TiO$_2$-Based Nanoheterostructures for Promoting Gas Sensitivity Performance: Designs, Developments, and Prospects

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Abstract: Gas sensors based on titanium dioxide (TiO$_2$) have attracted much public attention during the past decades due to their excellent potential for applications in environmental pollution remediation, transportation industries, personal safety, biology, and medicine. Numerous efforts have therefore been devoted to improving the sensing performance of TiO$_2$. In those effects, the construct of nanoheterostructures is a promising tactic in gas sensing modification, which shows superior sensing performance to that of the single component-based sensors. In this review, we briefly summarize and highlight the development of TiO$_2$-based heterostructure gas sensing materials with diverse models, including semiconductor/semiconductor nanoheterostructures, noble metal/semiconductor nanoheterostructures, carbon-group-materials/semiconductor nanoheterostructures, and organic/inorganic nanoheterostructures, which have been investigated for effective enhancement of gas sensing properties through the increase of sensitivity, selectivity, and stability, decrease of optimal work temperature and response/recovery time, and minimization of detectable levels.

Keywords: TiO$_2$; nanoheterostructures; gas sensor

1. Introduction

Since the 20th century, atmospheric pollution has been proved to be one of most urgent issues. For the sake of controlling the exhaust emissions, gas sensors for the quantitative detection of various toxic and harmful gases have been widely developed as a result of their high response, outstanding selectivity, excellent repeatability, and good stability [1–3]. So far a variety of gas sensors, such as metal oxide semiconductor-based gas sensors [4–9], solid electrolyte-based gas sensors [10], electrochemical gas sensors [11], carbon-based gas sensors [1,12–14], organic gas sensors [2,3], and so on, have been extensively investigated. Amongst these different types of gas sensors, resistance type metal oxide gas sensors offering low cost, simple manufacturing approaches, and excellent sensitivity to the great majority of gases, have attracted considerable attention during the past several years [15,16]. Since Seiyama [17] reported metal oxide-based gas sensors for the first time, a large amount of effort has been expended in exploring the sensing properties of metal oxide-based gas sensors [7,18,19].

As a representative semiconductor metal oxide, titanium dioxide (TiO$_2$) has attracted much attention since Fujishima et al. observed the photocatalytic splitting of water on a TiO$_2$ electrode
As a representative semiconductor metal oxide, titanium dioxide (TiO$_2$) has attracted much attention since Fujishima et al. observed the photocatalytic splitting of water on a TiO$_2$ electrode under the irradiation of UV light in 1972 [20]. In the past decades, it has been discovered that TiO$_2$ could be employed in many promising fields including photovoltaics [21], photocatalysis [22, 23], sensors, etc. [24–26]. In particular, because of its high stability, harsh environmental tolerance, and environmentally-friendly properties, TiO$_2$ has been widely investigated and is regarded as one of the sensing materials for gas detection with the most potential [27–30].

Naturally, TiO$_2$ mainly exists in three polymorph forms: rutile phase (tetragonal, P42/mnm) [31], anatase phase (tetragonal, I41/amd), and brookite phase (orthorhombic, pbcn) (Figure 1a–c), whose bandgaps are 3.02, 3.2, and 2.96 eV, respectively [32]. Besides the abovementioned three crystal phases, there exists another phase, TiO$_2$(B) (monoclinic, C2/m). As shown in Figure 1d, TiO$_2$(B) possesses a layer structure, thus the density is lower and the specific capacity is larger comparing with other phases [33–35]. Among these diverse crystal phases, the most stable bulk phase is rutile, whereas for nanomaterials, anatase and brookite are commonly recognized to be more stable phases because of their relatively lower surface energy than rutile, although this fact is still argued in previous reports [36,37]. In the practical applications, TiO$_2$ performance is commonly affected by the crystal phases, which can be obtained through controlling the experimental conditions, such as fabrication methods, pH, duration annealing, temperature, and so on. As for the sensing applications, rutile TiO$_2$ and anatase TiO$_2$ are the most studied polymorphs.

![Figure 1. Crystal structures of TiO$_2$: (a) Rutile; (b) Anatase; (c) Brookite; and (d) TiO$_2$(B), red spheres represent Ti atoms, and the grey spheres represent O atoms.](image)

TiO$_2$ gas sensors are typical resistive-type sensors which can display a decrease or increase in resistance when probing a reductive gas (H$_2$, H$_2$S, NH$_3$, CO, VOCs) or oxidative gas (NO$_2$, O$_2$) [29,30,38], respectively. The sensing mechanism of TiO$_2$-based gas sensors can be described by the following two-step process: receptor process and transducer process, as shown in Figure 2 [39].

The receptor process occurs at the TiO$_2$ surface, and it involves physisorption and chemisorption processes [40]. Firstly, oxygen molecules can be physically absorbed on the surface when TiO$_2$ is exposed to an air environment at room temperature; the process is determined by Van der Waals and dipole interactions; secondly, oxygen molecules on the TiO$_2$ surface will capture electrons from the conductive band (CB) of TiO$_2$ to form chemisorbed oxygen species (O$_2^-$) on the surface. The reactions taking place on the surface of TiO$_2$ are as follows:
whereas the rate of chemisorption process may be influenced by activation energy.

In fact, it is well known that the surface structure and specific surface area can play substantial effort has been invested in increasing the specific surface area, decreasing the grain size, and enhancing the conductivity of TiO$_2$-based materials play important roles. Consequently, in recent years, substantial effort has been invested in increasing the specific surface area, decreasing the grain size, and enhancing the conductivity of TiO$_2$ through nanostructured materials, element doping, heterostructural materials and so on [27,30,43–46].

The transducer process includes the transportation of electrons in the TiO$_2$ and the transformation of electrons into the outward resistance signal. This can be influenced by the three typical electron transfer modes which are divided as surface-controlled mode, grain-controlled mode, and neck-controlled mode, respectively, [41,42] as shown in Figure 2. As for surface-controlled mode, compact layer structures determined by the thin film thickness of the materials are universally considered as the main pattern [39], where the gases can only affect the materials surfaces other than the internal body. On the contrary, in real polycrystalline materials, the TiO$_2$ grains connect to each other through grain boundaries or necks, in this way, the grain boundaries or necks will contribute significantly to the electroconductibility and gas sensing performance of the TiO$_2$. It has been reported that materials with large grain size would possess large neck cross sections, so accordingly the neck resistance is less significant than the grain-boundary resistance. However, for materials with much smaller grain size, the neck resistance is higher than the grain boundary resistance because of the much smaller neck cross section, in this case the neck resistance becomes more significant [41].

\[
\begin{align*}
\text{O}_2(g) & \rightarrow \text{O}_2(ads) \quad (1) \\
\text{O}_2(ads) + e & \rightarrow \text{O}_2^- \quad (2)
\end{align*}
\]

During the process, receptor capability is determined by the physisorption process and chemisorption process together, where the physisorption can be influenced by the temperature, whereas the rate of chemisorption process may be influenced by activation energy.

In these two typical processes presented above, surface-to-volume ratio, grain size, and the electron transport ability of TiO$_2$-based materials play important roles. Consequently, in recent years, substantial effort has been invested in increasing the specific surface area, decreasing the grain size, and enhancing the conductivity of TiO$_2$ through nanostructured materials, element doping, heterostructural materials and so on [27,30,43–46].

Nano-scale is a key factor in studying the gas sensing properties of metal oxide semiconductor-based sensors. In fact, it is well known that the surface structure and specific surface area can play
very important roles in sensing properties [47]. Nanocrystallization is an efficient way to improve the gas sensing performance because of their much larger specific surface area and rich surface chemical properties on the nanostructure surfaces, which may potentially lead to miniaturized sensors with outstanding performance. In this regard, many kinds of TiO$_2$ nanostructures with various morphologies, such as zero-dimensional (0D) nanocrystals [48], 1D nanofibers or nanowires [43,49,50], 2D nanoplates [29], and 3D hierarchical microstructures [27] have been developed.

Another important strategy to enhance the sensing performance of TiO$_2$ is the formation of heterostructures. The heterojunction theory dates back to as early as the 1930s [51]. Since then, more and more applications of nanoheterojunctions have been extensively investigated owning to the superinjection of charge carriers. Since 2005, a great many nanoheterostructural materials have been widely researched and applied in many fields, including solar cells [52], Li-ion batteries [53], photoelectrochemical cells [54], photocatalysis [55], and gas sensors [5,56]. As a matter of fact, several TiO$_2$-based nanoheterostructures, such as semiconductor/semiconductor, noble metal/semiconductor, carbon-group-material/semiconductor and organic/inorganic nanoheterostructures, have attracted widespread interest in the preparation and investigation of their properties and applications. Various types of TiO$_2$-based nanoheterostructures including composite nanoparticles [57–59], quantum dots in nanowires/nanofibers [60–63], core/shell nanowires/nanofibers/ nanospheres [64,65], etc., have been studied intensively. Compared with the pure oxide, these nanoheterostructures achieve higher sensing performance. As a well-known strategy, the modification of TiO$_2$ nanostructures using noble metal nanoparticles, like platinum (Pt), palladium (Pd), silver (Ag), and gold (Au), forming noble metal/TiO$_2$ heterostructured sensor materials can further improve the sensing performance, including enhancement of sensitivity and selectivity and shortening of response/recovery times [66,67]. The enhanced properties can be generally ascribed to the catalytic activity of noble metal nanoparticles, increased active surface area, reduced electrical resistance, enhanced optical absorption, facilitated chemical adsorption of oxygen molecules and/or reaction of oxygen ions with probing gases, and improved gas diffusion inside the heterostructures [68]. In addition, the Schottky barrier formed at the interface of noble metal/TiO$_2$ heterojunction yielding efficient electron/hole separation is considered as another important factor in enhancing sensing performance. In general, the electronic and chemical properties of the metal/oxide interface, as well as the morphology of the noble metal nanoparticles and metal oxides matrix, play important roles in promoting the overall performance of the noble metal/TiO$_2$ nanoheterostructures [57,60,69,70]. Comprehensive coverage of metal/semiconductor nanoheterostructured sensors have been available elsewhere for many decades, so accordingly, in this review, we briefly trace the application of TiO$_2$-based semiconductor/semiconductor, carbon-group-material/semiconductor and organic/inorganic nanoheterostructures in the area of gas sensors, summarize their major design and preparation methods, describe some of the improvements and resulting achievements, and discuss the future challenges and perspectives.

