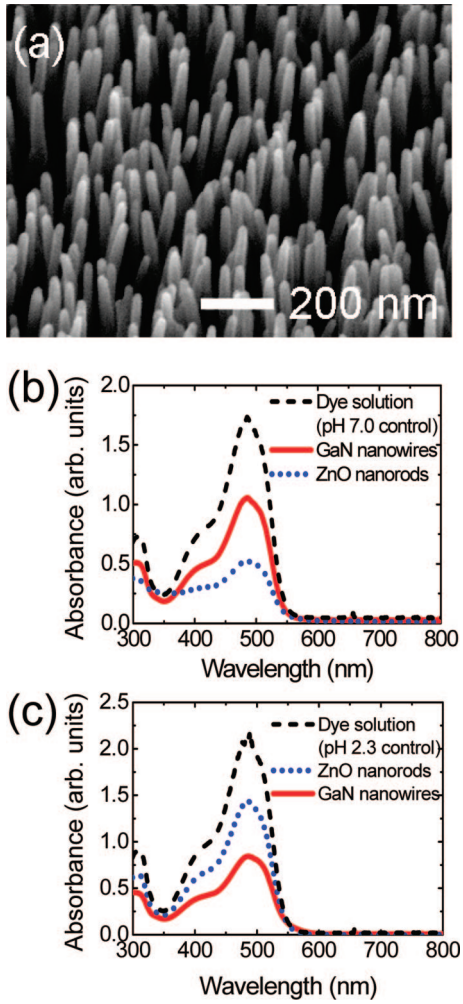

Figure 8. (a) FE-SEM image of ZnO nanowires grown by MOCVD. Absorption spectra of organic dye solution photodegraded by GaN and ZnO nanowires at (b) pH 7.0 and (c) pH 2.3 for 10 h.

eters and average length were 20–30 nm and 1 μm, respectively. We compared the absorption spectra of dye solutions photodegraded by GaN and ZnO nanowires. At pH 7.0, ZnO nanowires performed better than GaN nanowires, photodegrading an additional 31% of the organic dye (Figure 8b). However, in the strong pH region, *e.g.*, pH 2.3, the photocatalytic activity of ZnO nanowires decreased rapidly from 70% to 33%, whereas that of GaN nanowires exhibited a 60% increase (Figure 8c). The amount of organic dye photodegraded by GaN nanowires under acidic conditions was 27% greater than that photodegraded by ZnO nanowires. Furthermore, after the photodegradation experiment under the acidic condition, there was no significant change in the surface morphology of GaN nanowires, whereas the ZnO nanowires were completely dissolved and none of the ZnO nanowire could be observed.

CONCLUSION

The photocatalytic activity of GaN nanowires was investigated for photocatalyst applications under harsh conditions. GaN nanowires exhibited higher photocatalytic activity than both GaN thin films and submicron dot arrays because of their larger surface area and the high single crystallinity of the nanowires. Furthermore, the photocatalytic activity of GaN nanowires was enhanced in the acid pH region between pH 2 and 5, with much better photocatalytic properties than TiO_2 and ZnO nanowires. In addition, because of the strong chemical stability of GaN, no significant surface degradation was observed, even after GaN nanowires were reused several times in acidic solutions for the photodegradation of organic dye pollutants. Therefore, GaN nanowires would be a good photocatalytic material that can be used in both acidic and basic solutions.

METHODS

GaN nanowires were prepared using Ni catalyst-assisted MOCVD techniques. For the preparation of GaN nanowires, a very thin Ni layer with a thickness of 0.5−2 nm was deposited on *r*-plane sapphire substrates by *e*-beam evaporation. At 800 °C, the Ni layer was formed into many nanodroplets, which act as both nuclei and catalysts for nanowire growth. GaN submicron dot arrays were prepared using Ni layers thicker than 2 nm. For MOCVD of GaN thin films, no metal catalyst was used. Trimethylgallium (TMGa) and ammonia (NH_3) were used as precursors for the syntheses of all GaN materials. The details of GaN nanowire and thin film growth are described elsewhere.[11,12]

ZnO and TiO_2 nanowires were prepared to compare their photocatalytic activity with that of GaN nanowires. TiO_2 nanowires were grown on Ti metal substrates using a hydrothermal method.[9] Prior to TiO_2 nanowire growth, Ti metal substrates with a purity of 99.7% were treated in 2.5 M NaOH solution at 150 °C for 15 h, rinsed with deionized (DI) water, and left in DI water for 3 days. After cleaning with DI water, the substrate was dipped in 1 M HNO_3 and annealed at 450 °C for 5 h. ZnO nanowires were grown by catalyst-free MOCVD, and the details of ZnO nanowire growth are described elsewhere.[10]

The morphological investigation and structural analysis of GaN nanowires and thin films were carried out using field emission scanning electron microscopy (FE-SEM; Philips XL30SFEG) and TEM (JEM-20110 F). The nanowire specimens for TEM were prepared by scratching the as-grown sample surface, dispersing them in absolute ethanol, and depositing them on a carbon-coated copper grid.

The photocatalytic activity of the samples was determined by measuring the decoloration of Orange II [4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid] solution, a typical organic pollutant in photocatalysis experiments. The concentration of Orange II dye was controlled from 0.01 mM to 0.1 mM. To measure the photocatalytic activity of GaN nanowires under various pHs, the solution pH was controlled using KOH, NaOH, HNO_3, HCl, and H_2SO_4. For each set of photocatalysis experiments, a series of samples and a control (without any specimen) were simultaneously irradiated under ultraviolet light using an OSRAM lamp (Ultra Vitalux), which has a spectrum similar to that of solar light. The details of the photocatalytic activity measurements are described elsewhere.[6]

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