Glucose-Mediated Synthesis of Hierarchical Porous ZnGa$_2$O$_4$ Microspheres for Effective Photocatalytic Removal of Aromatic and Arsenic Pollutants

Qinfen Tian 1,2, Shiming Ren 2, Zaiwei Cai 2, Changhao Chen 2, Yi Zheng 1,*, and Jiandong Zhuang 2,*

1 State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350116, China; tianqinfen@163.com
2 College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China; ren064913sm@163.com (S.R.); cai709829984@163.com (Z.C.); cch545891208@163.com (C.C.)
* Correspondence: yizheng@fzu.edu.cn (Y.Z.); jdzhuang@gmail.com (J.Z.)

Received: 29 July 2019; Accepted: 19 September 2019; Published: 1 October 2019

Abstract: Porous ZnGa$_2$O$_4$ microspheres (P-ZGO) are synthesized by a facial glucose-mediated microwave hydrothermal method followed by annealing. The morphological, photoelectric and photocatalytic properties of the as-prepared P-ZGO sample are characterized in detail, and the results show that the P-ZGO photocatalyst has a good crystallinity, large specific surface area, hierarchical mesoporosity, and distinguished photoelectric properties. Under 254 nm UV irradiation, the P-ZGO sample shows a much higher activity and stability than TiO$_2$ in the photocatalytic degradation of gas-phase aromatic pollutants. The average conversion efficiencies of toluene and benzene over P-ZGO are ~56.6% and ~44.3%, and with corresponding mineralization rates of ~86.3% and ~65.2%, respectively. No remarkable deactivation of P-ZGO is observed in a 60 h heterogeneous photoreaction. Furthermore, the as-prepared P-ZGO sample also shows an excellent photocatalytic efficiency (up to 99.8%) for the liquid-phase As(III) removal from water. The distinguished photocatalytic performance of P-ZGO can be ascribed to its unique electronic structures and hierarchical morphologies. According to the results of our analysis, a possible mechanism is also proposed to elaborate the photocatalytic oxidation process in the pollutants/P-ZGO system.

Keywords: ZnGa$_2$O$_4$; glucose-mediated microwave hydrothermal method; hierarchical porous microspheres; aromatic pollutants mineralization; As(III) removal

1. Introduction

Photocatalytic oxidation technology using semiconductors (TiO$_2$, ZnO, etc.) as photocatalysts has been verified to be a “green” and sustainable approach for ecological environment remediation [1–4]. In the past decades, most applications have been focused on the purification of the indoor air environment (volatile organic compounds, VOCs) and water environment (heavy metal cations and organic pollutants) at a room temperature [5–8]. Nevertheless, the practical performance of most semiconductor photocatalysts requires a further enhancement due to its low quantum efficiency or easy deactivation. Intense efforts have therefore been carried out to promote the photocatalytic efficiency and service performance by modifying semiconductors [9–11], optimizing reaction conditions [12,13], and developing novel high-performance photocatalysts [14,15].

To date, many studies have reported that the p-block semiconductors are a new generation of extremely effective and stable photocatalysts for environmental remediation. Zinc Gallate (ZnGa$_2$O$_4$), a typical p-block wide bandgap semiconductor, exhibits an excellent photocatalytic performance in environmental purification [16–18], the reduction of CO$_2$ to methane [19] and water splitting [20,21].
The outstanding photocatalytic performance of ZnGa$_2$O$_4$ could be attributed to its subtle electronic structure and unique photoelectric feature. As shown in the density of states (DOS) spectra (Figure 1), the highly dispersed conduction band (CB) of ZnGa$_2$O$_4$, which is composed of the Ga 4s4p, Zn 4s4p and O 2p orbitals, could enhance the mobility of photo-generated electrons and thus be beneficial in improving the separation of charge carriers [20,22]. In combination with its width bandgap structure, the ZnGa$_2$O$_4$ is expected to provide photogenerated charges with a strong redox capability for an excellent photocatalytic performance [23,24].

Besides the electric structure, the rational design of the morphology also plays a significant role in regulating the photocatalytic performance of semiconductors [25,26]. Enormous ZnGa$_2$O$_4$ materials with different morphologies (such as nanoprisms [21], nanoflowers [25], nanocubes [27], core-shell spheres [28], etc.) have been reported for improving the photocatalytic performance. Among them, large specific surface areas combined with hierarchical porous architectures have proven to be a universally applicable model for the rapid mass transfer and high-efficient reaction of reactants. The one-pot hydrothermal/solvothermal synthesis of a mixture including metal salts and carbohydrate precursors has been confirmed to be an efficient and convenient approach for obtaining the mesoporous metal-oxides microspheres [29–32].

![Figure 1. The total and atomic densities of the states of ZnGa$_2$O$_4$.](image_url)

In this study, our “brick-mortar” strategy is therefore to use a carbonaceous polymer (from the polycondensation of a carbon precursor) as “mortar” to assemble ZnGa$_2$O$_4$ nanograins (as “brick”) into microspheres [33]. Then, after the simple removal of the “mortar” by calcination, the hierarchical mesoporous building (i.e., ZnGa$_2$O$_4$ microspheres) can be readily obtained. The photocatalytic performances of porous ZnGa$_2$O$_4$ microspheres under irradiation are evaluated via the photocatalytic efficiencies for VOC (i.e., benzene and toluene) degradation and Arsenite (As(III)) removal, respectively. It is found that the unique electric structure and the porous morphologies make ZnGa$_2$O$_4$ a highly potential photocatalyst for general environmental remediation applications.