2. Fabrication of TiO$_2$-Based Nanoheterostructures

In the past few decades, various fabrication methods, including chemical vapor deposition (CVD), atomic layer deposition (ALD), solid phase reaction, electrochemical deposition, chemical deposition, hydrothermal/solvothermal methods, sol-gel, electrospinning, etc., have rapidly developed and been successfully applied in preparing high quality TiO$_2$-based nanoheterostructures. Accordingly, in this section, most of the attention will be focused on the nanoheterostructure synthesis methods.

2.1. CVD and ALD Methods

The CVD route probably is one of most extensively explored approach in nanoheterostructure preparation, which can deposit various materials onto suitable substrates in order. Nanoheterostructures are generally synthesized using a two-step growth procedure. In the first step, the inner-core material is deposited on a suitable substrate through CVD or other synthetic routes. In the second step, the outer-layer shell material is subsequently grown on the core surface.
This method has the capability to control the components, morphology, thickness, and length of the materials by controlling some technological parameters including temperature, pressure, carrier gases, gas-flow rates, substrates, and deposition time. For example, ZnO-TiO\textsubscript{2} nanocomposites were fabricated via an innovative CVD technique \cite{46}, where TiO\textsubscript{2} nanoparticles were grown on the initially deposited ZnO nanoplatelet host. The process was carried out at a relatively low temperature of 350–400 °C, this avoiding the effect of unsuitable thermal treatment and maintaining the chemical properties of the materials. Barreca et al. \cite{71} have reported the fabrication of CuO-TiO\textsubscript{2} nanocomposites through a multistep vapor deposition process, where the first step was the synthesis of porous CuO nanomaterials on an Al\textsubscript{2}O\textsubscript{3} substrate via a CVD approach, and the final step was the controllable growth of TiO\textsubscript{2} nanoparticles on the porous CuO matrices.

Although involving a similar chemical process as the CVD route, ALD has attracted much attention in the synthesis of heterostructures because of the accurate control of film thickness at atomic scale and the conformal growth of complex nanostructures. The excellent conformability between two materials obtained by ALD makes them possible to form heterojunctions at the semiconductor interfaces. Through growth control, Katoch et al. \cite{72} have successfully prepared TiO\textsubscript{2}/ZnO inner/outer double-layer hollow fibers (TiO\textsubscript{2}/ZnO DLHFs), as shown in Figure 3. The TiO\textsubscript{2}/ZnO DLHFs were synthesized using a three-step process. First, polyvinyl acetate (PVA) fibers were prepared by an electrospinning process; subsequently, TiO\textsubscript{2} and ZnO were sequentially grown on the PVA fibers through the ALD method and, finally, a thermal treatment was carried out for the removal of the PVA support and the crystallization of TiO\textsubscript{2} and ZnO.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a–f) Scanning electron microscope (SEM) images of TiO\textsubscript{2} hollow fibers synthesized with 1000 ALD cycles (a); TiO\textsubscript{2}/ZnO double-layer hollow fibers synthesized with 20 ALD cycles (b); 50 ALD cycles (c); 90 ALD cycles (d); 220 ALD cycles (e); and 350 ALD cycles (f); (g) Transmission electron microscope (TEM) image of a single TiO\textsubscript{2}/ZnO DLHF; (h) High resolution transmission electron microscopy (HRTEM) image of the outer layer ZnO \cite{72}. Copyright 2014 American Chemical Society.

### 2.2. Solid Phase Reactions

Solid phase reactions are a quite facile process to synthesize composite sensing materials. In a typical process, pure powders are mixed uniformly using a physical method to electrostatically
self-assemble nanoheterostructures, which generally is a one-step procedure. For example, Zhou et al. have prepared Ag$_2$O/TiO$_2$ nanoheterostructures [73] through a solid phase reaction, where a certain amount of the pure Ag$_2$O and the corresponding amount of TiO$_2$ were uniformly mixed to get Ag$_2$O/TiO$_2$ nanoheterostructures. What’s more, some other nanoheterostructures, such as polyaniline-titanium (PANi-TiO$_2$) nanoheterostructures [74], reduced graphene oxide/titanium dioxide (rGO/TiO$_2$) layered nanofilm [75], ZnO–TiO$_2$ nanocomposites [59], and TiO$_2$/SnO$_2$ nanocomposites [76], have also been successfully synthesized using this facile method.

2.3. Electrochemical Deposition

Compared with the CVD route, electrochemical deposition can obtain large-scale nanostructures at relatively low temperature. The conventional technique is very propitious to the fabrication of ordered, uniform, and highly dense nanoheterostructures for widespread applications. Recent years, some types of TiO$_2$-based nanoheterostructures are prepared using a two-step electrochemical deposition process [60,77]. In the deposition process, the pre-grown nanomaterials on fluorine-doped tin oxide (FTO), indium-doped tin oxide (ITO), or other relevant substrates are treated as working electrode for the following deposition. For instance, Yang and co-workers [78] have reported the preparation of the Cu-Cu$_2$O/TiO$_2$ nanocomposites via the electrochemical deposition method. The fabrication process consisted of two main steps: in the first step, helical TiO$_2$ nanotube arrays (NTAs) were prepared through anodizing a Ti foil. The second step was the electrodeposition of Cu and Cu$_2$O nanoparticles on the TiO$_2$ NTAs surface.

![SEM images of (a) TiO$_2$ NTAs and (b) hydrothermally treated TiO$_2$ NTAs; (c) TEM image of a typical NiTiO$_3$/TiO$_2$ NTs, the inset is the corresponding energy dispersive spectrometer (EDS) spectrum [79]. Copyright 2015 Wiley. (d–i) SEM images of as-anodized TiO$_2$ NTs (d–f) and TiO$_2$ NTs filled by Co-precursor nanorods (g–i) in top view (d,g), cross-sectional view (e,h), and bottom view (f,i) [80]. Copyright 2013 Royal Society of Chemistry.](image)

Additionally, a great number of TiO$_2$-based nanoheterostructures were prepared using electrochemical deposition combined with other synthesis processes, where 1D TiO$_2$ arrays were commonly synthesized by electrochemical deposition, and then the as-prepared TiO$_2$ arrays would
be used as templates for heterostructure fabrication in the second synthesis step by other methods, including chemical deposition, hydrothermal/solvothermal methods, sol-gel method, and so on. For example, coaxial Ni/NiTiO$_3$/TiO$_2$ NTAs (Figure 4a–c) were synthesized by hydrothermally treating the as-anodized TiO$_2$ NTAs [79]. Nano-coaxial p-Co$_3$O$_4$/n-TiO$_2$ heterojunctions were synthesized first using electrochemical deposition and secondly using hydrothermal reaction [80]. The SEM images are shown in Figure 4d–i, where obviously the NTs with open top and closed bottom display high order and directionality. When soaking the as-anodized TiO$_2$ NTs in Co-based solutions, new nanorods with smaller diameter can be formed in the center of the TiO$_2$ NTs, representing the formation of nano-coaxial shaped of nanoheterostructures. Similarly, CdS/TiO$_2$ nanoheterostructures were fabricated by electrochemical deposition and sequential chemical deposition [81]; Pd/TiO$_2$ nanoheterostructures were synthesized by electrochemical deposition and a UV irradiation chemical method [82]; polypyrrole (PPy)/TiO$_2$ heterojunctions were fabricated by chemical deposition and electronchemical deposition methods [78,83].

2.4. Chemical Deposition

Chemical deposition is a convenient and low-cost technique for fabricating nanoheterostructures. For this method, the nanomaterials are obtained from the solid precipitation in the solution, and the concentration of the precursor, pH value, deposition temperature, and deposition time play important roles in the process. Nowadays, chemical deposition is generally applied in preparing either pure nanomaterials or composite nanomaterials. For example, brookite-TiO$_2$/a-Fe$_2$O$_3$ nanoheterostructures have been synthesized via two-step facile chemical deposition without using any templates or surfactants [65], as shown in Figure 5.

![Figure 5](image-url)
Furthermore, chemical deposition combined with other methods can also be used to fabricate nanoheterostructures. Our group has recently reported the fabrication of Ag$_2$O/TiO$_2$/V$_2$O$_5$ nanoheterostructures (STV NHs) [84] through a two-step synthesis approach: the first step was the preparation of continuous TiO$_2$/V$_2$O$_5$ nanofibers (TV NFs) using an electrospinning method, and the second step was the deposition of Ag$_2$O nanoparticles on the TV NFs surfaces by the reaction of AgNO$_3$ solution and NaOH solution. Based on this facile method, some other nanoheterostructures could be easily obtained, such as TiO$_2$/CuO [85], TiO$_2$/LiCl [86], and TiO$_2$/FeOOH [87] nanoheterostructures.

