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# Coral reef-like $Pt/TiO_2$ -Zr $O_2$ porous composites for enhanced photocatalytic hydrogen production performance



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## ABSTRACT

Keywords: Polystyrene Coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> Photocatalytic hydrogen evolution Polystyrene (PS) colloidal microspheres synthesized by the self-assembly technology were used as templates, a series of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> composites with TiO<sub>2</sub> anatase phase and ZrO<sub>2</sub> tetragonal phase were synthesized by sol–gel, vacuum impregnation and photoreduction based on the colloidal crystal template. The composites treated with PS microspheres as templates exhibited an overall shape similar to the natural formation of uneven grooves. Meanwhile, there were three-dimensional ordered macroporous structures on the surface of composites, showing a coral reef-like porous structure. In addition, the loading of the precious metal Pt significantly enhanced the absorption of the composite in the visible region. The plasma resonance effect and the larger work function of Pt prolonged the carrier lifetime, thus enhancing photocatalytic properties of coral reef-like porous composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>. The photocatalytic activity of coral reef-like porous composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> was higher in the experiment of multi-mode photocatalytic degradation of Rhodamine B, which had certain degradation of various dyes and organic pollutants. In the meanwhile, the experimental results of photocatalytic hydrogen production from water showed that the hydrogen production of coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> porous composites (7082.8  $\mu$ mol g<sup>-1</sup>) was more 600 times than that of TiO<sub>2</sub> (11.3  $\mu$ mol g<sup>-1</sup>) during 8 h, indicating that the loading of noble metal Pt, the synergistic effect of TiO<sub>2</sub> and ZrO<sub>2</sub>, and the coral reef-like porous structure of the composite enhanced the photocatalytic activity.

# 1. Introduction

The ideal source of new energy should be cheap, abundant and clean. Therefore, the use of solar energy in various ways has become a research goal [1,2]. In recent years, so as to achieve the high photo-catalytic activity of photocatalytic materials, solar energy has been applied to the field of photocatalysis to develop semiconductors with excellent electron separation and to combine with highly efficient co-catalysts. Efforts to further improve the photocatalytic properties of materials have been agreed upon by scientists [3,4].

In the study of hydrogen evolution from water by semiconductor photocatalysis,  $TiO_2$  photocatalyst is regarded as the excellent candidate material because of its low cost, non-toxicity, chemical stability and suitable energy band value for hydrogen production [5]. However, the ability of  $TiO_2$  photocatalyst to capturing light in the visible region is weak, of which the separation ability of photogenerated carriers is low [6,7]. To some extent, the enhancement of photocatalytic hydrogen evolution ability is restrained, and the practical application value is limited [8]. In order to solve these problems, researchers began to try to

adjust the oxygen vacancy, two semiconductor modifications and cocatalyst introduction and other aspects of research [9].  $ZrO_2$  is a widebandgap material with p-type semiconductor properties. The bandgap value ( $E_g$ ) is between 3.25 and 5.0 eV. Therefore, some researchers use the synergistic effect of two wide-bandgap semiconductors,  $TiO_2$  and  $ZrO_2$  to change the band gap of the composite, thereby changing the light absorption properties of the composite to enhance the photocatalytic activity of the composite. Sreethawong et al. [10] enhanced the photocatalytic hydrogen evolution ability of noble metal Ag on  $TiO_2$ - $ZrO_2$  by self-assembly technology. Rtimi et al. [11] enhanced the photocatalytic degradation of organic pollutants by Cu-modified  $TiO_2$ - $ZrO_2$  composites.

Furthermore, there are many research results on the enhancement of photocatalytic properties of materials by designing and obtaining different types of materials with various morphologies. Imhof et al. [12] prepared composites with macroporous structure by using emulsion droplets as the template. The composites not only had large specific surface area, high porosity, but also showed the characteristics of strong periodicity of pore structure and uniform pore size. Our research team

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had synthesized a kind of gully morphology by self-assembly technology, and the preparation process is simple and the morphology is easy to control [13]. In addition, Ren et al [14] synthesized  $Pt/TiO_2$ irregular pore materials using lotus pollen as a template agent. Because of large specific surface area and good electron trap effect of precious metal Pt, the composites had good hydrogen production properties.

The studies on the modification of semiconductors with precious metals as electronic traps are to improve the photocatalytic activity and hydrogen evolution of composites by changing the properties of composites. Among them, reports about Pt are more common. The hydrogen production of Pt/TiO<sub>2</sub> prepared by Lin et al. [15] was 60.0 mmol after 5 h irradiation. Therefore, if Pt can be doped into semiconductor TiO<sub>2</sub> and ZrO<sub>2</sub> composites, it can be used as a co-catalyst to enhance the photocatalytic performance of semiconductor materials [16–18].

According to as-results, a kind of coral reef-like porous composite was prepared by sol-gel and vacuum impregnation combined with photoreduction method using polystyrene (PS) colloidal microspheres synthesized by self-assembly technology as the template in this paper. On the one hand, by depositing precious metal Pt as an electron trap, the recombination of photogenerated electron-hole pairs in semiconductor TiO<sub>2</sub> and ZrO<sub>2</sub> is restrained, and the photogenerated electrons are effectively captured, thus facilitating the separation of photogenerated electron-hole pairs. At the same time, photogenerated electrons trapped by Pt can well participate in the photodissociation of water to produce hydrogen. For another, the coral reef-like porous structure has some advantages: firstly, the material has a groove structure and a porous structure, which is very favorable to capture photons. In addition, a comparison of the planar structure, the porous structure on the groove is advantageous to prolong the electron transfer path. Secondly, a large number of small particles are accumulated on the surface of the catalyst, which has a good diffuse reflection effect on the light, which can improve the utilization ratio of the catalyst to light and thus improve the photocatalytic activity. Meanwhile, the synthesized coral reef-like Pt/TiO2-ZrO2 porous material has the advantages of simple preparation conditions, high reproducibility, high yield, large specific surface area, excellent photocatalytic degradation of organic pollutants and excellent photolysis activity.

