Design of Hydrothermally Derived Fe₂O₃ Rods with Enhanced Dual Functionality Via Sputtering Decoration of a Thin ZnO Coverage Layer

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ABSTRACT: The Fe₂O₃−ZnO composite rods were successfully synthesized by combining hydrothermal growth of Fe₂O₃ rods and sputtering deposition of a thin ZnO coverage layer. Two types of the Fe₂O₃ rods with round and rectangular cross-sectional morphologies grown via control of the urea content in hydrothermal growth processes were used as rod templates to fabricate the Fe₂O₃−ZnO composite rods. The Fe₂O₃−ZnO composite rods exhibited an improved photoelectric conversion efficiency in the Fe₂O₃ rods via a construction of a heterogeneous structure. The photocatalytic degradation performance of rhodamine B dyes with Fe₂O₃ rods was substantially increased via sputtering decoration of a thin ZnO coverage layer on the Fe₂O₃ rods. Moreover, the Fe₂O₃−ZnO composite rods exhibited superior acetone vapor-sensing responses than the pristine Fe₂O₃ rods herein. The extended optical absorption ability together with the enhanced photoinduced charge separation efficiency via construction of the Fe₂O₃−ZnO heterogeneous system explained the improved photoactivity of the composite rods. Furthermore, the formation of a heterojunction between the Fe₂O₃ and ZnO increased the interfacial potential barrier height and enhanced the sensor resistance variation size upon exposure to the acetone vapor. This accounted for the improved gas-sensing performance of the Fe₂O₃−ZnO composite rods. The experimental results herein provide a promising approach to design Fe₂O₃-based composite rods with desirable photocatalytic and gas-sensing functionalities.

INTRODUCTION

Aligned one-dimensional binary oxide semiconductors on various substrates have attracted a lot of attention due to their potential applications in photocatalysts, photoelectrochemical (PEC) electrodes, and gas sensors.1−4 Hematite (α-Fe₂O₃) is gaining importance in photoactivated device and gas sensor applications because it is an n-type semiconductor, low cost, highly chemically and thermally stable, and nontoxic.5−8 Recently, one-dimensional hematite-based nanomaterials have been fabricated by employing various synthesis routes such as a hydrothermal method with a calcination process,9 solvothermal route with the assistance of ionic liquid,10 and thermal oxidation of iron foil.11 Among these synthesis routes, the hydrothermal method is an effective and low-cost method to produce a large and uniform aligned hematite nanorods with a desirable crystalline quality on various substrates.

The efficiency of the α-Fe₂O₃ for the photoactivated devices is still far from the theoretical values because of its short excited state life, short hole diffusion length, poor surface oxygen evolution reaction kinetics, and poor electrical conductivity.12 Moreover, the limited potential barrier numbers in the crystalline one-dimensional α-Fe₂O₃ rods also hinder their gas-sensing response upon exposure to various target gases.13 To overcome the abovementioned drawbacks, surface treatment and impurity doping of the hematite have been explored to enhance its electronic and optical properties.5,7,14 However, the surface treatment of the hematite crystals limits degrees of freedom in tuning their functionality, and effective doping with a desirable concentration in the hematite crystals is hard to be controlled during the hydrothermal growth because of their low reaction temperature. Due to peculiar properties that originated from their individual phases, composite or heterogeneous materials are a promising approach to design the hematite-based rods with enhanced and desirable functionalities.15 Sputtering has advantages of easy process control, large area thin-film deposition, and controllable microstructures for growing thin oxide layers.16 A two-step synthesis method integrated with a sputtering route to fabricate heterogeneous oxide rods has been widely realized in several composite oxide
rod systems.\textsuperscript{17,18} According to the thermodynamic requirement of a photocatalytic reaction, the redox potential of the valence band hole must be sufficiently positive to generate hydroxyl radicals and that of the conduction band electron must be sufficiently negative to generate superoxide radicals. Therefore, ZnO is reported to be used as a major component of photocatalysts;\textsuperscript{19} moreover, its stable chemical and n-type semiconducting properties make it suitable for use as gas-sensing materials.\textsuperscript{20} Based on the aforementioned discussions, the construction of $\alpha$-Fe$_2$O$_3$ rods coupled with the ZnO crystal to form a heterogeneous system is beneficial to isolate the oxidation reaction due to the holes, and the reduction reaction due to the electrons at two different phases further prevents the photoinduced charge recombination. Furthermore, the incorporation of the ZnO crystals into the $\alpha$-Fe$_2$O$_3$ rods increases the potential barrier heights at the $\alpha$-Fe$_2$O$_3$/ZnO heterojunctions, which might be an important factor in dominating the resistance variation of the heterogeneous rods upon exposure to target gases and enhancing their gas-sensing performance.

In this study, $\alpha$-Fe$_2$O$_3$ rod templates with two different morphologies were synthesized by hydrothermal methods. Furthermore, the Fe$_2$O$_3$–ZnO heterogeneous rods were synthesized via a sputtering-assisted ZnO growth method. The correlations among the phase constitution, microstructure, photoactivity, and gas-sensing activity of the heterogeneous rods were systematically investigated. The mechanisms for the description of enhanced photoactivity and gas-sensing activity of $\alpha$-Fe$_2$O$_3$–ZnO composite rods were also proposed herein to explore their possible scientific device applications.

\section*{RESULTS AND DISCUSSION}

Figure 1a,b shows the typical SEM images of the F-1 and F-2 rods, respectively. In Figure 1a, the exhibited side wall morphology of the F-1 rods grown with a lower urea addition was quite irregular and undulated, similar to a rod composed of interconnected spherical particles along its axis. The individual F-1 rods had an average diameter of approximately 45 nm; however, most of the F-1 rods were inclined to connect with the adjacent counterparts to form F-1 rod bunches with a substantially increased size of 120–200 nm. The individual F-2 rod formed with a higher urea addition exhibited a regular rectangular cross section and an average size of approximately 120 nm (Figure 1b). Comparatively, the F-2 rods exhibited a more free-standing rod-like feature without a seriously bunched feature among the rods. The chemical reactions leading to the formation of Fe$_2$O$_3$ rods herein followed the equations\textsuperscript{21}

\begin{align*}
\text{NH}_2\text{CONH}_2 + 3\text{H}_2\text{O} & \rightarrow 2\text{NH}_3\text{OH} + \text{CO}_2 \\
\text{FeCl}_3 + 3\text{NH}_3\text{OH} & \rightarrow \text{FeOOH} + 3\text{NH}_4\text{Cl} + \text{H}_2\text{O} \\
2\text{FeOOH} & \text{(heating)} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}
\end{align*}