2. Results and Discussion

2.1. Phase Compositions and Morphologies of ZnGa$_2$O$_4$

Figure 2 shows the XRD patterns of the as-prepared ZnGa$_2$O$_4$ powders. Obviously, the n-ZGO sample (curve a) is well-crystallized, and its diffraction peaks are well matched with the characteristic patterns of cubic phase ZnGa$_2$O$_4$ with a spinel structure (JCPDS-381240). The diffraction peaks at 18.42°, 30.33°, 35.71°, 57.35°, and 63.17° can be assigned respectively to the (311), (220), (111), (511), and (440) crystal planes of cubic ZnGa$_2$O$_4$. Meanwhile, for the ZGO@C, the diffraction peaks (curve c)
become broaden and weak, indicating that the glucose can suppress the grain growth of ZnGa$_2$O$_4$ nanocrystals under hydrothermal conditions. After the removal of the carbonaceous polymer from ZGO@C by calcination, well-crystallized ZnGa$_2$O$_4$ nanoparticles (P-ZGO, curve b) can be obtained. According to the Debye–Scherrer equation, the average crystallite sizes of these three ZnGa$_2$O$_4$ samples can be calculated based on the FWHM value of the (111) diffraction peak, and the results are listed in Table 1.

![Figure 2](image-url)  
**Figure 2.** The XRD patterns of the prepared ZnGa$_2$O$_4$ samples: (a) n-ZGO, (b) P-ZGO and (c) ZGO@C.

| Sample     | Crystallite Size (nm) | Band Gap (eV) | $S_{\text{BET}}$ (m$^2$/g) | Toluene Conversion (%) | $E_M$ (%) | As(III) Removal (%) | Surface Hydroxyl Density (mmol/g) |
|------------|-----------------------|---------------|----------------------------|------------------------|-----------|---------------------|-------------------------------|
| ZGO@C      | 12                    | 0.45          | 171.50                     | -                      | -         | -                   | AHG 0.72, BHG 1.05, Total 1.77 |
| P-ZGO      | 14                    | 4.58          | 134.80                     | 66.60                  | 86.30     | 99.80               | -                             |
| n-ZGO      | 21                    | 4.45          | 76.90                      | 37.80                  | 79.60     | 90.60               | 0.55, 0.83, 1.38              |
| P25        | 23                    | 3.20          | 50.10                      | 16.20                  | 19.10     | 80.50               | 0.23, 0.20, 0.43              |

The morphologies of the products are examined by field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM). Figure 3a, b represents the FESEM images of the ZnGa$_2$O$_4$ nanoparticles obtained without glucose (n-ZGO). As shown in Figure 3a, under pH = 8.5 and 180 °C conditions, the n-ZGO are agglomerated in an irregular massive block with a diameter of 25–30 nanometers (Figure 3b, c). The highly-resolved lattice fringes with a $\sim$0.48 nm interplanar distance (inset of Figure 3c) can be indexed as the (111) facet of ZnGa$_2$O$_4$. When D(+)-Glucose monohydrate is added (Figure 3d), the obtained ZnGa$_2$O$_4$@C product turns into relatively uniform spheres with an average diameter of 1–2 μm. Interestingly, the high-resolution SEM image (Figure 3e) shows that the ZGO@C spheres are constructed out of crystalline ZnGa$_2$O$_4$ nanoparticles with a diameter of 10–20 nm, with the carbonaceous polymer (mortar) deposition either on the surface or between the ZnGa$_2$O$_4$ nanoparticles (brick). The carbon content of ZGO@C estimated from the TG/DTA test is about 9.96 wt% (Figure 3f). After additional calcination, well-dispersed ZnGa$_2$O$_4$ spheres with a diameter of 1–2 μm (Figure 3g and inset) are produced. The high-resolution SEM image (Figure 3h) reveals that the porous sphere consists mainly of uniform ZnGa$_2$O$_4$ nanoparticles (10–20 nm). From the HRTEM image (Figure 3i), it is clear that the porous sphere is assembled by ZnGa$_2$O$_4$ nanocrystals with a diameter of approximately 10 nm. The results manifest that the deposited carbonaceous polymer can be readily removed by annealing.
Halenda (BJH) porous distribution curve has a doublet pore diameter distribution of ~3.86 nm and ~18.21 nm, respectively. The result confirms the hierarchically interconnected combination of independent sized pores, which can remarkably enhance the surface permeability of the catalyst. Meanwhile, for the n-ZGO samples, the hysteresis loop in the range of 0.7–1 clarifies the unimodal distributions of the sample. As depicted (inset in Figure 4a), the corresponding Barrett–Joyner–Halenda (BJH) porous distribution curve has a doublet pore diameter distribution of ~3.86 nm and ~18.21 nm, respectively. The result confirms the hierarchically interconnected combination of independent sized pores, which can remarkably enhance the surface permeability of the catalyst. Meanwhile, for the n-ZGO samples, the hysteresis loop in the range of 0.7–1 clarifies the unimodal distribution of the piled mesopores (~5.36 nm). The BET-specific surface areas of the different samples are also summarized in Table 1.