# 2. Experimental

#### 2.1. Materials

Titanium (IV) isopropoxide ( $C_{12}H_{28}O_4Ti$ , 98%) was purchased from Shanghai Darui Fine Chemical Co., Ltd.; Zirconium (IV) butoxide solution ( $C_{16}H_{36}O_4Zr$ , 80 wt%) was purchased from Shanghai Meryer Chemical Technology Co., Ltd.; Chloroplatinic acid hexahydrate ( $H_2PtCl_6\cdot6H_2O$ , 38.7%) was purchased from Shanghai Meryer Chemical Technology Co., Ltd.; Polyethylene-polypropylene glycol ( $C_5H_{10}O_2$ , P123) was purchased from Saan Chemical Technology (Shanghai) Co., Ltd.; Styrene ( $C_8H_8$ , 99%) was purchased from Shanghai Meryer Chemical Technology Co., Ltd.; Degussa P25 and  $K_2S_2O_8$  were purchased from Tianjin Tianda Purification Materials Fine Chemical Plant.; Methyl orange (MO), Congo red (CR), methylene blue (MB), Rhodamine B (RhB) and salicylic acid (SA) are commercially available analytical reagents and not further purified. All experimental water is deionized water.

# 2.2. Preparation of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> nanocomposites

Polystyrene microspheres template was synthesized by emulsion free polymerization [19]. Polystyrene (PS) microspheres suspension was centrifuged for 90 min. The lower emulsion of 8 mL was extracted in a beaker and 1 mL of tetraisopropyl titanium (TTIP) and 2 mL of n-butoxy zirconium ( $C_{16}H_{36}O_4Zr$ ) were added and hydrolyzed in time. The TiO<sub>2</sub>-ZrO<sub>2</sub> precursor was obtained by stirring for two hours.

Finally, the uniformly mixed  $TiO_2$ -ZrO<sub>2</sub> precursor was placed in a vacuum oven for 12 h under vacuum impregnation. The dry powder  $TiO_2$ -ZrO<sub>2</sub> was calcined at 600 °C for 7 h, then was labeled as  $TiO_2$ -ZrO<sub>2</sub>(C).

 $1.0 \text{ g TiO}_2\text{-}ZrO_2(\text{C})$  composite was uniformly dispersed into 50 mL of deionized water and placed in a photoreduction reactor, then sodium sulfide (3.0 g) was added as a sacrificial agent, and then the prepared 0.5 mL platinum standard solution was added. The mixture was uniformly mixed and then evacuated. Under the irradiation of 300 W xenon lamp for two hours, the photoreduction loading of Pt was carried out. Finally, the nanocomposites were washed with deionized water and ethanol for four times and dried in vacuum. The nanocomposites were labeled as Pt/TiO\_2-ZrO\_2(C). The TiO\_2 and ZrO\_2 used for comparison were synthesized by a sol–gel method in combination with calcination.

In addition, the contents of Pt,  $TiO_2$  and  $ZrO_2$  in  $Pt/TiO_2$ - $ZrO_2(C)$  samples were determined by ICP-AES. The results show that the weight percentages of Pt,  $TiO_2$  and  $ZrO_2$  in coral reef  $Pt/TiO_2$ - $ZrO_2(C)$  porous composites are 1.2%, 16.8% and 50.1%, respectively.

#### 2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were analyzed using an X-ray diffractometer from  $20^{\circ}$  to  $80^{\circ}$  with K $\alpha$  radiation  $(\lambda = 0.15406 \text{ nm})$  from Bruker-AXS (D8), Germany. The XPS spectrum of the sample was determined by using an ESCALAB250Xi X ray photoelectron spectrometer purchased from Thermo Company, USA, where the residual gas pressure of the Mg K-ADES source was less than  $10^{-8}$ Pa. The PL photoluminescence spectra of the samples were measured by the F-7000 fluorescence spectrophotometer of Hitachi, Japan. SEM analysis of the sample was carried out using the scanning electron microscope (SEM) of 5 kV, model S-4700, purchased from Hitachi, Japan, and the determination temperature was 77 K and the model was 3H-2000PS2, purchased from Bethesdale instrument Technology (Beijing) Co., Ltd. The HR-TEM photos of the sample were obtained by the Japanese electronic JEM-2100 F model. The accelerated voltage is 200 kV. The electrochemical impedance was measured using a PEC-1000 photoelectrochemical test system manufactured by Perfectlight Co., Ltd. The ICP-AES was carried on an Agilent Technologies 7500ce inductively coupled plasma atomic emission spectrum. The TU-1901 dual-beam UV-vis diffuse reflectance absorption spectra produced by Beijing General Analysis Company were used as a reference, and the BaSO<sub>4</sub> solid was used as a reference. The absorbance of the sample solution was determined by the TU-1901 UV-vis dual beam spectrophotometer produced by Beijing General Analysis Company.

# 2.4. Photocatalytic experiments

The photocatalytic experimental reaction devices of different modes are self-made. The ultraviolet light source is 125 W high pressure mercury lamp (the main emission wavelength is 313.2 nm), visible light source is 400 W xenon lamp (the main emission wavelength is more than 410 nm, the inner casing is made of special glass to filter the ultraviolet light emitted by Xe lamp), and the solar light is simulated. The source is 1000 W xenon lamp (external type, Shanghai Baoxin instrument Co., Ltd., emission spectrum is close to full spectrum). The microwave-assisted photocatalytic experiment uses H type microwave electrodeless lamp (main emission wavelength 280 nm) as the light source.