The SEM analysis revealed that the urea concentration (pH regulating agent) in the precursor solution affected the appearance of the $\alpha$-Fe$_2$O$_3$ rods. As the molar ratio of urea/FeCl$_3$ increased, the morphology of one-dimensional FeOOH precipitates on the FTO substrates changed due to the increase in the release of hydroxide ions in the intermediates, which is clearly evident from the SEM images.\textsuperscript{21} In the presence of urea, the hydrothermal crystal growth reaction can be regarded as composite coordination and recrystallization processes.\textsuperscript{22} The urea can coordinate with Fe ions to form complex compounds along with the release of OH to facilitate the recrystallization of products.\textsuperscript{23} The lower urea concentration in the reaction solution tends to slow down the formation reaction process of FeOOH, which consequently results in irregular side wall morphology when there is preferential crystal growth of one-dimensional intermediates according to eqs 1 and 2. The F-1 rods with a rugged side wall rod morphology were therefore formed after postannealing the intermediates because of the lower urea concentration in the reaction solution. Notably, tiny pores existed on the top region of the F-2 rods (Figure 1b); this is associated with the removal of H$_2$O from the precursor FeOOH rods during calcination (eq 3). These pores might increase the accessible surface area and provide more active sites for surface reactions with environmental molecule agents. Figure 1c,d shows SEM images of the F-1-Z and F-2-Z composite rods, respectively. Following the ZnO thin layer modification, the Fe$_2$O$_3$ crystals still maintained their one-dimensional geometry, and most regions of the rods are covered with 10–20 nm-sized ZnO nanoparticles. The decoration of the ZnO coverage layer through sputtering deposition engendered a rough surface and a coarsened rod diameter of the pristine Fe$_2$O$_3$ rods. Moreover, the corresponding cross-sectional view of the SEM micrographs in Figure 1e,f reveals that the average lengths of the F-1-Z and F-2-Z composite rods are approximately 1.5 $\mu$m; all composite rods are vertically aligned on the FTO substrates.

Figure 2 shows the XRD patterns of F-1, F-2, F-1-Z, and F-2-Z samples. Several distinct and sharp Bragg reflections of (012), (104), (110), (113), (024), and (116) rhombohedral $\alpha$-Fe$_2$O$_3$ (JCPDS no. 00-033-0664) are visibly presented in Figure 2a,b; the samples are in well-crystalline features. No impurity peaks for FeOOH, Fe$_3$O$_4$, and $\gamma$-Fe$_2$O$_3$ are presented in the XRD pattern, whose phases have been observed in several hydrothermally derived Fe$_2$O$_3$ crystals.\textsuperscript{24,25} Furthermore, the intensities of (104) and (110) main diffraction peaks in the F-2 sample are more intense than those of the F-1 sample, indicating a higher crystalline quality of the Fe-2 rods. Notably, extremely high intensity of the (110) peak was observed in the hydrothermally derived Fe$_2$O$_3$ rods herein, revealing the crystals were mostly inclined to a $<$110$>$ orientation. A similar crystal growth orientation feature has been observed in $\alpha$-Fe$_2$O$_3$ crystals synthesized via the chemical vapor deposition and hydrothermal method.\textsuperscript{21,26} Following the ZnO modification, Figure 1c,d shows additional two distinct Bragg reflections centered at
approximately 31.8 and 34.3°, which can be indexed to the (100) and (002) planes of hexagonal ZnO, respectively (JCPDS no.00-036-1451). The XRD results demonstrated that the Fe₂O₃−ZnO composite rods with a good crystallinity were successfully formed through the sputtering deposition of the ZnO coverage layer onto the surfaces of the hydrothermally derived Fe₂O₃ rods.

Figure 3a shows a low-magnification TEM image of the F-1-Z composite rod. The surface of the composite rod exhibited a rugged morphology, which is fully sheathed by a ZnO crystallite layer along the entire rod. The rod has a diameter ranging from 95 to 110 nm, which is consistent with the SEM observation. The high-resolution (HR) TEM images taken from various regions of the composite rod are displayed in Figure 3b−d. In these HR images, the distinct lattice fringes with distinguishable spacings of approximately 0.25 and 0.37 nm are ascribed to the interplanar distances of the (110) and (012) planes of the rhombohedral α-Fe₂O₃ phase, respectively. Furthermore, the measured ordered lattice fringe spacing of 0.26 nm was ascribed to the interplanar distance of the (002) plane for the hexagonal ZnO. The HRTEM images demonstrated the formation of the Fe₂O₃−ZnO composite rod with a good crystalline quality. Notably, in Figure 3d the distinguishable and sharp contacted lattice fringes between the α-Fe₂O₃ rod and ZnO coverage layer discovered that the Fe₂O₃−ZnO heterojunctions were sharply formed in the composite rod. Figure 3e depicts the selected area electron diffraction (SAED) pattern recorded from several composite rods. (f) Zn, Fe, and O elemental mapping images of the composite rod.
Diffraction from the (012), (104), and (110) planes corresponding to the α-Fe₂O₃ rods and the (100), (002), and (101) planes corresponding to the wurtzite ZnO coverage layer. The SAED analysis agrees with the XRD pattern, revealing that crystalline Fe₂O₃−ZnO composite rods were formed herein. The elemental mapping images were further used to analyze the distribution of Fe, Zn, and O in a Fe₂O₃−ZnO composite rod (Figure 3f). The EDS mapping images clearly identified the spatial distributions of Fe, Zn, and O in the composite rod structure. The O element existed in the entire region of the composite rod. The Fe element was confined in the inner region of the composite rod. In particular, the Zn element shows a more intense signal in the peripheral region of the composite rod, demonstrating the main element being distributed in the outer shell of the composite rod. It clearly shows a thin ZnO layer coated on the Fe₂O₃ rod with a thickness ranging from 24 to 41 nm.