It is worthy to note that room temperature chemical method is an efficient way to synthesize organic-functionalized TiO$_2$ nanoheterostructures, such as TiO$_2$/polypyrrole nanocomposites [88], TiO$_2$-diltiazem/tetrachlorobismuth core-shell nanospheres (TiO$_2$@DTMBi core-shell nanospheres) [89], polymer-functionalized TiO$_2$ nanorods [90], molecularly imprinted polymer on TiO$_2$ nanotubes (MIP@TiO$_2$ NTs) [91], polypyrrole/TiO$_2$ heterojunction (PPy/TiO$_2$ heterojunction) [78], and Prussian blue/TiO$_2$ nanowires (PB/TiO$_2$ NWs) [63]. Typically, Wang and his co-workers [92] have reported a simple, low cost, and effective chemical method to fabricate polythiophene/Pd/TiO$_2$ ternary composite nanoheterostructures, where TiO$_2$ spheres were synthesized in water/acetone solvent, and then the Pd species were loaded on the TiO$_2$ microspheres, finally the polythiophene was covered on the spheres to obtain polythiophene/Pd/TiO$_2$ ternary composites.

2.5. Hydrothermal/Solvothermal Technique

Hydrothermal/solvothermal methods are commonly applied in the synthesis of powdery nanostructures. In the typical process, reagents (such as amines) and precursors are firstly mixed with each other in an appropriate ratio and then injected into a solvent, which can not only speed up the precursor dissolution but also accelerate the reaction between reagent and precursor. Finally the solution is added into a special hydrothermal synthesis reactor for the reaction of reagent and precursor and the growth of nanomaterials at relatively high temperature and high pressure. For example, TiO$_2$/$\alpha$-V$_2$O$_5$ nanoheterostructures could be prepared through solvothermally treating TiO$_2$ nanoparticles in vanadium chloromethoxide precursor solution to growing V$_2$O$_5$ on TiO$_2$ nanoparticle surfaces [93]. Similarly, branched 1D $\alpha$-Fe$_2$O$_3$/TiO$_2$ nanoheterostructures [62] were synthesized by growing $\alpha$-Fe$_2$O$_3$ nanorods on the TiO$_2$ nanofibers using hydrothermal treatment. Figure 6 displays the SEM images of the branched $\alpha$-Fe$_2$O$_3$/TiO$_2$ nanoheterostructures, it can be observed that the sample is mainly formed by branch-like nanofibers with loose and rough surfaces. In addition, one-dimensional carbon nanotube (CNT)-TiO$_2$ heterostructures were prepared through a solvothermal route using multiwalled CNTs as templates [25]. As demonstrated by these examples, hydrothermal/solvothermal methods are suitable techniques to fabricate controlled nanoheterostructures.

Figure 6. SEM images of branched $\alpha$-Fe$_2$O$_3$/TiO$_2$ nanoheterostructures: (a,b) panoramic and (c,d) magnified [62]. Copyright 2013 American Chemical Society.
2.6. Sol-Gel Method

The sol-gel method is a representative wet chemistry technique for synthesizing TiO$_2$-based nanoheterostructures which involves relatively low growth temperatures and the morphology of the products can thus be controlled. The general process is as follows: first, prepare the sol gel, then heat the solution at high temperature combined with vigorous stirring to make it hydrolyze, finally carry out a condensation reaction to obtain nanomaterials. For instance, Lee et al. have fabricated a quartz crystal microbalance (QCZ) gas sensor based on the polyacrilic acid (PAA)/TiO$_2$ nanofilm, where the (TiO$_2$/PAA)$_n$ ($n = 5, 10,$ and $20$) nanofilms were deposited on gold-coated quartz crystal microbalance electrode using gas-phase surface sol-gel method [94].

2.7. Electrospinning

Since the electrospinning technique was first reported, more and more nanomaterials have been prepared by researchers via this simple method. During the typical process, a glutinous precursor solution is injected through a thin spinneret and then is stretched to form ultralong nanofibers; finally annealing the as-prepared samples at appropriate temperature can produce very highly crystalline nanofibers. In recent years, our group has successfully synthesized TiO$_2$/Ag$_{0.35}$V$_2$O$_5$ branched nanoheterostructures using a simple one-step electrospinning method [95,96]. The synthesis process of TiO$_2$/Ag$_{0.35}$V$_2$O$_5$ nanoheterostructures and characterization of the nanoheterostructures are presented in Figure 7.

![Figure 7](image-url)

**Figure 7.** (a) A diagram of the electrospinning process; (b–e) SEM images of (b,c) TiO$_2$ nanofibers and (d,e) TiO$_2$/Ag$_{0.35}$V$_2$O$_5$ branched nanoheterostructures; (f) N$_2$ adsorption/desorption isotherms and (g) XRD patterns of TiO$_2$ nanofibers and TiO$_2$/Ag$_{0.35}$V$_2$O$_5$ branched nanoheterostructures [95]. Copyright 2016 Nature.

In the typical electrospinning process, the consistence of the composite, working voltage, inner diameter of the spinneret, distance between the spinneret tip and the collector substrate, and annealing temperature can all affect the morphology of the nanomaterials. Furthermore, Ag/TiO$_2$ and TiO$_2$/V$_2$O$_5$ nanoheterostructures have also been prepared using the electrospinning process by our group [97–99]. What’s more, various type of TiO$_2$-based nanoheterostructures fabricated by electrospinning process
have been reported by other researchers, such as TiO$_2$/In$_2$O$_3$ [61], LiCl/TiO$_2$ [100], and Pt/TiO$_2$ [101] nanoheterostructures. Especially, Du’s group has synthesized TiO$_2$/ZnO core-sheath nanofibers using a coaxial electrospinning method [102].

3. Diverse Nanoheterostructural Gas Sensors

During the past decades, TiO$_2$ has attracted considerable attention because it was regarded as a promising candidate for waste gas detection. Unfortunately, the poor sensing activity of high resistance n-type TiO$_2$ seriously influences the development of TiO$_2$-based gas sensors. Recently, various heterostructured sensing materials have been reported. The coupling of different materials can result in improved sensing activity. In this section, we will focus on the sensing performance of multifarious TiO$_2$-based nanoheterostructure gas sensors, highlighting in particular, semiconductor/semiconductor nanoheterostructures.

3.1. Semiconductor/Semiconductor Nanoheterostructures

One of efficient ways to devise outstanding gas sensors is the modification of TiO$_2$ by coupling with other semiconductors to form nanoheterostructures, which could display enhanced sensitivity and selectivity, faster response/recovery times, and/or lower operational temperatures than pure TiO$_2$ [45,46,100,103,104]. Table 1 summarizes the different TiO$_2$-based semiconductor/semiconductor nanoheterostructures and their performance in the gas sensing detection field. For example, Zeng et al. [105] have successfully fabricated a novel gas sensor based on the SnO$_2$-TiO$_2$ hybrid nanomaterials.

Figure 8. (a–d) Gas response of the TiO$_2$ nanobelts and the SnO$_2$-TiO$_2$ hybrid oxides based sensors to 400 ppm methanol (a); ethanol (b); formaldehyde (c); and acetone (d) gases at different operating temperatures; (e) Response/recovery characteristics of the TiO$_2$ nanobelts and the SnO$_2$-TiO$_2$ hybrid oxides based sensors operated at 593 K to 400 ppm methanol, ethanol, formaldehyde, and acetone [105]. Copyright 2012 Royal Society of Chemistry.

They demonstrated that the SnO$_2$ nanospheres-functionalized TiO$_2$ nanobelts-based sensor displayed very outstanding sensing properties, higher response and lower operating temperature, than pure TiO$_2$ nanobelts-based sensors, as shown in Figure 8.
Table 1. Summary of the gas sensing properties of TiO$_2$-based semiconductor/semiconductor nanoheterostructure sensors.