In the ultraviolet, visible, simulated sunlight and microwave-assisted photocatalytic experiments, 0.15g, 0.3g, 0.15g, and 0.5g of catalyst were dispersed in a newly configured solution (concentration: 50 mg/L) in a volume of 90 mL, 220 mL, 100 mL, and 500 mL, respectively. The suspension was sonicated for 10 min, stirred in the dark for 30 min, and placed in a photocatalytic reactor for photocatalytic experiments. Samples were taken at regular intervals during the reaction and their absorbance values were measured at  $\lambda_{max}$  by a TU-1901



Fig. 1. SEM images of polystyrene microspheres (a–d) and Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites (e, f) (Inset : g is a sectional view of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composite; h is a natural coral reef structure image).

UV-vis dual beam spectrophotometer.

# 3. Results and discussion

# 3.1. SEM analysis

With a view to study the surface morphology of  $Pt/TiO_2$ - $ZrO_2(C)$  sample, polystyrene microspheres and  $Pt/TiO_2$ - $ZrO_2(C)$  were analyzed by scanning electron microscopy (SEM), and the results are shown in Fig. 1. As can be seen from Fig. 1(a–d), the synthesized polystyrene microspheres exhibite a monodisperse and closely packed structure, and its average diameter is about 320 nm. From Fig. 1e,  $Pt/TiO_2$ - $ZrO_2(C)$  has a coral reef-like structure, which is mainly composed of the accumulation of nanoparticles, and the pore structure and a small amount of nanoparticles can be clearly seen on the surface. The porous structure is formed by calcination of PS microspheres template, while a small amount of particles on the surface are photoreductively deposited Pt nanoparticles, which are very similar to the naturally formed coral reef-like morphology (the naturally formed coral structure is shown in Fig. 1h).

Most noteworthy, the coral reef surface morphology in Fig. 1(e–f) exhibits relatively uniform, good groove network structure and longrange periodic macropores with a pore size of 80–120 nm. It is also interesting to see that the gully morphology is parallel to each other and perpendicular to the outer surface of the particle. From Fig. 1f (in the illustration Fig. 1g), it is clear to see that the ravines arranged in parallel rows completely cross the whole material and extend; this special morphology can increase the optical transmission pathway as a channel, and can well introduce the light and molecules into the internal space of  $Pt/TiO_2$ -ZrO<sub>2</sub>(C). At the same time, in Fig. 1e, it can be seen that the composites have uneven ravines and porous structure, indicating that the synthesized composite material has certain permeability and a reflection and diffraction effect on light under the action of light.

This unique coral reef-like porous structure has good permeability and is conducive to the photon reflection path in the structure, increasing the effective optical path length caused by photon multiple reflection in the structure. Meanwhile, this unique coral reef-like porous structure contributes to capture more efficient photon, thereby improving light trapping efficiency.

For the purpose of revealing the role of PS microspheres as templates in the formation of porous structure materials, the possible formation mechanism of coral reef-like  $Pt/TiO_2$ - $ZrO_2(C)$  porous structure is inferred (Fig. 2).

During the synthesis process, after PS colloidal microspheres are centrifuged for a period of time, the PS colloidal microspheres self-assemble from the original monodisperse loose state into a denser arrangement state. Of course, PS colloidal microspheres not fully assembled also existe in the centrifugation process (Fig. 2a). The PS colloidal microspheres after centrifugation can fully absorb water. When the droplets of tetraisopropoxy titanium and n-butoxy zirconium contact with PS colloidal template, a thin and dense semi-permeable film is formed at the droplet interface, then hydrolyzes to produce part of TiO<sub>2</sub> and ZrO<sub>2</sub> particles (Fig. 2b). The TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles are then filled into the PS colloidal microspheres template under stirring (Fig. 2c). Due to the friction and the adsorption between the PS



Fig. 2. Schematic illustration of the formation process of coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> porous composites.

microspheres and the  $TiO_2$  and  $ZrO_2$  particles, a tightly packed cover layer can be formed under vacuum impregnation (Fig. 2d). As a result, the appearance of coral reefs has gradually formed, and the height and the depth of coral reefs also changes, showing the three-dimensional characteristics of coral reefs. During the formation process, the colloidal activity and hydrophilic properties of PS colloidal microspheres can accelerate the formation of coral reefs. The expansion of the PS colloidal microspheres and the increase of the adsorption force can obtain a coral reef composite with a large active surface. In addition, the PS colloidal template in the solution is adsorbed on the surface of the particles by vacuum impregnation to form a two-layer structure (Fig. 2e), and finally, by the calcination to remove the PS template, a "coral reef-like" porous structure is obtained (Fig. 2f).

# 3.2. XRD analysis

The crystallinity and phase composition of  $ZrO_2$ ,  $TiO_2$ ,  $TiO_2$ - $ZrO_2(C)$  and coral reef-like Pt/TiO\_2-ZrO\_2(C) samples were characterized by XRD method. The results are shown in Fig. 3. As shown in Fig. 3, the Pt/TiO\_2-ZrO\_2(C) presents strong diffraction peaks at  $2\theta = 25.4^{\circ}$ ,  $37.8^{\circ}$ ,  $48.2^{\circ}$ ,  $53.9^{\circ}$ ,  $55.2^{\circ}$ ,  $62.8^{\circ}$ , and  $75.2^{\circ}$ , corresponding to (110), (200), (212), (310), (301), (312) and (104) crystal surface of TiO\_2 anatase



Fig. 3. X-ray diffraction patterns of TiO\_2, ZrO\_2, TiO\_2-ZrO\_2(C) and Pt/TiO\_2-ZrO\_2(C).