Figure 4a presents a low-magnification TEM image of the F-2-Z composite rod. The diameter of the composite rod is obviously larger than that of the F-1-Z rod. The diameter of the F-2-Z composite rod was approximately 230 nm herein. Notably, following the ZnO modification, the surface of the F-2-Z composite rod was smoother than that of the F-1-Z rod as exhibited in Figure 3a. This is associated with the flat surface feature of the rectangular F-2 rod. In the HRTEM images (Figure 4b–d), the ordered lattice fringes in the outer region of the composite rod revealed the coverage of well-crystallized ZnO crystals on the surface of the composite rod. A lattice fringe spacing of approximately 0.37 nm corresponded to the interplanar distance of rhombohedral α-Fe₂O₃ (012). Furthermore, a lattice fringe spacing of 0.26 nm in the HR images demonstrated the interplanar distance of hexagonal ZnO (002). The SAED pattern taken from the several F-2-Z composite rods revealed a crystalline feature and a composite structure of the rhombohedral α-Fe₂O₃ rods sputtering coated with the hexagonal ZnO thin film (Figure 4e). Furthermore, elemental line-scan profiles of Fe, Zn, and O across the F-2-Z composite rod are displayed in Figure 4f. The cross-sectional line-scan profiles revealed that the Zn element was well distributed around the Fe₂O₃ rod, showing the formation of the compositionally defined composite structure of the F-2-Z rod. The EDS elemental mapping analysis corresponding to an individual F-2-Z composite rod (Figure 4g) further confirmed the spatial distributions of Fe, Zn, and O. The O signal was homogeneously distributed over the entire composite rod. Obviously, the Fe signal was detected as an inner rod structure, while Zn signals were detected in the whole region with more intense signals on the peripheral region of the composite rod, indicating the uniform distribution of the thin ZnO layer over the surface of the composite rod.
The thin ZnO layer covered on the Fe₂O₃ rod exhibited a thickness ranging from 25 to 45 nm. The XPS survey scan spectra of the F-1-Z and F-2-Z composite rods are displayed in Figure 5a,b, respectively. Obviously, the distinct Fe 2p, Zn 2p, O 1s, and external C 1s peaks appeared in the Fe₂O₃–ZnO composite rods, indicating ZnO was coated on the Fe₂O₃ surface. In addition to carbon contamination that originated from exposure of samples to ambient air, no other impurity elements existed in the samples. High-resolution core-level spectra of Zn 2p are presented in Figure 5c,d for the F-1-Z and F-2-Z composite rods, respectively. The distinct peaks centered at 1021.6 and 1044.8 eV corresponded to Zn 2p̃ and Zn 2p, respectively. The binding energy difference between the Zn 2p̃ and Zn 2p was in agreement with the Zn²⁺ binding state in the ZnO lattice. Figure 5e,f shows the Fe 2p core-level spectra of the F-1-Z and F-2-Z composite rods, respectively. The spectra can be mainly deconvoluted into two doublets. The first doublet has the Fe 2p₁/₂ at 710.9 eV and the Fe 2p₃/₂ at 724.6 eV. This doublet is associated with the Fe³⁺ oxidation state in the Fe₂O₃ lattice. Comparatively, the second doublet exhibited a substantially weaker intensity and lower binding energy; the binding energies of Fe 2p₃/₂ and Fe 2p₁/₂ occurred at 709.6 and 723.1 eV, respectively. These binding energies were associated with the Fe²⁺ oxidation state. In addition, the shake-up satellite peak presented at 717.6 eV is a characteristic of Fe³⁺ ions in Fe₂O₃. The Fe 2p analysis result demonstrated that the Fe atoms are mainly in the trivalent oxidation binding status in the Fe₂O₃ lattice. This is consistent with typical values for Fe₂O₃ nanorods formed by the thermal decomposition method. In Figure 5g,h, the O 1s spectra of the F-1-Z and F-2-Z can be deconvoluted into three subpeaks with the binding energies of 530.1, 531.2, and 532.4 eV. The subpeaks at 530.1 and 531.2 eV were indexed to lattice oxygen in the ZnO and Fe₂O₃, respectively. In addition, the subpeak at the 532.4 eV is a result of carbon contamination.
highest binding energy of 532.4 eV was ascribed to adsorbed water molecules or oxygen species on the oxide surface.\textsuperscript{27,30} The light absorption edges of various Fe\textsubscript{2}O\textsubscript{3} rods and Fe\textsubscript{2}O\textsubscript{3}−ZnO composite rods were located at approximately 580−610 nm as exhibited in Figure 6a. The optical bandgap of pure Fe\textsubscript{2}O\textsubscript{3} rods (F-1 and F-2) was calculated by converting the Kubelka−Munk equation.\textsuperscript{32} The estimated band gap is approximately 2.13 and 2.1 eV for the F-1 and F-2 rods, respectively (Figure 6b), which is close to the reported value of the Fe\textsubscript{2}O\textsubscript{3} nanorods prepared by a hydrothermal method with calcination treatments.\textsuperscript{33} Comparatively, the light harvesting ability of the F-2 rods are slightly higher than that of the F-1 rods herein. After the deposition of the ZnO coverage layer, the Fe\textsubscript{2}O\textsubscript{3}−ZnO composite rods presented a broader light absorption range and a slight redshift at the absorption edge in comparison with the pristine Fe\textsubscript{2}O\textsubscript{3} rods. Similarly, the coupling of different semiconductors with various bandgaps to form a heterogeneous system has been shown to extend their light harvesting ability.\textsuperscript{34,35} The optical absorbance results herein demonstrated that the formation of a Fe\textsubscript{2}O\textsubscript{3}−ZnO composite structure is beneficial to improve the photoactivity of the pristine Fe\textsubscript{2}O\textsubscript{3} rods.

The photoresponse properties of various rod photoelectrode samples under chopped illumination at 0.35 V are displayed in Figure 7a. The Fe-1 and Fe-2 photoelectrodes showed a distinct spike-like transient response under irradiation. The possible cause of this spike transient feature is associated with the whole process of the back reaction, which is regarded as the recombination of the photogenerated charges at the surface states.\textsuperscript{36} Notably, the large initial spike transient of the Fe\textsubscript{2}O\textsubscript{3} rods.
rods are extraordinarily decreased after covering the ZnO thin layer, indicating effective suppression of the electron−hole recombination on Fe$_2$O$_3$−ZnO heterogeneous rods (F-1-Z and F-2-Z). A similar substantial decrease in initial spike transient has been shown in the α-Fe$_2$O$_3$ nanostructures modified with Sb$_2$S$_3$ and cobalt phosphate. Moreover, the steady-state photocurrent density of the Fe$_2$O$_3$ nanorods was enhanced via decoration of the ZnO coverage layer in Figure 7a. F-1-Z and F-2-Z photoelectrodes retained a much higher current density than that of the parent F-1 and F-2 photoelectrodes, respectively. The F-1 and F-2 photoelectrodes demonstrated an average photocurrent density of 0.009 and 0.011 mA/cm$^2$, respectively, whereas the F-1-Z and F-2-Z photoanodes showed an average photocurrent density of 0.033 and 0.038 mA/cm$^2$, respectively. The photoresponse magnifications of the F-1 and F-2 photoelectrodes were 1.8 and 2.4, respectively, upon light irradiation. Moreover, the photoresponse magnifications of the F-1-Z and F-2-Z were 21.9 and 27.5, respectively, upon exposure to light. The F-2-Z exhibited the highest photoresponse among various rod samples herein.