The hierarchically mesoporous structure of the P-ZGO sample can be proven by the N2 sorption measurements. As is shown in Figure 4a, the N2 sorption isotherm of the P-ZGO sample possesses a spacious hysteresis loop in the region of relative pressure 0.4 to 1, revealing the multiple mesoporous distributions of the sample. As depicted (inset in Figure 4a), the corresponding Barrett–Joyner–Halenda (BJH) porous distribution curve has a doublet pore diameter distribution of ~3.86 nm and ~18.21 nm, respectively. The result confirms the hierarchically interconnected combination of independent sized pores, which can remarkably enhance the surface permeability of the catalyst. Meanwhile, for the n-ZGO samples, the hysteresis loop in the range of 0.7–1 clarifies the unimodal distribution of the piled mesopores (~5.36 nm). The BET-specific surface areas of the different samples are also summarized in Table 1.

The XRD patterns of the prepared ZnGa2O4 samples: (a) n-ZGO, (d,e) ZGO@C and (g–i) P-ZGO samples with different magnifications, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

The morphologies of the products are examined by field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM). Figure 3a,b represents the FESEM images of ZGO and P25 samples. Figure 3c shows the XRD patterns of the as-prepared ZnGa 2O4 powders. Obviously, the n-ZGO nanocrystals under hydrothermal conditions. After the removal of the carbonaceous polymer from the ZnGa2O4 nanocrystals with a diameter of approximately 10 nm. The results manifest that the grain size of the ZnGa2O4 nanoparticles (brick). The carbon content of ZGO@C estimated from the TG/DTA test is about 9.96 wt% (Figure 3f). After additional calcination, well-dispersed ZnGa 2O4 nanocrystals with a diameter of approximately 10–20 nm. From the HRTEM image (Figure 3i), it is clear that the porous sphere is assembled by cubic phase ZnGa 2O4 with a spinel structure (JCPDS-381240). The diffraction peaks at 18.42°, 30.33°, 35.71°, 57.35°, and 63.17° can be assigned respectively to the (311), (220), (111), (511), (422) planes of cubic phase ZnGa 2O4. When D(+)-Glucose monohydrate is added (Figure 3d), the obtained ZnGa 2O4@C product turns into relatively uniform n-ZGO samples. The SEM and TEM images of the (a–c) n-ZGO, (d,e) ZGO@C and (g–i) P-ZGO samples with different magnifications, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

Figure 3. The SEM and TEM images of the (a–c) n-ZGO, (d,e) ZGO@C and (g–i) P-ZGO samples with different magnifications, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

The XRD patterns of the prepared ZnGa2O4 samples: (a) n-ZGO, (d,e) ZGO@C and (g–i) P-ZGO samples with different magnifications, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

To determine the optical absorption properties of the as-prepared samples, the UV–vis DRS of ZGO and P25 samples.

The hierarchically mesoporous structure of the P-ZGO sample can be proven by the N2 sorption isotherms and corresponding pore size distribution curve, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

The hierarchical mesoporous structure of the P-ZGO sample can be proven by the N2 sorption isotherms and corresponding pore size distribution curve, and (f) shows the TG/DTA curves of the ZGO@C sample in flowing air.

Figure 4. (a) The N2-sorption isotherms and corresponding pore size distribution curve, and (b) the UV-vis diffuse reflection spectra and corresponding Kubelka-Munk transform (inset) of different ZGO and P25 samples.
To determine the optical absorption properties of the as-prepared samples, the UV–vis DRS of two ZGO samples and commercial TiO$_2$ (P25) are measured and compared in Figure 4b. Obviously, the wavelengths of the absorption edges ($\lambda$) of both ZGO samples, which are ascertained by the tangent line of the absorption spectrum and its intercept on the wavelength axis, show significant blue shifts as compared with that of TiO$_2$. The band gap widths of n-ZGO and P-ZGO (Figure 4b inset) are calculated to be approximately 4.45 and 4.58 eV, respectively. Obviously, the band gap of the ZGO samples is much wider than that of P25 (~3.2 eV), and the larger band gaps would contribute to a stronger redox ability for photocatalytic pollutant oxidation.