(JCPDS 21–1272) [20,21]. The tetragonal phase of ZrO<sub>2</sub> is observed at  $2\theta = 28.3^{\circ}, 30.3^{\circ}, 31.4^{\circ}, 35.3^{\circ}, 50.4^{\circ}$  and  $60.0^{\circ}$ , corresponding to (111), (102), (201), (211), (302) and (402) crystal plane (JCPDS 65-1024) [22]. The characteristic peaks of  $(Ti-Zr)O_2$  also appeares in the composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C), owing to the formation of (Ti-Zr)O<sub>2</sub> oxide during the calcination process, while the Pt characteristic peaks do not appear in the composite  $Pt/TiO_2$ - $ZrO_2(C)$ , which may be due to the low loading of Pt [23]. Compared with ZrO<sub>2</sub>, the diffraction peaks corresponding to (102) planes of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) and TiO<sub>2</sub>-ZrO<sub>2</sub>(C) are weakened, while the diffraction peaks corresponding to (111) and (201) planes are strengthened. The reason for the difference is that the peak strength of (111) and (201) faces of TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites is enhanced by further compounding between ZrO2 and TiO2 nanoparticles during the calcination process, and the peak strength of (111) and (201) faces increases after loading the noble metal Pt. However, the intensity of the characteristic peaks does not decrease but continued to increase after loading precious metal Pt, indicating that the intensity of characteristic peaks could be increased to a certain extent by photochemical reduction loading of precious metal Pt. At the same time, the  $2\theta = 30.3^{\circ}$  is the (102) surface of the ZrO<sub>2</sub>, and the composite material Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) corresponds to the (111) surface at  $2\theta = 28.3^{\circ}$ . The main characteristic peak position of the composite is offset, which is due to the inhibition of the growth of (102) crystal surface by TiO<sub>2</sub> and Pt nanoparticles. Meanwhile, the strength of the characteristic peaks on the (110) plane of the corresponding titanium dioxide continues to increase, indicating that the crystal form of titanium dioxide in the composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) is more perfect.

The grain size of the sample is calculated according to the Scherrer formula, and the results are shown in Table 1. By comparing the data of each group of samples in Table 1, it is found that the crystal size of the

Grain size (D\*), band gap energy (Eg), and cell parameters of different materials.

Sample	D* (nm)	Eg (eV)	Crystal parameters (TiO <sub>2</sub> )		Crystal parameters (ZrO <sub>2</sub> )	
			a(Å)	c(Å)	a(Å)	c(Å)
Pt/TiO <sub>2</sub> -ZrO <sub>2</sub> (C) TiO <sub>2</sub> -ZrO <sub>2</sub> (C) TiO <sub>2</sub> ZrO <sub>2</sub>	24.2 26.5 25.8 26.4	2.89 2.99 3.15 3.85	3.708 3.873 3.875 3.986	9.695 9.794 9.785 9.865	3.895 3.795 3.615 3.754	5.265 5.223 5.154 5.132



Fig. 4. X-ray photoelectron spectroscopy of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C): (a) full-spectrum; (b) O1s; (c) Ti2p; (d) Zr3d; (e) Pt4f.

noble metal Pt supported composite  $TiO_2$ -Zr $O_2(C)$  becomes smaller, the unit cell parameters of  $TiO_2$  decrease, and the cell parameters of  $ZrO_2$  increase. It is found from the data in Table 1 that the large grain size of the synthesized  $TiO_2$ -Zr $O_2(C)$  composites with Pt doping inhibits the formation of  $TiO_2$ -Zr $O_2(C)$  grains [24]. This belongs to PtO or Pt nanoparticles with good dispersion can be uniformly loaded on  $TiO_2$ -Zr $O_2(C)$ , thus inhibiting the growth of Pt/TiO\_2-Zr $O_2(C)$  crystal, resulting in the reduction of grain size [25–31].

# 3.3. XPS analysis

The element composition and valence state in Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites are analyzed by XPS analysis, as shown in Fig. 4. It can be observed from the full spectrum of Fig. 4(a) that Ti, O, Zr, C, and Pt are mainly present in the Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> composite. The characteristic peaks of carbon appeared in the whole spectrum, which can be attributed to the fact that the calcination process of polystyrene microspheres may not be burned out, or the characteristic peaks of C appeared in the instrument itself and the absorption of carbon dioxide in the air [32]. Fig. 4(b) is a characteristic peak of O1s. In the Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> porous composite, oxygen is mainly present in the form of lattice oxygen and adsorbed oxygen, and the valence state of oxygen is -2 [33]. In

Fig. 4(c), the binding energies of Ti at 459.0 eV and 465.2 eV correspond to  $Ti2p_{3/2}$  and  $Ti2p_{1/2}\text{,}$  respectively, indicating that Ti in the composite exists in the form of Ti<sup>4+</sup> [34]. The electron binding energies of Zr3d orbits are 181.9 eV and 184.8 eV, respectively, corresponding to the characteristic peaks of  $Zr3d_{5/2}$  and  $Zr3d_{3/2}$  in Fig. 4(d), indicating that Zr in the composite mainly exists in the form of  $Zr^{4+}$  [35]. Fig. 4(e) is the Pt4f peak of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C). From Fig. 4(e), it can be clearly found that Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) has four peaks at 71.7, 73.2, 75.1 and 76.1 of Pt 4f. The characteristic peaks at 71.7 and 76.1 eV correspond to the metal PtO states of Pt4f7/2 and Pt4f5/2, respectively, while the characteristic peaks at 73.2 and 75.1 eV correspond to  $Pt4f_{5/2}$  and  $Pt4f_{7/2}$ , respectively, belonging to elemental Pt<sup>0</sup>. Therefore, the coexistence of platinum oxide (PtO) and Pt elemental (Pt<sup>0</sup>) in the coral reef-like Pt/ TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composite was confirmed [36,37]. Among them, the PtO in the composite can provide more active sites, and their active sites will promote photocatalytic hydrogen evolution [38,39].