| TiO$_2$-Based Nanoheterostructures | Fabrication Method | Size | Detection Gas | Detection Range | Operation Temperature ($^\circ$C) | Sensitivity | Response/Recovery Time | Concentration |
|------------------------------------|--------------------|------|---------------|----------------|-------------------------------|-------------|------------------------|--------------|
| TiO$_2$/Co$_3$O$_4$ acicular nanowires | hydrothermal + pulsed laser deposition | length: 1–3 μm; diameter: 200 nm | ethanol | 10–500 ppm | 160 | $R_a/R_a$, 65 | 100 ppm | [104] |
| nano-cylindrical Mn$_2$O$_3$/TiO$_2$ | electrochemical anodization + hydrothermal process | nanotubes diameter: ~150 nm; core nanorods diameter: ~50 nm | ethanol | 260 | $R_a/R_a$, 40 | 14.7/2 s | 100 ppm | [80] |
| TiO$_2$/TiO$_2$ tube-like nanostructures | hydrothermal + chemical deposition | diameter: 120 nm; length: 400 nm; outer wall thickness: 23.5 nm | ethanol | 0.5–500 ppm | 270 | $R_a/R_a$, 19.4 | 500 ppm | [107] |
| SnO$_2$-coated TiO$_2$ nanobelts | hydrothermal | TiO$_2$ nanobelts: length: over ten micrometers; width: 0.5–200 nm; SnO$_2$ nanosheets: length: 50–200 nm, thickness: 20 nm | ethanol | 10–500 ppm | 43 | $R_a/R_a$, 11.2 | 10 ppm | [108] |
| TiO$_2$/SnO$_2$ core-shell nanocomposites | hydrothermal treatment + chemical deposition | | ethanol | 500–5000 ppm | 200 | $R_a/R_a$, 12.7 | ≤5/50 s | 1000 ppm | [109] |
| SnO$_2$/TiO$_2$ composites | hydrothermal | | ethanol | 500–400 ppm | 320 | $R_a/R_a$, 27.5 | 400 ppm | [105] |
| Ag/SnO$_2$/TiO$_2$ nanocomposites | chemical deposition | nanobelts diameter: 50–200 nm; | ethanol | 100–800 ppm | 320 | $R_a/R_a$, 27.5 | 400 ppm | [104] |
| TiO$_2$/Ag$_2$O$_3$/V$_2$O$_5$/TiO$_2$ nanocomposites | electrospinning | nanobranches diameter: 10–20 nm; | ethanol | 20–1000 ppm | 350 | $R_a/R_a$, 24.6 | 100 ppm | [97] |
| ZnO/TiO$_2$ nanocomposites | electrospinning | nanobranchies diameter: 5–20 nm; | ethanol | 20–1000 ppm | 350 | $R_a/R_a$, 31.8 | 100 ppm | [97] |
| brush-like ZnO/TiO$_2$ heterostructure nanofilms | electrospinning + hydrothermal process | ZnO nanorods diameter: 100–300 nm; TiO$_2$ nanobelts diameter: 100 nm | ethanol | 20–500 ppm | 320 | $R_a/R_a$, 50.6 | 5/10 s | 500 ppm | [110] |
| TiO$_2$/ZnO nanocomposites | hydrothermal method + ALD | core width: 120 nm; shell width: 20 nm | ethanol | 5–25 ppm | 150 | $R_a/R_a$, 2.37 | 100/70 s | 10 ppm | [64] |
| ZnO/TiO$_2$ nanocomposites | | nanofibers diameter: 70–130 nm; ZnO nanosheets diameter: 500 nm | ethanol | 10–200 ppm | 280 | $R_a/R_a$, 15.7 | 5/3 s | 100 ppm | [111] |
| ZnO/TiO$_2$ nanocomposites | CVD | | ethanol | 400 | $R_a/R_a$, 5 | ~1/1 min | 50 ppm | [11] |
| brookite TiO$_2$ decorated a-Fe$_2$O$_3$ nanoheterostructures | chemical deposition | length: 50–100 nm; diameter: ~10 nm | butanol | 10–500 ppm | 320 | $R_a/R_a$, 27.6 | 5/6 s | 100 ppm | [62] |
| ZnO/TiO$_2$ nanocomposites | CVD | diameter: 5–20 nm | acetone | 20–100 ppm | 350 | $R_a/R_a$, 32.7 | 1/1 min | 100 ppm | [48] |
| ZnO/TiO$_2$ nanocomposites | CVD | | acetone | | $R_a/R_a$, 32 | | 100 ppm | [48] |
| CuO/TiO$_2$ heterostructure nanofibers | electrospinning + hydrothermal process | TiO$_2$ nanofibers: length: several tens micrometers; diameter: 200 nm; CuO nanorods: diameter: 40–800 nm | formaldehyde | 5–100 ppm | 200 | $R_a/R_a$, 15.5 | 50 ppm | [112] |
| ZnO/TiO$_2$ nanocomposites | sol-gel | | formaldehyde | 100–500 ppm | 320 | $R_a/R_a$, 52 | 25/17 s | 200 ppm | [113] |
| a-Fe$_2$O$_3$/TiO$_2$ branch-like hierarchical heterostructures | electrospinning + hydrothermal method | diameter: 600 nm; length: several micrometers | trimethylamine | 10–200 ppm | 250 | $R_a/R_a$, 13.9 | 0.5/1.5 s | 50 ppm | [62] |
| hierarchically assembled ZnO nanorods on TiO$_2$ nanobelts | hydrothermal process | ZnO nanorods: length: 50–200 nm; | trimethylamine | 5–500 ppm | 200 | $R_a/R_a$, 25 | 5 ppm | [114] |
| SnO$_2$/TiO$_2$ composites | sol-gel | | methanol | 50–400 ppm | 360 | $R_a/R_a$, 60 | 10–15/14–20 s | 200 ppm | [113] |
### Table 1. Cont.

| TiO$_2$-Based Nanoheterostructures | Fabrication Method | Size | Detection Gas | Detection Range | Response | Ref. |
|-----------------------------------|-------------------|------|---------------|-----------------|----------|------|
| ZnO/TiO$_2$ nanocomposites        | physical mixture  |      | humidity      | 5%–90% RH       | RT       | [59] |
| TiO$_2$/TiO$_2$ electrospin nanofibers | electrospinning | diameter: 150–260 nm | humidity | 11%–95% RH | RT | [100] |
| ZrSnO$_2$/TiO$_2$ nanofibers heterojunction | electrospinning + hydrothermal treatment | TiO$_2$ nanofibers diameters: 200–300 nm; ZrSnO$_2$ nanorods diameters: 0.5–1.5 nm; ratio of length to diameter: ~9.6 | humidity | 11%–95% RH | RT | [114] |
| ZrSnO$_2$/TiO$_2$ nanofibers heterojunction | electrospinning + hydrothermal treatment | TiO$_2$ nanofibers diameters: 200–300 nm; ZrSnO$_2$ nanorods diameters: 30–50 nm | humidity | 11%–95% RH | RT | [114] |
| CuO/TiO$_2$/SnO$_2$ thin film | sol-gel | polypyrrole-coated TiO$_2$ nanofibers heterojunction | electrospinning + hydrothermal treatment | TiO$_2$/SnO$_2$ core diameter: 100 nm; PPy shell thickness: 7 nm | NH$_3$ | 0.5–45 ppm | RT | [118] |
| nanocrystalline TiO$_2$/SnO$_2$ composites | commercial powder | TiO$_2$/SnO$_2$ nanoneedles | wet chemical method | diameter: 40–80 nm; length: 60–100 nm | NH$_3$ | 150 | (ΔR/R$_0$) × 100%: 300% | 3/5 min | 1000 ppm | [120] |
| TiO$_2$/SnO$_2$ thick film | sol | TiO$_2$/SnO$_2$ inner/outer double-layer hollow fibers | electrospinning + ALD mode | TiO$_2$/SnO$_2$ core diameter: 320 nm; TiO$_2$ layer thickness: 30 nm; ZnO outer layer thickness: 20 nm | CO | 0.1–10 ppm | 375 | ΔR/R$_0$: 20.3 | 1 ppm | [72] |
| TiO$_2$/Fe$_3$O$_4$ nanorods thin film | sputtering | Fe$_3$O$_4$ nanoparticles/TiO$_2$ nanocomposites | sputtering method | diameter: 20–30 nm | CO | ΔR/R$_0$: | 15 | ~0.5/s | 1000 ppm | [122] |
| TiO$_2$/Al$_2$O$_3$/Pd composites | sol | nanocrystalline CuO/ZnO/TiO$_2$ | ppyrolization | TiO$_2$ | H$_2$ | 200–1000 ppm | 225 | log(R/R$_0$) / (Ω/R): 0.9 | 1000 ppm | [40] |
| TiO$_2$ decorated CuO nanorods | thermal evaporative + sputtering | diameter: 50–100 nm; length: a few tens of micrometers | H$_2$ | 0.1–5 ppm | 300 | R$_p$/R$_0$: 8.57 | 5 ppm | [124] |
| TiO$_2$/SnO$_2$ nanocomposites | physical mixture | diameter: 8–20 nm | H$_2$ | 10–300 ppm | 375 | 50% | [76] |
| TiO$_2$ fibers supported β-FeOOH nanorods | electrospinning + hydrothermal method | nanofiber diameter: ~50 nm | H$_2$ | 100–500 ppm | RT | R$_p$/R$_0$: 52.5 | 500 ppm | [97] |
| nanocomposite Ni$_2$O$_3$/TiO$_2$ | sol-gel | diameter: 4.1 nm | H$_2$ | 450 ppm | R$_p$/R$_0$: 0.5 | 500 ppm | [121] |
| TiO$_2$/NO thin film | sputtering | NO$_2$ nanotubes | diameter: ≤200 nm; length: several micrometers | NO$_2$ | 0.9–97 ppm | RT | ΔR/R$_0$: 70–80% | 6/1 min | 97 ppm | [45] |
| Pd/TiO$_2$ thin film | sol-gel | Au nanorods | thermal evaporation + sputtering | Pd/TiO$_2$ | H$_2$ | 1%–10% | 140 | ΔR/R$_0$: 100%: | ~10/2 min | 2% | [103] |
| TiO$_2$-doped thin films | sol-gel | TiO$_2$ | diameter: 250 nm; length: several micrometers | NO$_2$ | 0.3–97 ppm | RT | ΔR/R$_0$: 1.25 | ~0.5/s | 1 ppm | [61] |
| SnO$_2$-core/V$_2$O$_5$-shell nanorods | thermal evaporation + sputtering | nanotube outer diameter ≤200 nm; length: several micrometers | NO$_2$ | 10–80 ppm | 300 | R$_p$/R$_0$: 1.03% | ≤4.5/4.5 min | 10 ppm | [127] |
| Al$_2$O$_3$ decorated anatase TiO$_2$ nanotubes | electrochemical anodization + thermal decomposition | nanotube outer diameter ≤200 nm; length: several micrometers | NO$_2$ | 0.97–97 ppm | RT | ΔR/R$_0$: 80–90% | 8/1 min | 97 ppm | [45] |
| CoO-TiO$_2$/Au nanosystems | CVD + sputtering | CoO | CVD | 300 ppm | [71] |
| V$_2$O$_5$/TiO$_2$ thin film | sputtering | V$_2$O$_5$ | thickness: 3–5 nm | CoO | 1 ppm–20.9% | 250 | R$_p$/R$_0$: 3.5 | 5/30 min | 120 ppm | [126] |
| CoO/TiO$_2$ thin film | sputtering | CoO | thickness: ~10,000 ppm | CoO | 0.5–450 ppm | 420 | R$_p$/R$_0$: | 3 | 40–60/80 | 1000 ppm | [129] |
| SnO$_2$/TiO$_2$ thin film | sputtering | SnO$_2$ | thickness: ~4–67 nm | SnO$_2$ | 0.5–200 ppm | 100 | R$_p$/R$_0$: | 2 | 1000 ppm | [130] |
Tomer and Duhan [104] reported a mesoporous Ag-(TiO$_2$/SnO$_2$) structure which exhibited high sensitivity, a low detection limit (1 ppm), and wide detection range (1 ppm to 500 ppm) to ethanol, as shown in Figure 9. Moreover, the mesoporous Ag-(TiO$_2$/SnO$_2$) nanohybrid sensor also displayed excellent stability and high selectivity for ethanol.