2.2. Photocatalytic Properties of ZGO Samples

2.2.1. Gas-Phase Photocatalytic Properties

A gas chromatographic analysis is used to determine the conversion and products of toluene over ZnGa$_2$O$_4$ at an atmospheric pressure and room temperature. Figure 5a,b show the temporal changes in the toluene conversion rate over various photocatalysts under UV-254 nm irradiation, and the corresponding concentrations of produced CO$_2$. In the initial stages, P25 (TiO$_2$) shows a fair photocatalytic activity for the toluene degradation, and the maximum toluene conversion is tested to be ~16.2%, with a ~29 ppm CO$_2$ production. It is worth noting that the conversion rate of TiO$_2$ decreases rapidly to less than 4.5% just after 2 h of reaction. Interestingly, with an increasing reaction time, the color of the white TiO$_2$ becomes darker, finally turning black (complete inactivation) after 60 h of reaction. This is also observed in previous studies, where TiO$_2$ would be completely deactivated in the aromatics photocatalytic process [34]. When the ZGO samples are used, the photoinduced toluene conversion is greatly enhanced, and the maximum conversion efficiencies of toluene over n-ZGO and P-ZGO are examined to be 37.8 and 56.6%, respectively. Additionally, the concentrations of produced CO$_2$ over n-ZGO and P-ZGO are respectively tested to be about 282 and 458 ppm, corresponding to toluene mineralization efficiencies of about 79.6 and 86.3%, respectively. Compared with n-ZGO, the P-ZGO sample shows a much higher photocatalytic capacity in both toluene conversion and mineralization, which can be attributed to the higher specific surface area and the unique hierarchical pore structure of the P-ZGO microspheres. As shown in Figure 5c, the excellent photocatalytic performance can be maintained for more than 60 h, and no obvious deactivation can be observed during the photocatalytic process, indicating the high catalytic stability of P-ZGO microspheres. Furthermore, benzene, which is more toxic and persistent, is used as another probe aromatic pollutant to investigate the photocatalytic oxidative capacity of P-ZGO. It can be clearly revealed in Figure 5d that the P-ZGO microspheres also display a high activity in terms of the photocatalytic mineralization of benzene to CO$_2$. The average conversion rate of benzene and the corresponding CO$_2$ production are tested to be about 44.3% and 520 ppm, respectively. The mineralization efficiency of benzene over P-ZGO is calculated to be 65.2%.

Interestingly, the P-ZGO powder remains white even after 60 h of continuous reaction, implying that it has a strong redox capacity to mineralize the organic pollutants into CO$_2$ and H$_2$O. This inference can also be established by the FT-IR spectra of photocatalysts after the reaction, and the results are shown in Figure 6. For the P-ZGO microspheres, there is no noticeable difference that can be observed between the sample before and after the reaction. Meanwhile, for the used TiO$_2$, some new peaks can be clearly observed in the spectrum. The peaks at wavenumbers 1400 and 1460 cm$^{-1}$ are assigned to the C–H bending in the aliphatic groups, and the 1684 cm$^{-1}$ and 1715 cm$^{-1}$ peaks can be assigned to the stretching C=O bond [35]. The FT-IR results reflect the relatively poor mineralization capacity of TiO$_2$, and the deactivation of TiO$_2$ is mainly caused by the inevitable deposition of carbonaceous byproducts during the photocatalytic process.
photocatalytic process. The surface density of hydroxyl sites on the as-prepared ZGO samples and P-ZGO are examined via a surface acid–base ion–exchange reaction method. The acidic hydroxyl group (AHG) and basic hydroxyl group (BHG) concentrations for various photocatalysts are also summarized in Table 1. The surface densities of the acidic or basic hydroxyl sites decrease in the order of P-ZGO > n-ZGO > P25, which is highly consistent with their photocatalytic degradation activities.

### 2.2.2. Surface Hydroxyl Group Analysis

In previous studies [35,36], surface hydroxyl groups have been proven to be a significant intermediate species for keeping the photocatalyst a clean surface during the heterogeneous photocatalytic process. The surface density of hydroxyl sites on the as-prepared ZGO samples and P25 are examined via a surface acid–base ion–exchange reaction method. The acidic hydroxyl group (AHG) and basic hydroxyl group (BHG) concentrations for various photocatalysts are also summarized in Table 1. The surface densities of the acidic or basic hydroxyl sites decrease in the order of P-ZGO > n-ZGO > P25, which is highly consistent with their photocatalytic degradation activities.
for aromatic pollutants. Obviously, a higher specific surface area combined with a hierarchical porous structure will provide more reactive sites for surface hydroxyl adsorption. Then, the adsorbed hydroxyl groups can readily react with the photogenerated carriers (i.e., holes) to form \( \bullet \)\( \text{OH} \) radicals and thus improve the charge separation efficiency of photogenerated carriers.

2.2.3. Liquid-Phase Photocatalytic Properties for As(III) Removal

Furthermore, the light-driven As(III) removal efficiency is also conducted to evaluate the liquid-phase photocatalytic performance of ZnGa\(_2\)O\(_4\). First, the adsorption capabilities of the as-prepared ZnGa\(_2\)O\(_4\) samples are estimated by As(III) immobilization in the dark. As shown in Figure 7a, the As(III) adsorption capabilities of the P-ZGO, n-ZGO and P25 samples are examined to be 32.6%, 24.3% and 21.3%, respectively. The highest As(III) adsorption capacity of P-ZGO is closely related to its high specific surface area. Figure 7b displays the temporal changes of the As(III) concentration in the photocatalytic system under irradiation. Under the control condition (without photocatalyst), the As(III) species is very stable against UV irradiation. With the presents of photocatalysts, the As(III) concentration declines rapidly. After a 40 min irradiation, the As(III) removal ratios of P25, n-ZGO and P-ZGO are 80.5%, 90.6% and 99.8%, respectively. Due to its abundant porous structures and larger band gaps, P-ZGO shows a much stronger photo-oxidation activity and removal ability than the TiO\(_2\) and n-ZGO nanoparticles, suggesting that P-ZGO can act as a high-effective photocatalyst for As(III) removal.

\[ \text{Figure 7. The temporal changes in the concentration of As(III) with various photocatalysts under different experimental conditions: (a) in the dark and (b) with UV-254nm irradiation.} \]

2.3. DMPO-ESR and Photoelectrochemical Analyses

The formation of \( \bullet \)\( \text{OH} \) and \( \bullet \)\( \text{O}_2^- \) radicals in the liquid system is examined via the DMPO-ESR technique [37]. As can be found in Figure 8, there are no obvious signals in the system without photocatalyst. With UV light irradiation, four characteristic peaks, assigned to DMPO-\( \bullet \)\( \text{OH} \), can be readily observed in all three aqueous suspension systems (Figure 8a), and peaks corresponding to the DMPO-\( \bullet \)\( \text{O}_2^- \) species could also be found in their methanolic suspension systems (Figure 8b). The intensities of both types of DMPO signals over different photocatalysts are in a descending order of P-ZGO > n-ZGO > P25, corresponding well with their surface hydroxyl densities and photocatalytic activities.