#### 3.4. UV-vis diffuse reflectance spectra

Due to research the light absorption properties of  $TiO_2$ ,  $ZrO_2$ ,  $TiO_2$ - $ZrO_2(C)$  and  $Pt/TiO_2$ - $ZrO_2(C)$  composites, UV–vis/DRS absorption spectra were analyzed, as shown in Fig. 5a. It can be seen from Fig. 5a



Fig. 5. UV-vis/DRS spectra of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub> and ZrO<sub>2</sub> (a) and Kubelka–Munk energy curve map (b). (For interpretation of the references to colour in this figure text, the reader is referred to the web version of this article.)

that TiO<sub>2</sub> shows the absorption in the ultraviolet region and its light absorption edge is located at 380 nm. The absorption of ultraviolet light by ZrO2 at 350 nm has dropped sharply, indicating that the absorption edge of ZrO<sub>2</sub> to ultraviolet light is lower than 350 nm. After the combination of titanium dioxide and zirconium dioxide, the prepared TiO<sub>2</sub>- $ZrO_2(C)$  composite has a certain visible light response and a red shift phenomenon [40]. However, the absorption intensity of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites of coral reef-like porous structure formed by photoreduction of noble metal Pt is obviously improved in the ultraviolet and visible regions, and a certain red shift occurs. This red shift can be attributed to the presence of surface effects, and the formation of coral reef-like porous structures increases surface tension, causing lattice distortion [41]. At the same time, to realize the merit of template in the synthesis method and morphology induced reactivity in photocatalysis, the composites are obtained via template free method, the optical absorption properties of the UV-vis diffuse reflection of Pt/TiO2-ZrO2, Pt/ TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> and Kubelka-Munk energy curve map are shown in support information Fig. S1(a, b). In addition, the composite Pt/TiO<sub>2</sub>- $ZrO_2(C)$  has a strong absorption in the range of 425–580 nm, which can be attributed to the plasmon resonance effect (SPR effect) of Pt [42,43]. The above results indicate that the loading of noble metal Pt is beneficial to the response of the composite in the visible region and enhances the absorption of visible light [44].

According to the Kubelka–Munk energy curve chart (Fig. 5b), the forbidden band widths of TiO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>-ZrO<sub>2</sub>(C) and Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) were obtained by the tangent method. The results are shown in Table 1. It can be seen from the values obtained in Table 1 that the  $E_g$  value of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composite is significantly reduced compared with the TiO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composite, which is due to the fact that Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) with coral reef-like porous structure has a strong absorption of visible light and the absorption of light extends to visible region. The results indicate that the coral reef-like porous structure Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) will have higher photocatalytic activity [45,46].

# 3.5. TEM and HR-TEM analysis

In order to further study the composition and structure of the composites, the TEM and HR-TEM analysis of the coral reef-like Pt/ $TiO_2$ -ZrO<sub>2</sub> porous structural materials were carried out. The results are shown in Fig. 6. Fig. 6a can be seen that the Pt/ $TiO_2$ -ZrO<sub>2</sub> composite formed by vacuum filling, calcination and photoreduction treatment with PS microspheres as a template has a coral reef-like porous structure. Among them, the bright portion is a porous structure of Pt/ $TiO_2$ -ZrO<sub>2</sub>.

Because of this special porous and surface gully, it provides favorable channel for photogenerated electrons, which reduces the mass transfer resistance of the material to some extent and enhances the carrier lifetime of  $Pt/TiO_2$ - $ZrO_2$  porous composites, providing more

active sites for photocatalytic reactions. It can be clearly seen from Fig. 6b that the Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> porous composite material is similar to the naturally formed gully, and the surface has a large number of pore structures. This further demonstrates the coral reef-like porous structure of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> composites (this is consistent with the SEM analysis). With the intention of further prove the crystal phase structure of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> composites. Fig. 6c, d is the selected area electron diffraction pattern of zirconium dioxide and titanium dioxide in Pt/TiO2-ZrO2 composites and different crystal faces of platinum by Fourier transform processing using Digital Micrograph software. At the same time, from Fig. 6c, d, it can be observed that Pt,  $TiO_2$  and  $ZrO_2$  lattice streaks appear in different selected regions of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub> composites, indicating that the coral reef-like Pt/TiO2-ZrO2 composites are successfully synthesized. Fig. 6e-g gave more specific information about different crystals, where the lattice spacing of  $ZrO_2$  is d = 0.244 nm, which belongs to the (111) crystal plane of ZrO<sub>2</sub> [47], and the interplanar spacing d = 0.340 nm corresponds to the (110) crystal plane of  $TiO_2$  [48]. The interplanar spacing d = 0.223 nm corresponds to the (111) crystal plane of Pt [49]. The lattice spacing of the clear crystals indicates the presence of Pt, TiO<sub>2</sub> and ZrO<sub>2</sub> in the synthesized composites and better crystallinity.