The photocurrent versus time curves demonstrated the remarkable improvement of photoelectric conversion efficiency in the Fe$_2$O$_3$ via a construction of a heterogeneous system with the ZnO in this study. The charge carrier concentration on the interface of the semiconductor electrode and electrolyte were investigated by Mott−Schottky (M-S) analysis. Normally, the greater the charge carrier concentration on the interface, the better the photocatalytic activity is. This is because more charge carriers are involved in photocatalytic reactions. The M-S analysis (Figure 7b) is employed to determine the charge separation efficiency and flat band potential ($E_{fb}$) at the interface of the rod samples and electrolyte. The calculation is based on the following equation:

$$1/C^2 = \left(\frac{2}{\varepsilon_o \varepsilon_r N_d}\right)[(V - V_{fb}) - kT/\varepsilon_o]$$  \hspace{1cm} (4)

Here, $C$ is the specific capacitance, $\varepsilon_o$ is fundamental electric charge, $\varepsilon_r$ is the dielectric constant of Fe$_2$O$_3$ (approximately 80), $N_d$ is the permittivity of vacuum, $T$ is the temperature, and $k$ is the Boltzmann constant. According to eq 4, a straight line can be drawn using a plot of $1/C^2$ versus $V$, and $V_{fb}$ is determined by the intercept with the $X$ axis (potential) as revealed in Figure 7b. A flat band potential of approximately $-0.55$ V (versus Ag/AgCl) was determined from the intercept on the $X$ axis for the F-1 and F-2, while for the F-1-Z and F-2-Z, the flat band exhibits a negative shift of approximately 20 mV, indicating that a quasi-Fermi level of the Fe$_2$O$_3$−ZnO band bends upward due to the decoration of ZnO crystals. All of the slopes of the M-S curves are negative, suggesting a p-type semiconducting behavior for the heterogeneous rods.
are positive, indicating the n-type feature of various rod samples, consistent with the semiconductor characteristic of pristine Fe$_2$O$_3$ and ZnO. In addition, the curves of Fe$_2$O$_3$–ZnO composite rods exhibited smaller tangent lines compared to those of the pristine Fe$_2$O$_3$ sample electrode, indicating an increased donor density in the Fe$_2$O$_3$–ZnO composite structures due to the formation of a heterojunction. The above result also proves that the ZnO decoration on the Fe$_2$O$_3$ rods effectively enhanced the charge separation efficiency of the Fe$_2$O$_3$. Furthermore, the slopes of tangent lines for M-S plots of the F-1-Z and F-2-Z composite rods were $6.6 \times 10^{-3}$ and $5.5 \times 10^{-2}$, respectively. The smaller linear fitting slope of the F-2-Z suggested its higher charge carrier concentration and photoactivity compared with F-1-Z. Figure 7c shows Nyquist plots of various rod samples under light irradiation. The semicircles obtained at the higher frequency region are smaller for the Fe$_2$O$_3$–ZnO as compared with that for pristine Fe$_2$O$_3$ rods, showing that the heterogeneous structure possessed a more effective separation of photogenerated electron–hole pairs and faster interfacial charge transfer. The corresponding equivalent circuit diagrams of Figure 7d,e were used to evaluate the charge-transfer resistance ($R_c$) of the Fe$_2$O$_3$ rod samples and Fe$_2$O$_3$–ZnO composite rod samples, respectively. Notably, the series resistance $R_s$ is composed of ionic resistance of the electrolyte. $C_{eq}$ is the equivalent circuit component. $Z_w$ is the Warburg impedance. By using the equivalent circuit illustrated, we obtained the $R_c$ of the Fe$_2$O$_3$ rods and Fe$_2$O$_3$–ZnO composite rods. The $R_s$ values of the F-1 and F-2 samples were 503 and 421 ohm, respectively, while the $R_s$ values of F-1-Z and F-2-Z were approximately 101 and 89 ohm, respectively. The heterostructured Fe$_2$O$_3$–ZnO demonstrated a higher charge separation ability than that of the pristine Fe$_2$O$_3$ herein. Moreover, the F-2-Z exhibited the highest charge transfer ability at the interfacial region. Overall, the results manifest that the decoration of the ZnO coverage layer successfully enhanced the charge separation and transportation in turn reduce the interfacial resistance. Room-temperature PL spectra of the F-1-Z and F-2-Z composite rods are shown in Figure 7e to further investigate the photoactivity difference among various composite rods. Each sample shows a sharp UV emission peak and a wide emission peak in the visible-light region is usually a consistent with the earlier PEC results.