An electrochemical analysis (chronoamperometry response) is further conducted to reveal the impact of a hierarchical mesoporous structure on the photoelectronic properties of various samples. As shown in Figure 8c, the UV-induced photocurrents \( (I_{\text{ph}}) \) of all samples at \(-0.2\) V are fairly stable, corresponding well with the switching of the irradiation, and implying their good light response speeds and stabilities. In addition, the \( I_{\text{ph}} \) density of P-ZGO is higher than that of n-ZGO, and increased by about 9-fold when compared to P25. Compared with TiO\(_2\), the increased \( I_{\text{ph}} \) densities of the ZnGa\(_2\)O\(_4\)
samples could be possibly attributed to its highly dispersed LUMO and larger band gap. Moreover, the porous structure can provide more reactive sites and can further promote the separation efficiency of photogenerated charge carriers. The evidence that the strongest signals of both the DMPO and photocurrent are on P-ZGO offers a clear indication that the photogenerated holes and electrons in P-ZGO can not only separate effectively, but also that they possess a strong enough redox capacity and lifetime to react with the surface-adsorbed $-\text{OH}$ and $\text{O}_2$.

![Figure 8](image_url)

**Figure 8.** The DMPO spin-trapping ESR spectra in an aqueous dispersion for (a) DMPO–•OH and (b) DMPO–•$\text{O}_2^-$, and (c) the transient photocurrent responses of the samples with a $-0.2 \ \text{V}$ bias versus Ag/AgCl electrodes in a 0.2 M Na$_2$SO$_4$ solution.

### 2.4. Band Gap Analysis and Tentative Photooxidation Mechanism of ZnGa$_2$O$_4$

Essentially, the photo-redox activity of a semiconductor photocatalyst closely depends on its band gap edge positions. The edge position of semiconductors’ conduction bands (CBs) can be calculated by Bulter’s equation:

$$E_{\text{CB}} = X - E^c - \frac{1}{2}E_g$$

where $E_{\text{CB}}$ is the edge potential of CB, $X$ means the absolute electronegativity of the chemical compounds. The absolute electronegativity values of individual Ga, Zn, and O atoms are reported to be 3.20, 4.45, and 7.54, respectively [38]; thus, the $X$ value of ZnGa$_2$O$_4$ is calculated to be ca. 5.74. The $E^c$ value is about 4.5 eV, referring to the free electron energy on the hydrogen scale, and $E_g$ means the direct band gap width (i.e., 4.58 eV for P-ZGO). Obviously, the $E_{\text{CB}}$ (vs. NHE) value of P-ZGO can be calculated, and its valence band potential ($E_{\text{VB}}$) can also be subsequently estimated. Here, the $E_{\text{CB}}$ and $E_{\text{VB}}$ values
(vs. NHE) of P-ZGO are determined to be −1.05 V and 3.53 V (vs. NHE), respectively. The band gap edge potentials of TiO2 and P-ZGO are compared in Scheme 1a.

A possible mechanism for the photoelectric and oxidation process in the pollutants/P-ZGO system is depicted in Scheme 1b. For p-block metal oxide semiconductors with highly dispersive LUMO, the mobility of the photo-generated charge carriers is greatly promoted because of the hybridization of orbitals, leading to the enhancement of the charge separation in ZnGa2O4. Additionally, the $E_{VB}$ of P-ZGO is more positive than the $E_0(\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
Catalysts 2019, 9, 828 10 of 13
electron microscope (TEM, JEM-2010, JEOL Ltd. Tokyo, Japan), Micromeritics ASAP 2010 system, and Cary 500 UV–visible diffuse reflectance spectrophotometer (DRS), respectively. A ZENNIUM electrochemical workstation (Zahner Elektrik, GmbH & Co., Kronach, Germany) with a conventional three electrode cell is used to investigate the photoelectrochemical properties of the samples. The working electrode is a 1 cm × 4 cm ITO conducting glass with a 0.5 cm × 0.5 cm photocatalyst coating, and the reference and counter electrodes are an Ag/AgCl electrode and Pt electrode, respectively.

3.3. Surface Hydroxyl Groups Measurements

The surface hydroxyl density of the photocatalyst is examined by a surface acid–base ion–exchange reaction. The detailed procedure is as follows: 80 mg of photocatalyst powders are dispersed in 50 mL of 0.002 mol L⁻¹ NaOH or HNO₃ solutions at room temperature. After being stirred for 12 h, the powders are removed from the suspensions by centrifugation. Then, the retrieved solution is titrated with HNO₃ or Na₂CO₃ standard solutions, and the concentration decrease of the retrieved NaOH or HNO₃ solutions represents the acidic hydroxyl groups (AHG) or basic hydroxyl groups (BHG) on the photocatalysts.