![Figure 9. Gas responses of different sensors (S-15: SBA-15, TS-s: TiO$_2$/SnO$_2$ (soft template), TS-h: TiO$_2$/SnO$_2$ (hard template), ATS-h: Ag-(TiO$_2$/SnO$_2$)) to ethanol operated at 275 °C, the inset is the calibration curve within the concentration ranging from 1 ppm to 50 ppm [104]. Copyright 2016 Royal Society of Chemistry.](image)

3.1.1. Sensing Mechanism

Although the mechanism of the heterostructures has not been investigated explicitly, it is clear that the enhanced sensing properties for semiconductor/semiconductor nanoheterostructures should be related to the heterojunction constructed at the interface between two semiconductors, where the changes of heterojunction energy barrier immersed into different gas atmospheres are benefit to the improvement of sensing properties.

One possible explanation for the enhancement of these heterostructure-based sensors is the heterojunctions formed between TiO$_2$ and other semiconductors. On the basis of band structures and conductivity type of the semiconductors, two main types of semiconductor/semiconductor heterostructures, n-n heterojunctions and p-n heterojunctions, can be considered. The work function (highest potential of valence band (VB)), electron affinity (lowest potential of CB), and bandgap of the coupled semiconductors determine the electron/hole dynamics in the heterojunctions. Since the work function of TiO$_2$ is different from that of coupling semiconductors, the electrons will transfer from one semiconductor to another, thus resulting in an additional depletion layer and an energy barrier at the interfaces of two semiconductors. Compared with the pure semiconductors, the conductivity of heterojunctions is mainly determined by the energy barrier, and the relationship between resistance and energy barrier of the heterojunctions can be presented by the following equation:

$$R \propto B \exp(q\Phi/kT)$$  \hspace{1cm} (3)

where $B$ is a constant, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $q\Phi$ is the effective energy barrier at the heterojunction. When the heterostructures are in an air atmosphere, the electrons can be adsorbed by oxygen molecules to turn into various oxygen ions including $O^-$, $O^{2-}$, and $O_2^-$, accordingly the height of the energy barrier in heterojunctions will increase, as shown in the first figure of Figure 10a. Similarly, the energy barrier height will further increase when put into oxidizing
gases, whereas in reducing gases, the gases can react with the oxygen ions and result in the release of adsorbed electrons, therefore the energy barrier height will decrease, as shown in the second figure of Figure 10a. According to Equation (3), $R_a/R_g$ is proportional to $\exp(\Delta \Phi q)$, thus the notable changes of energy barrier height can cause remarkable changes of the resistivity and superior enhancement of sensing properties for heterojunctions. For instance, $\text{Fe}_2\text{O}_3/\text{TiO}_2$ tube-like nanoheterostructures [107] and $\text{TiO}_2/\text{Ag}_{0.35}\text{V}_2\text{O}_5$ branched nanoheterostructures [95] based sensors exhibited improved ethanol sensing performance compared with pure matrix sensors.

![Figure 10](image.png)

Figure 10. The proposed sensing mechanism diagram of $\text{TiO}_2/\text{Ag}_{0.35}\text{V}_2\text{O}_5$ nanoheterostructures. (a) Schematic band structure of $\text{TiO}_2/\text{Ag}_{0.35}\text{V}_2\text{O}_5$ heterojunction exposed in air and ethanol gases ($q\Phi$: energy barrier); (b) Sensing model of the $\text{TiO}_2/\text{Ag}_{0.35}\text{V}_2\text{O}_5$ nanoheterostructured sensor in air (Steps 1–3) and in ethanol (Steps 4–5) [95]. Copyright 2016 Nature.

Additionally, a synergetic effect between different nanomaterials is also regarded as one of important reasons for the enhanced sensing properties of nanoheterostructures. In fact, the synergetic effect is related only to the situation where both of the pure materials exhibit high sensitivity to the tested gases [61].

It is well known that some metal oxide semiconductors are effective catalysts which can help decompose organic gases. Therefore, the catalytic effect of $\text{TiO}_2$ and other materials should be taken into account in the sensing performance enhancement of nanoheterostructures. For example, according to the previous reports by our group [98,131], the $\text{TiO}_2/\text{V}_2\text{O}_5$ nanoheterostructures can act as much more effective catalysts than pure $\text{TiO}_2$ nanofibers, and should be capable of promoting the sensing reaction between volatile organic solvents (VOCs) and oxygen ions adsorbed at the surface, thus a $\text{TiO}_2/\text{V}_2\text{O}_5$ nanoheterostructures-based ethanol sensor displays much higher sensitivity than a pure $\text{TiO}_2$-based sensor [97].

In addition to the heterojunction effect, synergetic effect, and catalytic effect, there may be other mechanisms in play for enhancing the sensing performance of nanoheterostructure. For example, Chen et al. [108] considered that the electron transfer are facilitated because of the formation of $\text{SnO}_2/\text{TiO}_2$ heterostructures, thus the gas sensing response including sensitivity and selectivity is efficiently enhanced as a result of increased charge carrier concentration.

Actually, there is more than one reason for the enhanced mechanisms of nanoheterostructure sensors. Park and coworkers [64] demonstrated that the improved ethanol sensing performance of $\text{TiO}_2$-core/$\text{ZnO}$-shell nanorods compared with that of pure $\text{TiO}_2$ nanorods might be due to more efficient catalytic activity of $\text{ZnO}$ and the potential barriers built in the heterojunctions. Wang and coworkers [61] found that the improved gas sensing activity of the porous single crystal $\text{In}_2\text{O}_3$
beads@TiO$_2$-In$_2$O$_3$ composite nanofibers (TINFs) could be ascribed to the Schottky junction formed between single crystal In$_2$O$_3$ beads and the Au electrode, the increased carrier density derived from the TiO$_2$ electron-donor, and the best gas absorption conditions provided by the surface-related defects, as shown in Figure 11.

![Figure 11. (a) Energy band diagram of In$_2$O$_3$ and TiO$_2$, EC: conduction band, EV: valence band; (b) I-V curves of In$_2$O$_3$ nanofibers (INFs) and In$_2$O$_3$ beads@TiO$_2$-In$_2$O$_3$ composite nanofibers (TINF2) thin film sensors in air at room temperature (the gate voltage Vg = 0.1); (c) The gas sensing reactions based on Schottky junction between Au electrode and In$_2$O$_3$ beads [61]. Copyright 2015 American Chemical Society.]

3.1.2. The Influence of Morphology on Sensing Performance

It is reasonable that the influence of nanoheterostructures morphology on sensing performance should be taken into account, where the gas sensitivity and the response/recovery time affected by gas absorption and gas diffusion can be improved by the large specific surface area and the especial morphology of materials. On the one hand, like for resistance-type gas sensors, the fundamental sensing process is the reaction of the target gases and the electrons at the surface of the sensing materials. Larger surface area means more surface active sites can be provided for gas absorption and reactions, resulting in more noticeable changes of resistance in different gases, consequently the sensitivity of the sensors can be improved. On the other hand, the electron exchange process can only occur within a thin layer, the width of this surface layer is determined by the Debye length ($L_D$) of the materials, which is defined by following equation:

$$L_D = \left( kT \varepsilon \epsilon_0 / q^2 n_c \right)^{1/2}$$  \hspace{1cm} (4)

where $T$ is the absolute temperature in Kelvin, $k$ is Boltzmann’s constant, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon$ is the static relative dielectric constant, $n_c$ is the carrier concentration, and $q$ is the electrical charge of the carrier. When $L_D$ is less or equivalent to the thickness of the nanostructures, the electrons in semiconductors can be totally depleted by the oxygen molecules adsorbed on the surface, thus will result in more evident resistance change after exposure in gases compared with that of not entirely depleted ones.