#### 3.6. N<sub>2</sub> adsorption-desorption analysis

In the interest of studying the surface physicochemical properties of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>, Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub> and ZrO<sub>2</sub> samples, the results of N<sub>2</sub> adsorption-desorption test are shown in the support information Fig S3 and Fig. 7. According to the definition of IUPAC, the above isotherms of Pt/TiO2-ZrO2(C), TiO2-ZrO2(C), TiO2 and ZrO2 belong to the type IV isotherm and have the H3 type hysteresis loop. The type of this isotherm and its hysteresis loop is caused by capillary condensation and special coral reef-like porous structure [50]. From the pore size distribution curve of Fig. 7 (shown in the inset), the pore size distribution of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) has certain broadness. From this it can be observed in the inset of Fig. 7(a) that the mesopores at ① and ② are 2.35 nm and 27.07 nm, respectively, due to the accumulation of TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles and the formation of gullies, which are respectively microporous and mesoporous structures. The pore size of 3 sites is about 85 nm, which is due to the macroporous structure on the coral reef surface after vacuum impregnation, timely calcination and photoreduction (Fig. 8a). Therefore, there is a porous structure on the surface of the Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composite. Because of the existence of this structure, the composite has more photocatalytic active sites, thereby enhancing the photocatalytic activity of the composite [51,52]. In the meanwhile, the porous structure can serve as a mass transfer channel for the substance, which is beneficial to the photocatalytic activity of the photogenerated electrons [53].

In addition, from this it can be the data in Table 2, the specific surface area of  $Pt/TiO_2$ -Zr $O_2(C)$  is higher than that of monomers  $TiO_2$ 



Fig. 6. HR-TEM images of (a-d) and FFT line plots (e-g) of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C).

and  $ZrO_2$ , and  $TiO_2$ - $ZrO_2(C)$ . This is mainly caused by the photoreduction of the noble metal Pt, which makes the surface area of the composite rough, resulting in the increase of the specific surface area. In general, we think that the special structure of the coral reef-like  $Pt/TiO_2$ -ZrO<sub>2</sub>(C) porous composite can promote the separation of electron–hole pairs, and the separated electrons and holes can



Fig. 7. N<sub>2</sub> adsorption-desorption isotherms of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) (a), TiO<sub>2</sub>-ZrO<sub>2</sub>(C) (b), ZrO<sub>2</sub> (a), and TiO<sub>2</sub> (d) (insets show the BJH pore size distribution curves).



Fig. 8. Photoluminescence spectra (excitation: 320 nm) of different samples.

Table 2

Specific surface area, average pore size, and pore volume of  $Pt/TiO_2$ - $ZrO_2(C)$ ,  $TiO_2$ - $ZrO_2(C)$ ,  $TiO_2$  and  $ZrO_2$ .

Sample	$S_{BET} (m^2 g^{-1})$	D (nm)	Vtotal (cm <sup>3</sup> g <sup>-1</sup> )
Pt/TiO <sub>2</sub> -ZrO <sub>2</sub> (C)	14.2	27.5	0.101
TiO <sub>2</sub> -ZrO <sub>2</sub> (C)	12.5	15.6	0.071
TiO <sub>2</sub>	12.2	12.8	0.054
ZrO <sub>2</sub>	11.0	13.0	0.036

successfully migrate to the surface and then transfer to the surface to react to organic pollutants degraded to  $CO_2$  and water. The porous and gully structures on the surface of the coral reef-like  $Pt/TiO_2$ - $ZrO_2(C)$  composites increase the charge transfer and inhibit the electron–hole recombination to improve the photocatalytic activity of the material.

# 3.7. PL analysis

The photo-luminescence spectra were investigated to examine the charge separation efficiency in different samples. As shown in Fig. 8, the PL spectra of all samples are included in the range of 200–800 nm.

Among them,  $TiO_2$  and  $ZrO_2$  have the strongest emission in the region, indicating that the combination of photogenerated electrons and holes is faster. The emission intensity of composite  $TiO_2$ - $ZrO_2(C)$  in the region decreases, indicating that the recombination rate of excited electron hole pairs caused by electron transfer after  $ZrO_2$  and  $TiO_2$  recombination is slower; among them, after loading Pt nanoparticles on the surface of  $TiO_2$ - $ZrO_2(C)$ , the intensity of the peak is further reduced, which indicates that the loaded Pt nanoparticles have accelerated electron migration, so reducing electron—hole pairs recombination and prolonging photocarrier carrier lifetime. Therefore, the loaded Pt nanoparticles can correspondingly improve the photocatalytic performance of Pt/TiO\_2-ZrO\_2(C).

#### 3.8. Photocatalytic activity

For the sake of studying the photocatalytic properties of composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C), the photocatalytic degradation experiments were carried out in UV, visible, simulated sunlight and microwave-assisted modes. The experimental results are shown in Fig. 9. It can be seen from Fig. 9(a) that the degradation of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites is higher than that of direct photolysis, P25, TiO2, ZrO2, Pt/TiO2, Pt/ZrO2 and TiO<sub>2</sub>-ZrO<sub>2</sub>(C) under ultraviolet light irradiation. The results show that the synergistic effect of TiO<sub>2</sub> and ZrO<sub>2</sub> combined with the loading of noble metal Pt and the synthesis of coral reef porous structure can effectively improve the photocatalytic activity of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) composites. The kinetic curves of rhodamine B degraded by different catalysts under ultraviolet light irradiation, as shown in Fig. 9(b). It can be seen from Fig. 9(b) that  $lnC_0/C_t$  has a linear relationship with the reaction time t, which indicates that follows the quasi-first-order reaction kinetics. The rate constants of direct photolysis, P25, TiO<sub>2</sub>, ZrO<sub>2</sub>, Pt/ TiO<sub>2</sub>, Pt/ZrO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub>(C) and Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) by UV photocatalytic degradation of rhodamine B were calculated as:  $0.0056 \,\mathrm{min}^{-1}$ ,  $0.007 \, \mathrm{min}^{-1}$ ,  $0.0016 \,\mathrm{min}^{-1}$  $0.0068 \,\mathrm{min}^{-1}$  $0.0062 \min^{-1}$ ,  $0.0135 \min^{-1}$ ,  $0.0194 \min^{-1}$ ,  $0.0249 \min^{-1}$ , respectively. Fig. 9(c-e) shows photocatalytic degradation of rhodamine B under visible light, simulated sunlight and microwave-assisted irradiation. It can be seen that Pt/TiO2-ZrO2(C) has relatively high