3.4. Photocatalytic Activity Measurements

VOCs mineralization: A fixed-bed quartz tube surrounded by four 4 W lamps with a wavelength centered at 254 nm (4W/G4T5, Philips, Amsterdam, Netherlands) is designed for the gas-phase photocatalytic experiments. A 300 mg photocatalyst is loaded into the reactor with an air-cooled device (~303 K). Benzene/Toluene diluted in oxygen (20 mL/min) is used as the reactant stream, and the initial concentrations of Benzene and Toluene are measured to be 300 ppm and 280 ppm, respectively. The concentrations of VOCs and CO₂ are simultaneously detected with an online gas chromatograph (HP6890). Benzene or Toluene is very stable in the dark, and no photolysis can be observed without photocatalysts in these conditions.

As(III) removal experiments: A stock solution (1 g/L) of arsenite [As(III)] was prepared by dissolving 1.734 g of NaAsO₂ into a 1 L 20% HCl solution. The reaction solutions (2 mg/L AsO₂⁻) used for the As(III) removal experiments were made by diluting the stock solution and adjusting the pH value to the neutral state (~ 7.0) using 1 mol/L NaOH. Typically, in a quartz tube surrounded by four 254 nm UV-lamps (4W/G4T5, Philips), 50 mg of photocatalyst are suspended in the 50 mL dilute arsenite solution (pH ≈ 7.0). Under vigorous stirring, 1 mL of the suspension is extracted at the given irradiation time intervals and centrifuged to collect the upper clear liquid. Then, the pH value of the supernatant is adjusted to ~4.0 by 1 mol/L HCl. The As(III) content in the supernatant is analyzed by using atomic fluorescence spectrometry (PF6, Beijing purkinje general instrument Co., Ltd. Beijing, China).

4. Conclusions

Porous ZnGa₂O₄ microspheres with diameters of 1~2 µm are fabricated via a facile microwave hydrothermal method followed by annealing. Due to the wide band gap and highly dispersed LUMO electron structure, the photogenerated charge carriers in ZnGa₂O₄ have a high mobility and strong redox capacity. In the gas-phase photocatalytic degradation of aromatic pollutants, P-ZGO shows a much higher activity and stability than commercial TiO₂. The average conversion efficiencies of toluene and benzene over P-ZGO are up to ~56.6% and ~44.3%, with corresponding mineralization rates of ~86.3% and ~65.2%, respectively. No remarkable deactivation of the P-ZGO photocatalyst is observed during the 60 h gas-phase photoreaction, and the excellent catalytic stability can be ascribed to the abundant surface-adsorbed hydroxyl groups on the photocatalyst. Furthermore, the photocatalytic As(III) removal efficiency over P-ZGO is up to 99.8% in water. The excellent photocatalytic performance of the porous ZnGa₂O₄ microspheres can be ascribed to its unique electronic structure and hierarchical morphology. The results suggest that the carbohydrate-assisted hydrothermal synthesis method can provide an effective way to fabricate porous multi-metal oxide
microspheres, and that the as-prepared porous ZnGa$_2$O$_4$ microspheres have potential applications in related fields of environmental remediation.

**Author Contributions:** Conceptualization, J.Z.; Data curation, Q.T. and S.R.; Investigation, Q.T., S.R., Z.C. and C.C.; Project administration, Y.Z.; Supervision, Y.Z.; Writing – original draft, Q.T.; Writing – review & editing, Y.Z. and J.Z.

**Funding:** This work is financially supported by the National Natural Science Foundation of China (No. 21673044, 21303244), Natural Science Foundation of Fujian Province (No. 2016J01207), and Outstanding Youth Fund of Fujian Agriculture and Forestry University (No. XJQ201419, CXZX2017292). and Youth Education and Scientific of Fujian Province (No. JAT170154).