Figure 8a–d shows the typical irradiation time-dependent absorption spectra of the RhB solution after photodegradation with the F-1, F-2, F-1-Z, and F-1-Z rod photocatalysts, respectively. With irradiation duration increased, the intensity of the RhB characteristic absorption peak decreased gradually, suggesting that the RhB dyes were gradually photodegraded by the Fe$_2$O$_3$ rods and Fe$_2$O$_3$–ZnO composite rods. Figure 8e summarizes the results of $C/C_0$ versus irradiation duration. The nearly complete photodegradation (approximately 88%) of the RhB dyes was achieved for the RhB solution containing the F-2-Z photocatalyst after 60 min of irradiation; the F-1-Z photocatalyst degraded 82% of RhB dyes under the same irradiation duration. By contrast, pristine F-1 and F-2 Fe$_2$O$_3$ rods exhibited low photodegradation performances and only degraded 34 and 40% of RhB dyes after 60 min of irradiation, respectively. Comparatively, all the Fe$_2$O$_3$–ZnO composite rods exhibited better photocatalytic degradation efficiency than the pristine Fe$_2$O$_3$ rods. Furthermore, the photodegradation reaction of the RhB catalyzed by the oxide semiconductors herein follows a first-order rate law, $\ln(C/C_0) = kt$, where $k$ is the apparent rate constant of the degradation. Figure 8f shows the $-\ln(C/C_0)$ versus time curves of different rod samples on photodegrading RhB dyes. The $k$ was found to be 0.006, 0.008, 0.028, and 0.035 min$^{-1}$ for the rod samples of F-1, F-2, F-1-Z, and F-2-Z, respectively. The result demonstrates that the photodegradation performance of the rod samples follows the order F-2-Z > F-1-Z > F-2 > F-1. The photodegradation efficiency of the Fe$_2$O$_3$–ZnO composite rods is better than that of pristine Fe$_2$O$_3$ rods, which is associated with the complex band configuration of the Fe$_2$O$_3$/ZnO heterostructures. As shown in Figure 8g, the enhancement of the photocatalytic efficiency of composite rods toward RhB dyes could be ascribed to the favorable synergistic effect between Fe$_2$O$_3$ and ZnO. The position of ZnO and Fe$_2$O$_3$ bands has a type II alignment where the conduction band edge ($-0.4$ eV) of ZnO is located between the conduction band ($-0.55$ eV) and the valence band ($1.55$ eV) of Fe$_2$O$_3$. The photogenerated electrons in the conduction band of Fe$_2$O$_3$ can transfer to the conduction band of ZnO under irradiation. This heterogeneous band alignment can promote the separation of photogenerated electrons and holes at the Fe$_2$O$_3$/ZnO interface and reduce the electron–hole recombination probability in the composite rods.

Consequently, the photogenerated holes and electrons were transferred to the surfaces of Fe$_2$O$_3$ and ZnO, respectively, according to the proposed heterogeneous band alignment. The holes in the Fe$_2$O$_3$ surface will act with water molecules and finally form as hydroxyl radicals (OH). Moreover, the super oxygen radicals ($O_2^\cdot$) would be formed by the combination of electrons with O$_2$ adsorbed on the surface of ZnO. These super oxygen radicals acted with water molecules and further formed hydroxyl radicals to decompose RhB dyes. A similar band alignment effect in the heterogeneous systems composed of wide band gap and narrow band gap semiconductors, leading to the high transfer rate of photoinduced charge carriers at the interface, has been shown in TiO$_2$–ZnFe$_2$O$_4$ and ZnO–Sn$_2$S$_3$ systems.

The operating-temperature-dependent 500 ppm acetone vapor-sensing responses of the sensor made from F-2-Z composite rods are shown in Figure 9a. The acetone vapor-sensing response increased along with the operating temperature and reached a maximum value at 325 °C, suggesting that a resultant equilibrium between the surface reaction with acetone vapor molecules and the diffusion of acetone vapor molecules to the composite rods’ surfaces occurred at 325 °C. Therefore, the optimal operating temperature is determined to be 325 °C for the subsequent gas-sensing tests of the Fe$_2$O$_3$–ZnO composite rods. Figure 9b–e shows the dynamic response curves of the sensors made from F-1, F-2, F-1-Z, and F-2-Z rods, respectively.
respective, exposed to 25−500 ppm acetone vapor at an operating temperature of 325 °C. The well acetone vapor concentration-dependent cyclic resistance change curves of various rod-based gas sensors were shown in this study. The dynamic-sensing response curves herein can be described as a decrease in the sensor resistance upon exposure to acetone vapor, and the sensor resistance completely recovers to the initial state upon the removal of acetone vapor. This is attributable to the gas-sensing behavior of the n-type oxide semiconductors. The acetone vapor-sensing responses versus the acetone concentration for various sensors based on rod samples are summarized in Figure 9f. The responses of the F-1, F-2, F-1-Z, and F-2-Z sensors upon exposure to 25 ppm acetone vapor are 2.1, 2.5, 3.2, and 4.1, respectively. Moreover, the responses of the F-1, F-2, F-1-Z, and F-2-Z sensors upon exposure to 500 ppm acetone vapor are approximately 5, 7, 28, and 36, respectively. Notably, the Fe₂O₃−ZnO composite rods showed a higher acetone vapor detection ability than the pristine Fe₂O₃ rods. Moreover, the F-2-Z sensor showed the highest acetone vapor response among all samples at the given test conditions. Compared with the pristine Fe₂O₃ rods, the improved acetone vapor-sensing property of the Fe₂O₃−ZnO composite rod sensors can be mainly attributed to the heterojunction formed between the Fe₂O₃ and ZnO. The work function of ZnO is lower than that of α-Fe₂O₃, thus the electrons in the Fermi level of ZnO would transfer to the Fermi level of α-Fe₂O₃ until their Fermi levels equalized. Hence, an electron depletion layer is formed at the heterojunction interface, which plays an important role in the resistance variation of the sensor upon exposure to the target gas. Several reports have demonstrated that the formation of a heterojunction can improve the gas-sensing responses of various composites or heterostructures. For metal oxide gas sensors, the change of sensor resistance is mainly caused by the adsorption and desorption of gas molecules on the surface of the sensing materials. The difference of the acetone vapor sensing mechanisms of the pristine Fe₂O₃ and Fe₂O₃−ZnO sensors can be explained by the modulation model of the depletion layer. In Figure 10a, oxygen molecules were adsorbed on the surface of the Fe₂O₃ rod and ionized to surface-adsorbed oxygen species by capturing free electrons from Fe₂O₃ in ambient air, as shown in eq 5

\[ \text{O}_2 + e^- = 2\text{O} \]  

\[
\text{(5)}
\]

Figure 9. (a) Gas-sensing responses versus the operating temperature of the F-2-Z sensor upon exposure to 500 ppm acetone vapor. Cyclic resistance change curves of various sensors exposed to 25−500 ppm acetone vapor concentrations. (b) F-1, (c) F-2, (d) F-1-Z, and (e) F-2-Z. (f) Summarized acetone vapor-sensing responses of various sensors exposed to 25−500 ppm acetone vapor.