**Fig. 9.** Degradation of Rhodamine B by different catalysts irradiated by ultraviolet light (a), kinetic results of degradation of Rhodamine B with different catalysts under UV irradiation (b), visible light irradiation (t = 210 min) (c), simulated sunlight irradiation(t = 300 min) (d), photocatalytic degradation of Rhodamine B under microwave-assisted irradiation(t = 120 min) (e), photocatalytic degradation profiles of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) for different dyes and organic solutions under UV irradiation (f).

photocatalytic activity under the above experimental conditions, which is mainly due to the unique coral reef-like porous structure of the synthesized  $Pt/TiO_2$ -ZrO<sub>2</sub>(C) composite.

In addition, it should be emphasized that the high activity of Pt/ TiO<sub>2</sub>-ZrO<sub>2</sub>(C) microwave assisted photocatalysis is also related to its special morphology and microwave radiation. Microwave-assisted photocatalysis is to produce ultraviolet radiation by microwave electrodeless lamp, directly destroy the structure of organic pollutants by bond breakage. At the same time, microwave can produce additional defect sites on the catalyst. The polarizing effect of high defect catalyst can improve the possibility of photoelectron transfer. The surface defect of porous can become the trapping center of photogenerated electron and hole and restrain their recombination. Thus, the photocatalytic activity of the catalyst is further enhanced.

In order to investigate the practical application of the catalyst, the photoabsorption of the catalyst in UV region was evaluated under simulated sunlight condition, but the proportion of ultraviolet light in simulated solar light is very small. Under these conditions, the catalyst still degrades the model molecule to a certain extent, which indicates that the catalyst has certain practical application value. Fig. 9(f) is the result diagram of  $Pt/TiO_2$ - $ZrO_2(C)$  UV-photodegradation of different dyes. It has the best degradation effect on Rhodamine B, but also has different degrees of degradation on other dyes, indicating that the composite has certain universality.

#### 3.9. Photocatalytic hydrogen evolution

It can be seen from Fig. 10(a) that under the same experimental conditions, coral reef porous structure composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) has better hydrogen evolution ability in photolysis of water than that of TiO<sub>2</sub> and ZrO<sub>2</sub>. After 8 h reaction with methanol as the sacrificial agent, the total hydrogen production of was 7064.3  $\mu$ mol g<sup>-1</sup>, which was obviously higher than that of TiO<sub>2</sub>-ZrO<sub>2</sub>(C), TiO<sub>2</sub> and ZrO<sub>2</sub>, and was more 600 times than that of TiO<sub>2</sub>. The high hydrogen production of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) can be attributed to the following: (1) Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) has unique coral reef porous structure and high efficiency lighting ability, which can effectively capture the irradiated light energy. (2) The composite of TiO<sub>2</sub> and ZrO<sub>2</sub> is a factor. By combining TiO<sub>2</sub> with



Fig. 10. Result diagram of hydrogen production from different catalysts (8 h) (a); cycle diagram of Pt/TiO2-ZrO2(C) photolysis water to hydrogen production (b).

strong light stability and ZrO2 with redox property, the obtained composite will have the advantages of both. Moreover, the different energy levels between the two semiconductors can improve the separation of photogenerated charges and facilitate the transfer of photogenerated carriers from ZrO<sub>2</sub> to TiO<sub>2</sub>. (3) The photoabsorption property of the catalyst is enhanced by doping precious metal Pt. The SPR effect of Pt increases the transport pathway of photogenerated carriers and reduces the photoelectron-hole pair recombination. Pt acts as the active site of surface reaction, which further improves the activity of hydrophotolysis to produce hydrogen. In addition, a small amount of PtO present in the coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composite can promote the production of hydrogen by photolysis. The beneficial effects of PtO in promoting activity (hydrogen evolution) are as follows: (1) PtO can capture electrons as a cocatalyst during photocatalytic hydrogen evolution, promote separation of photogenerated charges, and prolong photogenerated carriers and improve the photocatalytic hydrogen evolution performance of composite materials. (2) PtO nanoparticles act as active sites to improve charge separation and migration at the interface between the promoter and the semiconductor. At the same time, the interaction between Pt and PtO reduces the recombination of photogenerated electron-hole pairs. (3) Pt<sup>2+</sup> and PtO nanoparticles provides an additional photocatalytic active site and inhibits the oxidation of hydrogen during the reaction.

The cycle stability of the coral reef-like  $Pt/TiO_2$ - $ZrO_2(C)$  porous composite was studied by photohydrolysis of hydrogen production cycle. The results are shown in Fig. 10(b). It can be seen from Fig. 10(b) that after the coral reef-like  $Pt/TiO_2$ - $ZrO_2(C)$  porous composite material is recycled five times; its hydrogen production still maintains a high level, indicating that the stability of the material is better. However, it can be seen from Fig. 10(b) that the stability of the material decreases after repeated cycles. The possible reason is that the noble metal Pt deposited on the  $TiO_2$ - $ZrO_2(C)$  composite produces hydrogen in photolysis water. A certain oxidation occurred during the process, and Pt oxide (PtO) is formed. The hydrogen production capacity of PtO is still slightly different from that of Pt.