**Acknowledgments:** The authors are very much appreciate Prof. Ping Liu for his technical support in As(III) removal experiments.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* 1995, 95, 69–96. [CrossRef]
2. Bhatkhande, D.S.; Pangarkar, V.G.; Beenackers, A.A.C.M. Photocatalytic degradation for environmental applications— A review. *J. Chem. Technol. Biotechnol.* 2002, 77, 102–116. [CrossRef]
3. Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.; Hamilton, J.W.; Byrne, J.A.; O’shea, K.; et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B. Environ.* 2012, 125, 331–349. [CrossRef]
4. Zhuang, J.; Dai, W.; Tian, Q.; Li, Z.; Xie, L.; Wang, J.; Liu, P.; Shi, X.; Wang, D. Photocatalytic Degradation of RhB over TiO$_2$ Bilayer Films: Effect of Defects and Their Location. *Langmuir* 2010, 26, 9686–9694. [CrossRef] [PubMed]
5. Jo, W.K.; Park, K.H. Heterogeneous photocatalysis of aromatic and chlorinated volatile organic compounds (VOCs) for non-occupational indoor air appli cation. *Chemosphere* 2004, 57, 555–565. [CrossRef] [PubMed]
6. Ren, L.; Li, Y.; Hou, J.; Bai, J.; Mao, M.; Zeng, M.; Zhao, X.; Li, N. The pivotal effect of the interaction between reactant and anatase TiO$_2$ nanosheets with exposed {0 0 1} facets on photocatalysis for the photocatalytic purification of VOCs. *Appl. Catal. B. Environ.* 2016, 181, 625–634. [CrossRef]
7. Boyjoo, Y.; Sun, H.; Jian, L.; Pareek, V.K.; Wang, S. A review on photocatalysis for air treatment: From catalyst development to reactor design. *Chem. Eng. J.* 2017, 310, 537–559. [CrossRef]
8. Dai, J.; Tian, Q.; Sun, Q.; Wei, W.; Zhuang, J.; Liu, M.; Cao, Z.; Xie, W.; Fan, M. TiO$_2$-alginate composite aerogels as novel oil/water separation and wastewater remediation filters. *Compos. Part B. Eng.* 2019, 160, 480–487. [CrossRef]
9. Lin, W.; Xie, X.; Xiao, W.; Yan, W.; Segets, D.; Jing, S. Efficient adsorption and sustainable degradation of gaseous acetaldehyde and o-xylene using rGO-TiO$_2$ photocatalyst. *Chem. Eng. J.* 2018, 349, 708–718. [CrossRef]
10. Fagan, R.; Mccormack, D.E.; Dionysiou, D.D.; Pillai, S.C. A review of solar and visible light active TiO$_2$ photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern. *Mater. Sci. Semicond. Process.* 2016, 42, 2–14. [CrossRef]
11. Tian, Q.; Wei, W.; Dai, J.; Sun, Q.; Zhuang, J.; Zheng, Y.; Liu, P.; Fan, M.; Chen, L. Porous core-shell TiSn1-xO$_2$ solid solutions with broad-light response: One-pot synthesis and ultrahigh photooxidation performance. *Appl. Catal. B. Environ.* 2019, 244, 45–55. [CrossRef]
12. Li, X.; Zhuang, J.; Xie, L.; Liu, P.; Yuan, R.; Shi, X.; Wang, D. High-efficient degradation of benzene over Pt/TiO$_2$ by adding a small amount of H$_2$ under a mild condition. *Catal. Comm.* 2011, 12, 621–624. [CrossRef]
13. Subrahmanya, C.; Renken, A.; Kiwi-Minsker, L. Novel catalytic non-thermal plasma reactor for the abatement of VOCs. *Chem. Eng. J.* 2007, 134, 78–83. [CrossRef]
14. Shao, Z.; Zeng, T.; He, Y.; Zhang, D.; Pu, X. A novel magnetically separable CoFe$_2$O$_4$/CdO. 9Zn0. 1S photocatalyst with remarkably enhanced H2 evolution activity under visible light irradiation. *Chem. Eng. J.* 2019, 359, 485–495. [CrossRef]
15. Gao, M.; Yang, J.; Sun, T.; Zhang, Z.; Zhang, D.; Huang, H.; Lin, H.; Fang, Y.; Wang, X. Persian buttercup-like BiOBrxCl1-x solid solution for photocatalytic overall CO2 reduction to CO and O2. *Appl. Catal. B: Environ.* 2019, 243, 734–740. [CrossRef] [PubMed]

16. Zhang, X.; Huang, J.; Ding, K.; Hou, Y.; Wang, X.; Fu, X. Photocatalytic decomposition of benzene by porous nanocrystalline ZnGa2O4 with a high surface area. *Environ. Sci. Technol.* 2009, 43, 5947–5951. [CrossRef] [PubMed]

17. Li, X.; Zhang, X.; Zheng, X.; Shao, Y.; He, M.; Wang, P.; Fu, X.; Li, D. A facile preparation of ZnGa2O4 photonic crystals with enhanced light absorption and photocatalytic activity. *J. Mater. Chem. A* 2014, 2, 15796–15802. [CrossRef]

18. Chen, X.; Xue, H.; Li, Z.; Wu, L.; Wang, X.; Fu, X. Ternary wide band gap p-block metal semiconductor ZnGa2O4 for photocatalytic benzene degradation. *J. Phys. Chem. C* 2008, 112, 20393–20397. [CrossRef]

19. Yan, S.C.; Ouyang, S.X.; Gao, J.; Yang, M.; Feng, J.Y.; Fan, X.X.; Wan, L.J.; Li, Z.S.; Ye, J.H.; Zhou, Y. A Room-temperature reactive-template route to mesoporous ZnGa2O4 with improved photocatalytic activity in reduction of CO2. *Angew. Chem. Int. Ed.* 2010, 122, 6544–6548. [CrossRef]

20. Ikarashi, K.; Sato, J.; Kobayashi, H.; Saito, N.; Nishiyama, H.; Inoue, Y. Photocatalysis for water decomposition by RuO2-dispersed ZnGa2O4 with d(10) configuration. *J. Phys. Chem. B* 2002, 106, 9048–9053. [CrossRef]

21. Zheng, T.; Xia, Y.; Jiao, X.; Wang, T.; Chen, D. Enhanced photocatalytic activities of single-crystalline ZnGa2O4 nanoprism and nanowires. *Nanoscale* 2019, 12, 28045–28054. [CrossRef]

22. Suresh, K.S.; Kanhere, D.G.; Ravindra, P. Electronic structure of spinel oxides: Zinc aluminate and zinc gallate. *J. Phys. Condens. Matter* 1999, 11, 3635.