Hierarchical nanostructures are a particularly promising choice for further enhancing the sensing performance because of their extremely large specific surface area and/or thin thickness (less or
equivalent to \( L_D \)). As a matter of fact, several hierarchical TiO\(_2\)-based nanoheterostructures, such as branch-like \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) hierarchical heterostructure [62], hierarchically assembled ZnO nanorods on TiO\(_2\) nanobelts [114], SnO\(_2\) nanospheres functionalized TiO\(_2\) nanobelts [105], have been fabricated into gas sensors. In particular, Zhu and coworkers have reported that \( \beta\text{-FeOOH}/\text{TiO}_2 \) hierarchical heterostructures exhibited remarkably high sensitivity and reversibility [87]. Our group [95] demonstrated that the enhancement of the TiO\(_2\)/Ag\(_{0.35}\)V\(_2\)O\(_5\) gas sensor could be attributed to the extraordinary branched-nanofiber structures with large surface area and thin branch diameter (the semidiameter of the branches was equivalent to the depletion layer of the Ag\(_{0.35}\)V\(_2\)O\(_5\)), where more gas molecules could be absorbed and electrons in the Ag\(_{0.35}\)V\(_2\)O\(_5\) nanobranches could be totally depleted by the oxygen molecules adsorbed on the surface (Figure 10(b)). Furthermore, Deng et al. [110] have found that the enhanced performance of the ZnO-TiO\(_2\)-based gas sensors could be ascribed to the hierarchical structures, as shown in Figure 12, where the high specific surface area could result in a large number of gas molecules absorbed on the surface of ZnO-TiO\(_2\) nanoheterostructures when compared with the pure TiO\(_2\) nanofibers, additionally, well aligned structures of the nanoheterostructures would cause the unhindered gas diffusion to the whole surface of the sensor.

Figure 12. (a–d) SEM images of TiO\(_2\) nanofibers (a); ZnO nanorods (b); and ZnO-TiO\(_2\) nanoheterostructures (c,d); (e,f) Schematic diagram of catalytic reactions (e) and ideal band structure (f) of ZnO-TiO\(_2\) nanoheterostructures [110]. Copyright 2013 Elsevier.

In addition to island type hierarchical heterostructured sensors, core/shell type and hollow type nanoheterostructures have also attracted much attention in gas sensor research. Recently, Zhu et al. [107] synthesized tube-like Fe\(_2\)O\(_3\)/TiO\(_2\) core/shell nanoheterostructures (Figure 13). The special core/shell nanoheterostructures could act as a superior ethanol sensor material with
respect to the pristine one, as shown in Figure 13. Katoch and coworkers [72] demonstrated that TiO$_2$/ZnO double layer hollow fibers exhibited superior CO sensing performance compared to the ZnO single layer hollow fibers, as shown in Figure 14a. The enhancement was ascribed to the fact that the electrons in ZnO outer layer could be easily absorbed to TiO$_2$ inner layer, thus ZnO would become more resistive owing to the noticeable loss of electrons, as shown in Figure 14(b,c). When exposed in CO gas atmosphere, the resistance of ZnO outer layer would partially regain its original value, this could lead to more noticeable resistance change for the TiO$_2$/ZnO double layer hollow fibers in detecting CO gas.

**Figure 13.** (a) Sensing response of the Fe$_2$O$_3$/TiO$_2$ tube like nanoheterostructures to ethanol at different temperatures; (b) Time dependent sensing response of the Fe$_2$O$_3$/TiO$_2$ tube like nanoheterostructures to ethanol vapor at 270 °C [107]. Copyright 2012 American Chemical Society.

**Figure 14.** Cont.
Third, since TiO$_2$ displays n-type semiconductor characteristic and carbon group-materials (graphene, CNTs) display p-type semiconductor characteristic, hence, a competitive mechanism may occur surrounding the carbon-group-materials/TiO$_2$ heterojunctions, which can lead to enhanced gas sensitivity owing to the decrease of the work function (barrier height) or increase of the conductivity of TiO$_2$ sensitive layer [144,145]. Furthermore, the catalytic activity of TiO$_2$ should also be considered as one of important reasons for the improved sensing performance of carbon-group-materials/TiO$_2$ nanoheterostructures [146,147].

As an emerging carbon material, graphene is regarded as a promising candidate for application in gas sensors due to its huge surface area, high electrical conductivity, inherently low electrical noise, environmental ultra-sensitivity, and ease microfabrication. In particular, the combination of graphene and TiO$_2$ can achieve efficiently improved sensing performance.

3.2. Carbon-Group-Materials/Semiconductor Nanoheterostructures

The formation of carbon-group-materials/semiconductor heterostructures is also an important technique to improve the gas sensing performance of TiO$_2$. In recent years, carbon-group-materials have attracted much attention for applications in gas sensors [1,12,15,132]. The nanostructured carbon materials including carbon nanotubes (CNTs) and graphene possess outstanding physical, chemical and electrical properties, such as good flexibility, large surface area, high chemical stability, and high electrical conductivity [14,133]. These excellent features make them extremely suitable for use as candidates in enhancing semiconductors’ sensing properties [132,134–136]. It has been demonstrated that the absorptivity, conductivity, and/or electrochemical reaction of some small gas molecules of carbon/TiO$_2$ nanoheterostructures could be promoted, thus the nano-heterostructures can display remarkably improved sensing performance [75,137–139]. Table 2 summarizes the carbon/TiO$_2$ nanoheterostructures and their performance in the detection of gases.

The mechanism of enhanced gas sensing performance of the carbon/TiO$_2$ nanoheterostructures is proposed to occur as follows: first, carbon-group-materials possess huge specific surface areas and nanoscale structures, thus a large number of surface sites are exposed for reacting with gases, therefore various gases can be easily detected at lower operating temperatures [140,141]. Second, the electric conductivity of carbon-group-materials is much higher in comparison with TiO$_2$, this can reduce the resistance and enhance the electrons transport capability of heterostructured sensors, thus making the nanoheterostructures based sensors work at lower operating temperature [142,143]. Third, since TiO$_2$ displays n-type semiconductor characteristic and carbon group-materials (graphene, CNTs) display p-type semiconductor characteristic, hence, a competitive mechanism may occur surrounding the carbon-group-materials/TiO$_2$ heterojunctions, which can lead to enhanced gas sensitivity owing to the decrease of the work function (barrier height) or increase of the conductivity of TiO$_2$ sensitive layer [144,145]. Furthermore, the catalytic activity of TiO$_2$ should also be considered as one of important reasons for the improved sensing performance of carbon-group-materials/TiO$_2$ nanoheterostructures [146,147].

![Schematic diagrams of sensing mechanism](image_url)
Table 2. Summary of the gas sensing properties of carbon-group-materials/TiO\textsubscript{2} nanoheterostructure sensors.

| TiO\textsubscript{2}-Based Nanoheterostructures | Fabrication Method                  | Size                  | Detection Gas | Detection Range | Operation Temperature (°C) | Sensitivity | Response/Recovery Time | Concentration |
|-----------------------------------------------|-------------------------------------|-----------------------|---------------|-----------------|-----------------------------|-------------|------------------------|---------------|
| Pd/TiO\textsubscript{2}/reduced graphene oxide ternary composite | one-pot polyol                      | NH\textsubscript{3}   | 5–150 ppm     | RT              | \((\Delta R/R_a) \times 100\%: 39.9\%\) |             | 100 ppm                |               |
| PPy/graphene nanoplatelets decorated TiO\textsubscript{2} nanoparticles | sol-gel + chemical polymerization  | TiO\textsubscript{2} nanoparticles diameter: 10–30 nm | NH\textsubscript{3} | 1–200 ppm     | RT \((\Delta R/R_a) \times 100\%: 102.2\%\) | 36/16 s     | 50 ppm                 |               |
| CNTs/TiO\textsubscript{2} nanocomposites    | screen-printing + dip-coating techniques | NH\textsubscript{3}   | RT            | \(\Delta R/R_a: 93\) | 9/2 min                    |             | 1%                     |               |
| Pt/TiO\textsubscript{2}/MWCNTs nanocomposites | sol-gel                            | diameter: 100 nm, length: 14 \textmu m | H\textsubscript{2} | 5–100%         | RT \((\Delta R/R_a) \times 100\%: 30\%\) | 50          | 70%                    |               |
| CNTs/Pt-TiO\textsubscript{2} NTs            | anodization                        |                       | H\textsubscript{2} | 0.5–3%         | 100 \((\Delta R/R_a) \times 100\%: 2\%\) |             | 1%                     |               |
| Pt-TiO\textsubscript{2}/MWCNTs hybrid composites | wet chemical procedure             | H\textsubscript{2}   | 0.5–3%        | 150             | 0.5%                     |             | 0.5%                   |               |
| rGO/TiO\textsubscript{2} thin film          | formaldehyde                       | formaldehyde         | 0.1–1 ppm     | RT              | \((\Delta R/R_a) \times 100\%: 0.64\) | 70/128 s    | 1 ppm                  |               |
| MWCNTs/TiO\textsubscript{2} nanocomposites | sol-gel                            | diameter: 20–40 nm   | CO             | 350             | \(R_0/R_\infty: 15.8\) | 4/16 s      | 50 ppm                 |               |
| MWCNTs/TiO\textsubscript{2} thin film       | sol-gel                            | CO                    | 400           | \(R_0/R_\infty: 89.2\) | 5.16/2.72 s | 100 ppm               |               |
| graphene-TiO\textsubscript{2} nanocomposite | sol-gel                            | TiO\textsubscript{2} nanoparticles: ~35 nm | CO\textsubscript{2} | 500–15,000 ppm | 200 \(R_0/R_\infty: 1.34\) |               | 10,000 ppm            |               |
| TiO\textsubscript{2}/carbon black           | sol-gel                            | CO2                  | 1–100 ppm     | 150             | \(\Delta R/R_\infty: 100\%: 7\%\) |             | 100 ppm                |               |
| single-walled carbon nanotube/TiO\textsubscript{2} hybrid      | sol-gel                            | NO\textsubscript{2}   | 50 ppb–1 ppm  | RT \((\Delta R/R_a) \times 100\%: 9\%\) |               | 50 ppb                 |               |
| CNT/TiO\textsubscript{2} hybrid films       | sol-gel                            | O\textsubscript{2}   | 10 ppm        | 350             | \(\Delta R/R_\infty: 6.5\) | 8/s         | 10 ppm in CO\textsubscript{2} |               |
| graphene oxide/nano-anatase TiO\textsubscript{2} | sol-gel                            | humidity            | 35–95%        |                 | power loss/\(\Delta RH = 0.47\) dB/%RH | 0.74/0.91 s |               |               |