Figure 10. Acetone vapor-sensing mechanisms of the various sensors. (a) Pristine Fe₂O₃ rods and (b) Fe₂O₃−ZnO composite rods.
As a result, an electron depletion layer forms on the surface region of the Fe₂O₃ rod, leading to a high resistance of the sensor. In the presence of acetone vapor, the acetone molecules will react with the former adsorbed oxygen species and make the captured electrons be released back to the conduction band of the Fe₂O₃ according to the following equation:

\[
\text{CH}_3\text{COCH}_3 + 8\text{O}^– \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 8\text{e}^- \quad (6)
\]

Thus, the free electron concentration increases, and the measured resistance of the sensor decreases finally. By contrast, Figure 10b shows the schematic diagram of the acetone vapor-sensing mechanism of the Fe₂O₃-ZnO sensor. When the Fe₂O₃-ZnO rods are exposed in ambient air, an electron depletion layer would be formed near the surface of the ZnO shell layer, and an additional electron depletion layer would form at the interface between the Fe₂O₃ and ZnO. Furthermore, it has been revealed that the semiconductor oxides exhibit obvious gas-sensing capability when the crystal size is comparable to their Debye length.27,49 In this work, the coverage thickness of ZnO rods highly resistive compared to the pristine Fe₂O₃ after introducing acetone vapor. Moreover, the acetone vapor-sensing tests show that the sensors made of Fe₂O₃-ZnO composite rods are more sensitive to detect acetone vapor than that of pristine Fe₂O₃ rods. Furthermore, the acetone vapor-sensing tests show that the sensors made of Fe₂O₃-ZnO composite rods are more sensitive to detect acetone vapor than the sensors made of pristine Fe₂O₃ rods at the given test conditions. The formation of the Fe₂O₃/ZnO heterojunctions in the composite rods accounted for the enhanced acetone vapor-sensing ability of the composite rods herein. Design and tuning crystalline Fe₂O₃ rods with desirable photocatalytic and gas-sensing properties can be achieved through sputtering-assisted decoration of the thin ZnO coverage layer onto the Fe₂O₃ rod templates in this study.

### CONCLUSIONS

In summary, the crystalline Fe₂O₃-ZnO composite rods were initially synthesized through a combination of hydrothermal and sputtering methods. The low content of urea in the hydrothermal process resulted in the round cross-sectional Fe₂O₃ rods; moreover, a high urea concentration caused formation of the Fe₂O₃ rods with a rectangular cross-sectional morphology. The decoration of a thin ZnO coverage layer onto the surfaces of the Fe₂O₃ rod templates enhanced the composite rods’ light harvesting ability. Moreover, the PEC and EIS results show an increased photoinduced charge separation efficiency in the Fe₂O₃-ZnO composite system because of the suitable type II band alignment between the Fe₂O₃ and ZnO. These factors explained the superior photodegradation performance of the RhB solution containing the Fe₂O₃-ZnO composite rods than that of pristine Fe₂O₃ rods. Furthermore, the acetone vapor-sensing tests show that the sensors made of the Fe₂O₃-ZnO composite rods are more sensitive to detect acetone vapor than the sensors made of pristine Fe₂O₃ rods at the given test conditions. The formation of the Fe₂O₃/ZnO heterojunctions in the composite rods accounted for the enhanced acetone vapor-sensing ability of the composite rods herein. Design and tuning crystalline Fe₂O₃ rods with desirable photocatalytic and gas-sensing properties can be achieved through sputtering-assisted decoration of the thin ZnO coverage layer onto the Fe₂O₃ rod templates in this study.

### EXPERIMENTAL METHODS

One-dimensional Fe₂O₃ rods were synthesized using a hydrothermal method. FeCl₃·6H₂O (0.757 g) and 0.27 g (or 0.36 g) of urea dissolved in distilled water (15 mL) were used as the precursor solution. Then, 12.5 mL of the precursor solution was transferred into a Teflon-lined autoclave. The hydrothermal crystal growth was carried out at 100 °C for 24 h. After the hydrothermal reaction, the autoclave was cooled to room temperature naturally. Subsequently, the deposited samples were rinsed repeatedly with deionized water and annealed at 500 °C for 30 min to get the desired crystalline phase (α-Fe₂O₃). The notations for the Fe₂O₃ rod samples prepared with 0.27 g and 0.36 g urea are F-1 and F-2, respectively.

The Fe₂O₃-ZnO composite rods were synthesized using radio frequency (rf) sputtering deposition of a ZnO thin film onto the surfaces of the Fe₂O₃ rod templates. During the ZnO thin film deposition, the working pressure was kept at 20 mTorr. The rf sputtering power was performed at 90 W with a ZnO target (3 inches in diameter), and the Ar/O₂ ratio was maintained at 4/1. The thin film growth temperature was maintained at 375 °C during the sputtering processes. Herein, F-1-Z and F-2-Z were denoted as F-1 and F-2 Fe₂O₃ rods coated with the ZnO thin film layer, respectively.

### Table 1. Acetone Vapor-Sensing Performance of Various Fe₂O₃-Based Composites Prepared Using Various Routes under Similar Gas-Sensing Test Conditions

| materials                          | synthesis method                  | morphology       | operating temperature (°C) | concentration (ppm) | response (Rf/Rp) |
|-----------------------------------|-----------------------------------|------------------|-----------------------------|---------------------|-----------------|
| Fe₂O₃-ZnO (this work)             | hydrothermal + sputtering         | nanorod          | 325                         | 500                 | 36              |
| CuFe₂O₄–Fe₂O₃                    | facile template-induced + hydrothermal | hollow sphere   | 300                         | 500                 | 23              |
| rGO–Fe₂O₃                        | homotaxial electrophinning method  | nanotube         | 375                         | 250                 | 8               |
| Fe₂O₃–CuO                        | facile carbon sphere template method | hollow sphere   | 380                         | 500                 | 16              |
| Fe₂O₃/C₃N₄                       | hydrothermal + pyrolysis          | nanotube         | 350                         | 500                 | 5               |

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Sample crystal structures were investigated by X-ray diffraction (XRD). The morphologies of various rod products were characterized by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used to investigate the microstructure and composition of the composite rod samples. The diffuse reflectance spectra of various rod samples were recorded by using a UV–vis spectrophotometer. The elemental binding states of the as-synthesized samples were explored by X-ray photoelectron spectroscopy (XPS). Photoluminescence (PL) spectra of the synthesized samples were recorded by using a UV–vis spectrophotometer. In order to quantify the photodegradation degree of the synthesized rod photocatalysts toward RhB dyes, absorbance intensities at \( t = 0 \) and at any irradiation duration \( t \) were used to evaluate the photodegradation degree in which \( C_0 \) and \( C \) are the initial and residual concentration of the RhB dye at \( t = 0 \) and at any irradiation duration \( t \), respectively; and \( I_0 \) and \( I \) are the absorbance intensities at irradiation duration \( t \) and at \( t = 0 \), respectively. The gas sensors made from various as-synthesized rod samples were placed in a closed vacuum chamber, and various concentrations of acetone vapor (25, 50, 100, 250, and 500 ppm) were introduced into the test chamber, using dry air as the carrier gas. The sputtering-deposited patterned Pt electrodes with a film thickness of 80 nm were prepared for electric measurements. The gas-sensing response of the gas sensors to acetone vapor is defined as the \( R_0 / R_g \). \( R_g \) is the sensor electrical resistance in the dry air, and \( R_0 \) is that with introduction of the acetone vapor into the test chamber.