23. Bae, S.Y.; Lee, J.; Jung, H.; Park, J.; Ahn, J.P. Helical structure of single-crystalline ZnGa2O4 nanowires. *J. Am. Chem. Soc.* 2005, 127, 10802–10803. [CrossRef] [PubMed]

24. Liu, Q.; Wu, D.; Zhou, Y.; Su, H.; Wang, R.; Zhang, C.; Yan, S.; Xiao, M.; Zou, Z. Single-crystalline, ultrathin ZnGa2O4 nanosheet scaffolds to promote photocatalytic activity in CO2 reduction into methane. *ACS Appl. Mater. Interfaces* 2014, 6, 2356–2361. [CrossRef]

25. Zhuang, J.D.; Tian, Q.F.; Lin, S.; Yang, W.B.; Chen, L.H.; Liu, P. Precursor morphology-controlled formation of perovskites CaTiO3 and their photo-activity for As(III) removal. *Appl. Catal. B: Environ.* 2014, 156, 108–115. [CrossRef]

26. Zhuang, J.; Tian, Q.; Zhou, H.; Liu, Q.; Liu, P.; Zhong, H. Hierarchical porous TiO2@C hollow microspheres: One-pot synthesis and enhanced visible-light photocatalysis. *J. Mater. Chem. B* 2012, 22, 7036–7042. [CrossRef]

27. Yan, S.; Wang, J.; Gao, H.; Wang, N.; He, Y.; Li, Z.; Yong, Z.; Zou, Z. An Ion-Exchange Phase Transformation to ZnGa2O4 Nanocube Towards Efficient Solar Fuel Synthesis. *Adv. Funct. Mater.* 2013, 23, 758–763. [CrossRef]

28. Zhang, Y.; Li, P.; Tang, L.Q.; Li, Y.Q.; Zhou, Y.; Liu, J.M.; Zou, Z.G. Robust, double-shelled ZnGa2O4 hollow spheroids for photocatalytic reduction of CO2 to methane. *Dalton Trans.* 2017, 46, 10564–10568. [CrossRef]

29. Titirici, M.M.; Antonietti, M.; Thomas, A. A Generalized Synthesis of Metal Oxide Hollow Spheres Using a Hydrothermal Approach. *Chem. Mater.* 2006, 18, 3808–3812. [CrossRef]

30. Yu, J.; Yu, X. Hydrothermal Synthesis and Photocatalytic Activity of Zinc Oxide Hollow Spheres. *Environ. Sci. Technol.* 2008, 42, 4902–4907. [CrossRef]

31. Zhuang, J.; Tian, Q.; Liu, Q.; Liu, P.; Cui, X.; Li, Y.; Fan, M. New insight into binary TiO2@C nanocomposites: The crucial effect of an interfacial microstructure. *Phys. Chem. Chem. Phys.* 2017, 19, 9519–9527. [CrossRef] [PubMed]

32. Tian, Q.; Wei, W.; Dai, J.; Sun, Q.; Zhuang, J.; Liu, P.; Zheng, Y. Furfural-Mediated Synthesis of Mesoporous TiO.5Sn0.5O2 Solid-Solution Microspheres for Effective Photocatalytic Removal of As(III). *J. Phys. Chem. C* 2018, 122, 28045–28054. [CrossRef]

33. Szeifert, J.M.; Fattakhova-Rohlfing, D.; Georgiadou, D.; Kalousek, V.; Rathousky, J.; Kuang, D.; Wenger, S.; Zakeeruddin, S.M.; Grätzel, M.; Bein, T. “Brick and Mortar” strategy for the formation of highly crystalline mesoporous titania films from nanocrystalline building blocks. *Chem. Mater.* 2009, 21, 1260–1265. [CrossRef]

34. Einaga, H.; Futamura, S.; Ibusuki, T. Complete oxidation of benzene in gas phase by platinized titania photocatalysts. *Environ. Sci. Technol.* 2001, 35, 1880–1884. [CrossRef] [PubMed]

35. Einaga, H.; Futamura, S.; Ibusuki, T. Photocatalytic decomposition of benzene over TiO2 in a humidified airstream. *Phys. Chem. Chem. Phys.* 1999, 1, 4903–4908. [CrossRef]
36. d’Hennezel, O.; Pichat, P.; Ollis, D.F. Benzene and toluene gas-phase photocatalytic degradation over H2O and HCL pretreated TiO2: By-products and mechanisms. *J. Photochem. Photobiol. A* 1998, 118, 197–204. [CrossRef]

37. Wu, T.; Lin, T.; Zhao, J.; Hidaka, H.; Serpone, N. TiO2-Assisted Photodegradation of Dyes. 9. Photooxidation of a Squarylium Cyanine Dye in Aqueous Dispersions under Visible Light Irradiation. *Environ. Sci. Technol.* 1999, 33, 1379–1387. [CrossRef]

38. Pearson, R.G. Absolute electronegativity and hardness: Application to inorganic chemistry. *Inorg. Mater.* 1988, 27, 734–740. [CrossRef]

39. Li, Z.; Dong, T.; Zhang, Y.; Wu, L.; Li, J.; Wang, X.; Fu, X. Studies on In(OH)ySz Solid Solutions: Syntheses, Characterizations, Electronic Structure, and Visible-Light-Driven Photocatalytic Activities. *J. Phys. Chem. C* 2007, 111, 4727–4733. [CrossRef]