Ref. [142] [146] [148] [149] [150] [140] [151] [152] [144] [153] [140] [154] [141]
In Ye’s research [75], rGO/TiO$_2$ layered thin film were prepared on the interdigital electrode substrates via a spray method. Formaldehyde sensing tests demonstrated that the layered thin film exhibited high sensitivity (0.905 ppm$^{-1}$), and a reversible and linear response to 0.1–0.5 ppm formaldehyde at room temperature, and that this could be ascribed to the positive synergetic effect of the two materials, as shown in Figure 15. Xiang and coworkers [146] developed a room-temperature sensitive NH$_3$ gas sensor using TiO$_2$@PPy-graphene nanocomposites. The sensor displayed high sensitivity (102.2%), superior reproducibility, and excellent selectivity to 50 ppm NH$_3$. Additionally, Wang et al. [147] synthesized TiO$_2$/graphene composite film for O$_2$ sensing upon exposure to UV light. They found that the outstanding sensitivity of the composite film could be ascribed to the synergetic effect of the ultrasensitivity of single-layer graphene to the environment and photocatalytic activity of TiO$_2$.

![Figure 15. (a) response curves and (b) response values of pure rGO and rGO/TiO$_2$ layered films to 0.1–0.5 ppm CH$_2$O [75]. Copyright 2015 Elsevier.](image)

Like graphene, CNTs have also been widely studied as preeminent gas sensing materials. Recently, multifarious effort has been devoted to the design and fabrication of CNTs/metal oxide nanocomposites [138,139,149,155]. The new composite materials will maintain the original properties of each component, or even show a synergistic effect, which is exceedingly significate to sensing performance. For example, Llobet et al. [154] proposed an effective O$_2$ sensor based on CNTs/TiO$_2$ hybrid films. The researchers compared the sensing properties of CNTs/TiO$_2$ hybrid film and Nb-doped TiO$_2$ films, and the results showed that the sensitivity of former was four times higher than that of latter, as shown in Figure 16. The outstanding sensing performance of CNTs/TiO$_2$ hybrid films arose from their very large surface area because of the central hollow cores and outside walls of CNTs. Luca and coworkers [149] have developed a room temperature sensor using Pt/TiO$_2$/MWCNTs composites. The results showed that increased resistance in response to H$_2$ possibly indicated a p-type conduction mechanism of the composite sensing material. Lee et al. [151] have demonstrated that the MWCNTs/TiO$_2$ xerogel composites film possessed better sensing performance. Compared with pure TiO$_2$ xerogel, the nanocomposites displayed improved sensitivity (15.8), and lower response/recovery times (4/16 s), as shown in Figure 17. The improved sensing properties could be attributed to the increased surface-to-volume area and enhanced conductivity which were benefit from the p-n heterojunction formed at the interface of MWCNTs and TiO$_2$. This result could also be confirmed by Kim et al. [152] who prepared a MWCNTs-modified direct-patternable TiO$_2$ thin film based CO gas sensor. It was found that the incorporation of MWCNTs could induce increase of surface morphology and roughness and thus resulted in promoted sensing performance.
Figure 16. (a,b) HRTEM images of CNT/TiO$_2$ nanocomposites; (c–e) Response to 10 ppm of O$_2$ in CO$_2$ flow at 450 °C for (a) a TiO$_2$/MWCNT sensor annealed at 500 °C; (b) a TiO$_2$/MWCNT sensor annealed at 600 °C; and (c) a Nb-doped TiO$_2$/MWCNT sensor annealed at 500 °C [154]. Copyright 2008 Institute of Physics.

Figure 17. (a) SEM image of MWCNTs/TiO$_2$ xerogel film; (b) CO sensing properties of pure TiO$_2$ xerogel film and MWCNTs/TiO$_2$ xerogel film to 50 ppm CO at 350 °C [151]. Copyright 2013 Elsevier.

3.3. Organic/Inorganic Nanoheterostructures

Nowadays, more and more requirements for gas sensors applied in the safety control and environmental monitoring have been put forward. In these efforts, designing and manufacturing suitable and efficient sensing materials is an important factor in obtaining highly efficient sensors [156]. In recent years, conductive polymers were considered a promising sensing element because of the...
significant changes in electrical and optical properties of such materials exposed in different gas atmospheres. In particular, the simple preparation and high sensing performance at room temperature of these polymers make them more acceptable for applications in many fields [157].

Conducting polymer-based nanocomposites composed of metal oxides nanomaterials and conducting polymers have been well developed, and the corresponding sensors exhibit great potential in probing various hazardous gases [91] due to their enhanced sensing properties, such as fast and reversible responses to target gases at room temperature [92], and more noticeably, that defined organic material modified semiconductor sensors exhibit outstanding sensing selectivity to a single gas species because of their exclusive chemical and electronic conditions [6,158–160]. Particularly, organic-functionalized TiO$_2$ nanoheterostructures also exhibit significantly improved characteristics in gas sensing compared with pure TiO$_2$ nanomaterials [83,91,94,161,162] and thus have been investigated by several research groups, as shown in Table 3.

Till now, a number of literatures proposed the sensing mechanism of polymer/TiO$_2$ nanoheterostructures. One of generally accepted factor is that the nanostructures of the heterostructures are beneficial to the high sensing properties, which mainly result from their large specific surface areas and much more active sites for the adsorption and interactions with the gases [163–165]. What is more, the formation of heterojunction at the interface between TiO$_2$ and polymers is usually regarded as a main factor for the ultrahigh sensitivity of the nanoheterostructures [83]. At the heterostructure interface, the electrons will transfer from the material with higher Fermi level to another with lower Fermi level, while the holes will transfer rightabout until the Fermi levels is equalized. In this process, electron depletion layer, an efficient current switch, will form at the interface of the heterostructures, thus leading to high gas sensitivity [166–168].

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**Figure 18.** (a,b) Atomic force microscope (AFM) images of the surface morphology of PAA25 (a) and PAA400 (b) deposited on TiO$_2$ gel-immobilized mica; (c) Dynamic responses of the quartz crystal microbalance (QCM) electrode coated with a (TiO$_2$/PAA400)$_{20}$ film to ammonia at different concentrations. The inset shows a comparison of the calibration curves with data taken at different times; (d) Calibration curves for (TiO$_2$/PAA)$_n$ ($n = 5, 10,$ and $20$) films [94]. Copyright 2010 American Chemical Society.
Table 3. Summary of the gas sensing properties of TiO$_2$-based organic/inorganic nanoheterostructure sensors.