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**REFERENCES**

(1) Liang, Y.-C.; Chiang, K.-J. Design and tuning functionality of rod-like titanium dioxide–nickel oxide composites via a combinational methodology. Nanotechnology 2020, 31, 195709.

(2) Liang, Y.-C.; Liu, Y.-C.; Hung, C.-S. Sputtering control of Ag2O decoration configurations on ZnO nanorods and their surface arrangement effects on photodegradation ability toward methyl orange. Nanotechnology 2019, 30, 495701.

(3) Liang, Y.-C.; Liu, Y.-C. Design of Nanoscaled Surface Morphology of TiO2–Ag2O Composite Nanorods through Sputtering Decoration Process and Their Low-Concentration NO2 Gas-Sensing Behaviors. Nanomaterials 2019, 9, 1150.

(4) Liang, Y.-C.; Hung, C.-S. Effects of sputtering deposited homoseed layer microstructures on crystal growth behavior and photoactivity of chemical route-derived WO3 nanorods. CrystEngComm 2019, 21, 5779–5788.

(5) Ning, J.; Shi, P.; Jiang, M.; Liu, C.; Li, X. Effect of Ce Doping on the Structure and Chemical Stability of Nano-α-Fe2O3. Nanomaterials 2019, 9, 1039.

(6) Jiao, Y.; Liu, Y.; Qu, F.; Wu, X. Dendritic α-Fe2O3 hierarchical architectures for visible light driven photocatalysts. CrystEngComm 2014, 16, 575–580.

(7) Wei, K.; Zhao, S.; Zhang, W.; Zhong, Z.; Li, T.; Cui, B.; Gao, S.; Wei, D.; Shen, Y. Controllable Synthesis of Zn-Doped α-Fe2O3 Nanowires for H2S Sensing. Nanomaterials 2019, 9, 994.

(8) Wang, Y.; Tang, X.; Cao, S.; Chen, X.; Rong, Z. The Synthesis of the Pomegranate-Shaped α-Fe2O3 Using an In Situ Corrosion Method of Scordrite and Its Gas-Sensitive Property. Nanomaterials 2019, 9, 977.

(9) Almeida, T. P.; Fay, M. W.; Hansen, T. W.; Zhu, Y.; Brown, P. D. Insights from in situ and environmental TEM on the oriented attachment of α-Fe2O3 nanoparticles during α-Fe2O3 nanorod formation. CrystEngComm 2014, 16, 1540–1546.

(10) Xie, S.; Jia, H.; Lu, F.; Sun, N.; Yu, J.; Liu, S.; Zheng, L. Controlled synthesis of α-Fe2O3 nanostructures with the assistance of ionic liquid and their distinct photocatalytic performance under visible-light irradiation. CrystEngComm 2015, 17, 1210–1218.

(11) Vincent, T.; Gross, M.; Dotan, H.; Rothschild, A. Thermally oxidized iron oxide nanoarchitectures for hydrogen production by solar-induced water splitting. Int. J. Hydrogen Energy 2012, 37, 8102–8109.

(12) Wang, D.; Chen, H.; Chang, G.; Lin, X.; Zhang, Y.; Aldalbahi, A.; Peng, C.; Wang, J.; Fan, C. Uniform Doping of Titanium in Hematite Nanorods for Efficient Photoelectrochemical Water Splitting. ACS Appl. Mater. Interfaces 2015, 7, 14072–14078.

(13) Liang, Y.-C.; Chao, Y. Enhancement of Acetone Gas-Sensing Responses of Tapered WO3 Nanorods through Sputtering Coating with a Thin SnO2 Coverage Layer. Nanomaterials 2019, 9, 864.

(14) Xi, L.; Chiam, S. Y.; Mak, W. F.; Tran, P. D.; Barber, J.; Loo, S. C.; Jong, W. L. A Novel Strategy for Surface Treatment on Hematite Photoanode for Efficient Water Oxidation. Chem. Sci. 2013, 4, 164–169.

(15) Kment, S.; Riboni, F.; Pausova, S.; Wang, L.; Wang, L.; Han, H.; Hubicka, Z.; Krysa, J.; Schmuki, P.; Zboril, R. Photoanodes based on TiO2 and α-Fe2O3 for solar water splitting - superior role of 1D nanoarchitectures and of combined heterostructures. Chem. Soc. Rev. 2017, 46, 3716–3769.

(16) Liang, Y.-C.; Chang, C.-W. Preparation of Orthorhombic WO3 Thin Films and Their Crystal Quality-Dependent Dye Photo-degradation Ability. Coatings 2019, 9, 90.

(17) Liang, Y.-C.; Liu, Y.-C. Microstructures and Photodegradation Performance toward Methylene Orange of Sputtering-Assisted Decoration of ZnFe2O4 Crystallites onto TiO2 Nanorods. Nanomaterials 2019, 9, 205.
(18) Liang, Y.-C.; Chang, C.-W. Improvement of Ethanol Gas-Sensing Responses of ZnO–WO3 Composite Nanorods through Annealing Induced Local Phase Transformation. Nanomaterials 2019, 9, 669.

(19) Liang, Y.-C.; Lung, T.-Y.; Xu, N.-C. Photoexcited Properties of Tin Sulfide Nanosheet-Decorated ZnO Nanorod Heterostructures. Nanoscale Res. Lett. 2017, 12, 258.

(20) Liang, Y.-C.; Lin, T.-Y.; Lee, C.-M. Crystal growth and shell layer crystal feature-dependent sensing and photoactivity performance of zinc oxide–indium oxide core–shell nanorod heterostructures. CrystEngComm 2015, 17, 7948–7955.