#### 3.10. Possible photocatalytic reaction mechanism

In order to study the main active species of coral reef-like  $Pt/TiO_2$ - $ZrO_2(C)$  porous composites in photocatalytic reaction, the capture experiments of rhodamine B degradation by  $Pt/TiO_2$ - $ZrO_2(C)$  composites were carried out in this paper. Among them, p-benzoquinone (BQ) was used to capture superoxide radical ( $O_2^-$ ), and ethylenediamine tetraethylamine diamine (EDTA) was used to capture (h<sup>+</sup>), methanol (CH<sub>3</sub>OH) to capture hydroxyl radical ('OH). It can be seen from Fig. 11 that in the absence of a capture agent, the degradation of rhodamine B by the composite material reaches 95.0% after almost 120 min of ultraviolet light irradiation, and is almost completely degraded. The degradation effect of the coral reef-like porous structure composite Pt/



Fig. 11. UV photocatalytic degradation of Rhodamine B under different trapping agents.

 $\rm TiO_2\text{-}ZrO_2(C)$  on rhodamine B has reduced in varying degrees after adding the capture agent, indicating that the active species of Pt/TiO\_2-ZrO\_2(C) in the photocatalytic reaction system are mainly 'O\_2<sup>-</sup>, 'OH and h<sup>+</sup>.

As shown in Fig. 12(a), when ultraviolet light is irradiated on coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composites, the photon energy is greater than or equal to the band gap energy of TiO<sub>2</sub> and ZrO<sub>2</sub>. The electrons in the valence band (VB) of TiO<sub>2</sub> and ZrO<sub>2</sub> are excited to the conduction band (CB), and the electrons on the ZrO<sub>2</sub> conduction band (CB) are transferred to the conduction band of TiO<sub>2</sub>, then it is captured by the precious metal Pt. In addition, due to the lower Fermi level of Pt, the hole (h<sup>+</sup>) generated in the valence band of ZrO<sub>2</sub> is transferred to the valence band of TiO<sub>2</sub>. The electron trapping of TiO<sub>2</sub>-ZrO<sub>2</sub>(C) surface by Pt as an electron trap not only reduces the recombination of photogenerated electrons, thus improving the photocatalytic activity of the composites.

Fig. 12(b) shows the possible photocatalytic reaction mechanism of coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composites under visible light irradiation. Because both TiO<sub>2</sub> and ZrO<sub>2</sub> are broadband gap semiconductors, they almost do not absorb visible light, and hardly produce electrons and holes when exposed to visible light. Compared with pure TiO<sub>2</sub> and ZrO<sub>2</sub> under visible light, the photocatalytic properties of coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composites were significantly enhanced, mainly due to the SPR effect of Pt nanoparticles. Coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) due to the SPR effect of metal Pt porous composites can respond in the visible light region and generate hot plasma



Fig. 12. Possible photocatalytic reaction mechanism of Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C).

electrons. The resulting hot plasma electrons transfer first to the conduction band of ZrO<sub>2</sub> and then to the conduction band of TiO<sub>2</sub>. In order to return to the original state, Pt needs to accept electrons from the TiO<sub>2</sub> and ZrO<sub>2</sub> valence bands. These factors can increase the charge carrier lifetime and inhibit the recombination of electrons and holes. In addition, the near resonance energy transfer of Pt can accelerate the generation and separation of electron-hole pairs in TiO<sub>2</sub> and ZrO<sub>2</sub>.

In addition, under the irradiation of UV + vis light, the thermal plasma electrons of Pt can be transferred to the conduction band of  $ZrO_2$  and  $TiO_2$ , thereby increasing the rate of formation of H<sub>2</sub>, as shown in Fig. 12(c). Pt nanoparticles play two roles in this photocatalytic system. The first is to transfer electrons to the surface of ZrO<sub>2</sub> and TiO<sub>2</sub>, and then react with H<sup>+</sup> in water to form H<sub>2</sub>. The other is that Pt surface plasmon photogenerated electrons can be injected into the conduction bands of ZrO2 and TiO2 to improve the separation of electrons and holes. Therefore, this not only improves the absorption of visible light, but also reduces the composite probability of photogenerated electron-hole pairs, thereby improving the photocatalytic activity of the coral reef-like Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) porous composite.

#### 4. Conclusion

Using polystyrene (PS) colloidal microsphere template technique, the coral reef-like porous structure composite Pt/TiO2-ZrO2 was successfully prepared by sol-gel, vacuum impregnation and photoreduction. The composite Pt/TiO<sub>2</sub>-ZrO<sub>2</sub>(C) has a unique coral reef-like porous structure and high-efficiency lighting ability, which can effectively capture light energy. At the same time, different energy levels between TiO<sub>2</sub> and ZrO<sub>2</sub> semiconductors facilitate the transfer of photogenerated carriers from ZrO<sub>2</sub> to TiO<sub>2</sub>, which improves the separation of photogenerated charges. The plasmon resonance effect (SPR effect) of the noble metal Pt can promote the migration mode of photogenerated carriers and suppress the recombination of photogenerated electrons and holes pairs. Meanwhile, the presence of PtO promotes the separation and transfer of electrons and holes, provides more active sites for H<sub>2</sub> production and inhibits the oxidation of H<sub>2</sub>. Therefore, as a surface reactive site, Pt and PtO further enhances its photocatalytic degradation of organic pollution and photohydrolysis of hydrogen.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110482.

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