| TiO$_2$-Based Nanoheterostructures | Fabrication Method | Size | Detection Gas | Detection Range | Operation Temperature (°C) | Sensitivity | Response Time | Concentration |
|-----------------------------------|--------------------|------|---------------|-----------------|----------------------------|-------------|---------------|---------------|
| TiO$_2$/PPy nanocomposites        | in situ chemical polymerization | 33–67 nm | NH$_3$ | 20–140 ppm | RT | $(\Delta R/R_a) \times 100\%: 7.95\%$ | 19/85 s | 141 ppm | [88] |
| PPy-coated TiO$_2$/ZnO nanofibers | electrospinning + chemical deposition | TiO$_2$/ZnO core diameter: 100 nm; PPy shell thickness: 7 nm | NH$_3$ | 0.5–450 ppm | RT | $\Delta R/R_a$: 0.35 | 450 ppm | [118] |
| PPy/TiO$_2$ nanocomposites        | layer by layer self-assembly technology | NH$_3$ | 10–1600 ppm | RT | frequency shift (AF): 50 Hz | ~100/200 s | 10 ppm | [165] |
| PPy/TiO$_2$ nanofibers            | in situ polymerization | NH$_3$ | 20–500 ppm | RT | $\Delta R/R_a$: 0.13 | 100 ppm | [169] |
| PANi/TiO$_2$ nanocomposites       | electrosprinning | diameter: 600 nm | NH$_3$ | >50 ppt | RT | $\Delta R/R_a$: 0.018 | <10/10 s | 200 ppt | [49] |
| PANi/TiO$_2$ thin film heterojunction | chemical polymerization + sol-gel | NH$_3$ | 20–100 ppm | RT | $(\Delta R/R_a) \times 100\%: -11\%$ | 41/s | 100 ppm | [74] |
| polyaniline/TiO$_2$ nanorods heterostructure | hydrothermal method | NH$_3$ | 5–100 ppm | RT | $(R_g/R_a) \times 100\%: 610\%$ | 40/60 s | 100 ppm | [167] |
| cellulose/TiO$_2$/PANI composite nanofibers | electrosprinning | NH$_3$ | 10–250 ppm | RT | $\Delta R/R_a$: 0.584 | 10 ppm | [168] |
| TiO$_2$/PANI/PA6 nanofibers        | electrospinning + sputtering | NH$_3$ | 50–250 ppm | RT | $\Delta R/R_a$: 18.3 | <50/50 s | 250 ppm | [170] |
| PANi/TiO$_2$ nanocomposite thin film | in situ self-assembly technique | diameter: 90 nm | NH$_3$ | 20–140 ppm | RT | $\Delta R/R_a$: 0.3 | 2–3/~60 s | 1 ppm | [88] |
| CSA/PANI/TiO$_2$ thin film | sol-gel | NH$_3$ | 20–100 ppm | RT | $\Delta R/R_a$: 0.75 | 49/413 s | 100 ppm | [171] |
| TiO$_2$–PANI nanocomposite thin film | spin coating | CO$_2$ | 53–1000 ppm | RT | $R_g/R_a$: 53 | 9.2/5.7 min | 1000 ppm | [164] |
| PANi doped TiO$_2$ nanocomposite thin film | spin coating | LPG | 21 nm | RT | $R_g/R_a$: 2.37 | 2.6/2.4 min | 200 ppm | [164] |
| TiO$_2$/PPy/poly 3-[methacryloylaminopropyl trimethylammonium chloride] (PMAPTAC) nanocomposite thin film | in situ photopolymerization | humidity | 13–90% RH | RT | log Z: ~6 | 30/45 s | 60% | [172] |
| TiO$_2$/PPy nanocomposite film | in situ photopolymerization | humidity | 30–84% RH | RT | log Z: ~5.5 | 40/20 s | 30% | [173] |
Polyacrylic acid (PAA) is one of the appropriate choices for probing NH$_3$ gas because the free carboxylic functional groups present on the PAA surface possess high sensitivity and selectivity to NH$_3$ molecules [174]. The incorporation of PAA and metal oxide nanomaterials may solve the long recovery time at higher NH$_3$ concentration (>1 ppm) and undesired sensitivity to humidity of the existing inorganic semiconductor sensors [175]. For instance, Lee and coworkers [94] have demonstrated that TiO$_2$/PAA-based amine gas sensors exhibited fast and stable response in a wide relative humidity range of 30%-70%, furthermore, a good linear response was also observed in the NH$_3$ concentration range between 0.3 ppm and 15 ppm, as shown in Figure 18. One of possible reasons for the decreased influence of humidity on gas sensitivity was that the presence of the TiO$_2$ would suppress the mobility of PAA, therefore the influence of water molecules on the sensing response would be reduced. As another very interesting conducting polymer, polypyrrole (PPy) has been widely investigated due to its relatively good environmental stability and easily controlled surface carrier properties adjusted by altering the dopant species in PPy during the synthetic process [169]. Accordingly, a number of researchers have attempted to enhance the gas sensing performance of TiO$_2$ by introducing PPy to form organic/inorganic nanoheterostructures. For example, Bulakhe and coworkers [83] have prepared a PPy/TiO$_2$ heterojunction-based liquefied petroleum gas (LPG) sensor which could operate at room temperature. The maximum sensing sensitivity of 55% to 1040 ppm LPG was observed, as shown in Figure 19. Compared with other room temperature LPG sensors, the PPy/TiO$_2$ heterojunction-based sensor could work at low LPG concentrations and showed promoted response/recovery times (112/131 s), indicating the PPy/TiO$_2$ heterojunction was a promising choice for a room temperature LPG sensor. Furthermore, Tai et al. [88] have investigated the NH$_3$ sensing performance of TiO$_2$/PPy nanocomposite ultrathin films. The results revealed that the TiO$_2$/PPy ultrathin film presented outstanding sensing performance, such as shorter response/recovery time comparing with pure PPy thin film based sensor. Additionally, in the work of Wu et al. [169], the PPy/TiO$_2$ composite thin film based sensor displayed much lower detection limit of 2 ppm to NH$_3$ gas. The improvement of sensing performance of PPy/TiO$_2$ heterostructures is mainly attributed to the formation of p-n junctions at the interface between TiO$_2$ and organic PPy.

![Figure 19. Gas response of a PPy/TiO$_2$ heterojunction at a fixed voltage of +0.6 V at concentration of 1040 ppm of LPG [83]. Copyright 2013 Elsevier.](image)

Moreover, polyaniline (PANi) has attracted much attention in commercial applications due to its excellent environment stability, novel photoelectrical and electrical characteristics, and easy fabrication [170]. It has been demonstrated that combining TiO$_2$ with PANi can enhance the sensitivity, selectivity, and stability of the resulting sensors [88]. For example, Gong et al. [49] have reported an
ultrasensitive NH$_3$ gas sensor based on PANi/TiO$_2$ fibers p-n heterojunctions, it was found that the p-n heterojunctions could act as electronic transmission switches when NH$_3$ gas was absorbed by PANi, thus resulting in the enhancement of sensing properties. Similarly, using TiO$_2$ nanoparticles modified PANi fibers as sensor, a fast response of 2–3 s and a low detection limit of 1 ppm at room temperature were obtained by Tai et al. [88]. Additionally, Pawar et al. [74] have also investigated the sensing performance of nanostructured PANi/TiO$_2$ films synthesized via a spin-coating method on glass substrates, the results revealed that the nanocomposites film exhibited much enhanced sensing performance, such as higher sensitivity and lower response/recovery time toward NH$_3$ at room temperature, as shown in Figure 20.

Figure 20. (a–f) SEM images of PANi (a); TiO$_2$ (b); and PANi–TiO$_2$ (20–50 wt %) films (c–f); (g) Response of the pure TiO$_2$, pure PANi, and nanocomposite of the PANi-TiO$_2$ film toward 100 ppm NH$_3$ gas at room temperature [74]. Copyright 2012 Wiley.
4. Conclusions

In the last few decades, continuous breakthroughs in the fabrication, modification and application of TiO$_2$-based gas sensors have been reported. In this review, we describe the universal tactics and new progress in the preparation of TiO$_2$-based nanoheterostructures for exhaust gases detecting. We focus on then synthetic methods and sensing performances of TiO$_2$-based nanoheterostructures, including semiconductor/semiconductor nanoheterostructures, noble metal/semiconductor nanoheterostructures, carbon-group-materials/semiconductor nanoheterostructures, and organic/inorganic nanoheterostructures, which are summarized as follows:

1) Coupling TiO$_2$ by with other semiconducting materials to form heterostructures could result in enhanced sensitivity and selectivity, faster response/recovery times, and/or lower operational temperatures than pure TiO$_2$. The enhanced sensing properties could be related to the heterojunctions formed at the interface between two semiconductors, the synergetic effect and catalytic effect. Additionally, the influence of the nanoheterostructures' morphology on sensing performance should also be taken into account, where the gas sensitivity and the response/recovery time affected by gas absorption and gas diffusion can be promoted by the specific surface area and the special morphology of structures. As compared with other types of nanoheterostructure-based sensors, the minimization of detectable levels of the semiconductor/semiconductor nanoheterostructure-based sensors might not bear comparison with the carbon-group-materials/semiconductor nanoheterostructures, and their operation temperatures might be higher than that of noble metal/semiconductor nanoheterostructures and organic/inorganic nanoheterostructures, however, their most excellent stability make the semiconductor/semiconductor nanoheterostructures more acceptable when applied in many fields.

2) Combining carbon-group-materials with TiO$_2$ is considered an efficient way to improve the gas sensing performance of TiO$_2$. It has been demonstrated that the absorptivity, conductivity, and/or electrochemical reactions of some small gas molecules with carbon/TiO$_2$ nano- heterostructures could be promoted, thus the nanoheterostructures can display remarkably improved sensing performance. Remarkably, carbon-group-material/semiconductor nano- heterostructure-based sensors display the most outstanding minimum detectable levels as compared with other nanoheterostructures, which could be attributed to their large surface area and the high electrical conductivity of the carbon-group-materials.

3) Conducting polymer-functionalized TiO$_2$ nanoheterostructures have also been demonstrated to be some of most promising materials for gas detection. These nanoheterostructures possess fast and reversible responses at room temperature due to the formation of organic/inorganic heterojunctions. It is noticeable that defined organic material modified semiconductor sensors exhibit outstanding sensing selectivity to a single gas species because of their exclusive chemical and electronic conditions. As a type of typical room temperature sensor, the controllable sensing selectivity of organic/inorganic nanoheterostructures is an outstanding characteristic that other types of nanoheterostructures do not possess.

In summary, much progress has been achieved in investigation of TiO$_2$-based nanoheterostructured sensors, and they are widely applicable in the detection of various gases such as H$_2$, CO, NH$_3$, H$_2$O, VOCs, etc. However, there are still some challenges in designing high-performance nanoheterostructured gas sensors. First, although the TiO$_2$-based nano- heterostructured gas sensors can respond to various gases based on the resulting resistance changes, a single sensor cannot discriminate different analytes, and the response is susceptible to other gases. Thus, most current studies are focused on the quantitative analysis of target gases using only simple matrices rather than complex matrices and actual samples. To meet the needs of practical applications, one possible solution is combing multiple sensors in a multimodal module sensor system, which can display distinctive response patterns across the array in probing different actual samples. Second, the understanding to
the electrons transport and response on the interfaces of nanoheterostructures is not detailed enough, which is critical for the design and optimization of highly efficient sensors. Therefore it is necessary to further elucidate the dynamic behavior of electrons at the interface and surface of nanoheterostructures so that researchers can design TiO\(_2\) based nanoheterostructures more rationally. Furthermore, although a variety of synthetic methods have been successfully used for preparing TiO\(_2\)-based nanoheterostructured sensors in the laboratory conditions, but these are far away from the large quantity industrial production. In addition, the chemical stability of TiO\(_2\) based nanoheterostructures is still poor, which seriously hampers the performance and wide application of the sensors. Therefore, the in-depth understanding of the sensing mechanism and the establishing of general and reasonable design guidelines in TiO\(_2\) based nanoheterostructured sensors are significant to achieve substantial breakthroughs in the practical application of the sensors.

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