(21) Mulmudi, H. K.; Mathews, N.; Dou, X. C.; Xi, L. F.; Praman, S. S.; Lam, Y. M.; Mhaisalkar, S. G. Controlled growth of hematite (α-Fe2O3) nanorod array on fluorine doped tin oxide: Synthesis and photoelectrochemical properties. Electrochem. Commun. 2011, 13, 951–954.

(22) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect. Science 2004, 304, 711.

(23) Su, M.; He, C.; Sih, K. Facile synthesis of morphology and size-controlled α-Fe2O3 and Fe2O3 nano-and microstructures by hydrothermal/solothermal process: The roles of reaction medium and urea dose. Ceram. Int. 2016, 42, 14793–14804.

(24) Hu, X.; Yu, J. C.; Gong, J.; Li, Q.; Li, G. α-Fe2O3 Nanorings Prepared by a Microwave-Assisted Hydrothermal Process and Their Sensing Properties. Adv. Mater. 2007, 19, 2324–2329.

(25) Katsuki, H.; Komarneni, S. Microwave-Hydrothermal Synthesis of Monodispersed Nanophase α-Fe2O3. J. Am. Ceram. Soc. 2001, 84, 2313–2317.

(26) Xi, L.; Tran, P. D.; Chiam, S. Y.; Bassi, P. S.; Mak, W. F.; Mulmudi, H. K.; Batbayal, S. K.; Barber, J.; Loo, J. S. C.; Wong, L. H. CoOx-Decorated Hematite Nanorods as an Effective Photoanode for Solar Water Oxidation. J. Phys. Chem. C 2012, 116, 13884–13889.

(27) Liang, Y.-C.; Lo, Y.-J. High-temperature solid-state reaction induced structure modifications and associated photoactivity and gas-sensing performance of binary oxide one-dimensional composite system. RSC Adv. 2017, 7, 29428–29439.

(28) Li, N.; Zhang, J.; Tian, Y.; Zhao, J. H.; Zhang, J.; Zuo, W. Precisely controlled fabrication of magnetic 3D γ-Fe2O3@ZnO core-shell photocatalyst with enhanced activity: Ciprofl oxacin degradation and mechanism insight. Chem. Eng. J. 2017, 307, 377–385.

(29) Suresh, R.; Giribabu, K.; Manigandan, R.; Stephen, A.; Narayanan, V. Fabrication of Ni–Fe2O3 magnetic nanorods and application to the detection of uric acid. RSC Adv. 2014, 4, 17146.

(30) Liang, Y.-C.; Liao, W.-K.; Deng, X.-S. Synthesis and substantially enhanced gas sensing sensitivity of homogeneously nanoscale Pd- and Au-particle decorated ZnO nanorod structures. J. Alloys Compd. 2014, 599, 87–92.

(31) Sarkar, D.; Khan, G. G.; Singh, A. K.; Mandal, K. Enhanced Electrical, Optical, and Magnetic Properties in Multifunctional ZnO/α-Fe2O3 Semiconductor Nanoheterostructures by Heterojunction Engineering. Phys. Chem. C 2012, 116, 23540–23546.

(32) Ng, C.; Iwase, A.; Ng, Y. H.; Amal, R. Understanding Self-Photocatalytic Charge Transfer Kinetics of Fe2O3/CDs Composite Nanorods using Cobalt Phosphate as cocatalyst. Appl. Catal., B 2017, 218, 570–580.

(33) Zhu, T.; Song, Y.; Ji, H.; Xu, Y.; Song, Y.; Xia, J.; Yin, S.; Li, Y.; Xu, H.; Zhang, Q.; Li, H. Synthesis of γ-C3N4/Ag3VO4 composites with enhanced photocatalytic activity under visible light irradiation. Chem. Eng. J. 2015, 271, 96–105.

(34) Uddin, M. T.; Nicolas, Y.; Olivier, C.; Toupane, T.; Servant, L.; Müller, M. M.; Kleebe, H.-J.; Ziegler, J.; Jaegermann, W. Nanostructured SnO2–ZnO heterojunction photocatalysts showing enhanced photocatalytic activity for the degradation of organic dyes. Inorg. Chem. 2012, 51, 7764–7773.

(35) Watanabe, A.; Kozuka, H. Photoanodic Properties of Sol–Gel-Derived Fe2O3 Thin Films Containing Dispersed Gold and Silver Particles. J. Phys. Chem. B 2003, 107, 12713–12720.

(36) Chen, D.; Liu, Z.; Zhou, M.; Wu, P.; Wei, J. Enhanced photoelectrochemical water splitting performance of α-Fe2O3 nanostructures modified with Sb2S3 and cobalt phosphate. J. Alloys Compd. 2018, 742, 918–927.

(37) Narayanan, V. Fabrication of Ni-InAs Nanoparticle with Enhanced Activity: Ciprofloxacin degradation and enhanced photocatalytic activity under visible light irradiation. Sci. Rep. 2013, 3, 189, 307–312.

(38) Liang, Y.-C.; Lin, T.-Y. Fabrication and sensing behavior of one-dimensional ZnO-ZnO heterostructures. Nanoscale Res. Lett. 2014, 9, 344.

(39) Karunakaran, C.; Vinayagamoorthy, P. Superparamagnetic core–shell Fe3O4/ZnO nanoshells as photocatalyst cum bactericide. Catal. Today 2017, 284, 114–120.

(40) Wu, W.; Zhang, S.; Xiao, X.; Zhou, J.; Ren, F.; Sun, L.; Jiang, C. Controlled Synthesis, Magnetic Properties, and Enhanced Photocatalytic Activity of Spindlelike Mesoporous α-Fe2O3/ZnO Core–Shell Heterostructures. ACS Appl. Mater. Interfaces 2012, 4, 3602–3609.

(41) Liang, Y.-C.; Lin, T.-Y. Fabrication and sensing behavior of one-dimensional ZnO-ZnO heterostructures. Nanoscale Res. Lett. 2014, 9, 344.

(42) Chen, D.; Liu, Z.; Zhou, M.; Wu, P.; Wei, J. Enhanced photoelectrochemical water splitting performance of α-Fe2O3 nanocrystals modified with Sb2S3 and cobalt phosphate. J. Alloys Compd. 2018, 742, 918–927.