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The photocatalytic performance of Ta and Rh co-doped TiO_2 tuned by the average dopant valence

Xiao-yu Sun, Chang Liu, Zheng Chen, Yong-qing Ma*

Anhui Key Laboratory of Information Materials and Devices, School of Physics and Materials Science, Anhui University, Hefei 230039, People's Republic of China

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ABSTRACT

In order to reveal the effects of dopant average valence on the photocatalytic performance, Ta and Rh co-doped $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$ (x = 0, 0.008, 0.016, 0.02, 0.024, 0.032, and 0.04) samples were crystallized at 450 °C and 800 °C, respectively; then the 800 °C crystallized x = 0.02 sample was subsequently reduced in the H_2/N_2 mixture gases at 600, 700, 800, and 900 °C. Under different processing conditions, Ta remains the valence of +5, while the valence of Rh varies. Rh exhibits Rh^{3+} and Rh^{4+} in the 450 °C crystallized samples and is completely oxidized to Rh^{4+} in the 800 °C crystallized samples. In the reduced samples, Rh exists in the forms of Rh, Rh^{3+} and Rh^{4+}. The optimal photocatalyst is obtained as the ratio of Rh^{3+}/Rh^{4+} is 2.11 or the average valence of doped Ta and Rh is closest to the +4 valence of substituted Ti.

1. Introduction

Titanium dioxide (TiO_2) has the advantages of high efficiency, non-toxicity, chemical stability and low-cost, enabling it to become a benchmarking photocatalyst which has been widely used in degradation of organic pollutants [1–5], photo energy conversion or water splitting [6] and self-cleaning [7–9]. The 3.2 eV (387 nm) band gap energy of anatase TiO_2 limits the effective use of TiO_2 in the visible-light region. To solve this problem, one of the most effective ways is to create impurity energy levels in the forbidden band of TiO_2 through the doping of metallic ion at Ti^{4+} sites [10].

A majority of doping researches aim to reveal the effects of the dopant type and oxidation state on the photocatalytic performance. However their results are diverse and even contradictory [11–15]**. Therefore, it is important to unravel the intrinsic reasons for these conflicting results, which is indispensable for designing and developing the high effective photocatalyst.**

The dopants that substitutes Ti^{4+} in TiO_2 produce the multiple effects on the photocatalytic performance, because they have the different ionic radius and/or valences from that of Ti^{4+} in TiO_2, inevitably leading to the lattice distortion and/or changing the valence of Ti and the amount of oxygen vacancy (O_v) which synergistically affect the photocatalytic performance [14–16]**. Therefore, in order to reveal the effects of dopant valence on the photocatalytic performance, it is important to keep the dopant radius constant. Imaginably, this idea cannot be realized through the doping of a single element, so in the present work Rh and Ta co-doped $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$ is utilized to investigate the effects of dopant valence. The valence of Rh and Ta is commonly +3 and +5** [17–19]**, respectively, and the ionic radius of both Rh^{3+} and Ta^{5+} is 0.68 Å** [20–23]**, equal to that of Ti^{4+} in TiO_2. Therefore, with changing the concentration of Ta and Rh in $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$, the average ionic radius will keep constant, while the average valence of Ta and Rh can be tuned in the** region of +3 ~ +5. The Rh or Ta mono-doped TiO_2 was extensively reported [17,18,24,25]**, but the strategy to change the dopant average valence through Rh and Ta co-doping has not been reported before as far as we know.**

2. Experimental procedure

2.1. Synthesis of Rh^{3+} and Ta^{5+} co-doping TiO_2

The Rh^{3+} and Ta^{5+} co-doping $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$ (x = 0, 0.008, 0.016, 0.02, 0.024, 0.032 and 0.04) were synthesized through the sol-gel method. First, 3.895 mL titanium isopropoxide (TIP, $C_{12}H_{28}O_4Ti$, 95%, Aladdin, Shanghai, China) was added to 100 mL isopropyl alcohol (C_3H_8O, 99.7%, Aladdin, Shanghai, China) to form the solution A (titanium precursor solution). Then $TaCl_5$ (98%, Macklin, Shanghai, China) and $RhCl_3{\cdot}3H_2O$ (Rh 38.5%, Aladdin, Shanghai, China) with the Ta/Rh molar ratio being 100%, 80%, 60%, 50%, 40%, 20% and 0% were added to 100 mL isopropyl alcohol to form solution B. The molar ratio of (Ta + Rh): Ti was controlled to be 4:96. The solution A and solution B were continuously stirred for 60 min respectively; Subsequently they were mixed with continuously stirring for 120 min,

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* Corresponding author.
E-mail address: yqma@ahu.edu.cn (Y.-q. Ma).

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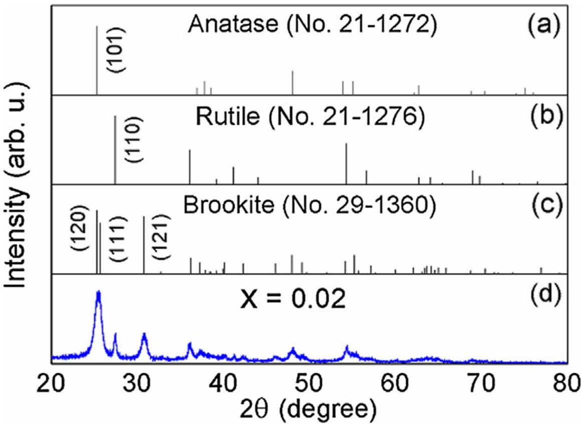

Fig. 1. The standard PDF cards of anatase (a), rutile (b), brookite (c) TiO_2 and the XRD pattern of $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ (x = 0.02) crystallized at 450 °C (d).

and then two drops of concentrated hydrochloric acid (36%–38%) were added. After stirring for 60 min, 50 mL diluted isopropanol with the volume ratio of isopropanol/water being 1:1 was dropwise added to initiate precipitation at 80 °C inwaterbath with stirring for 60 min.

The obtained precipitate was collected by centrifuge, washed with ethanol and distilled water twice, and then dried in a drying oven at 40 °C. All of the powders were crystallized at 450 °C and 800 °C, respectively.

2.2. Reduction of Rh^{3+} and Ta^{5+} co-doping TiO_2

The 800 °C crystallized $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$ (x = 0.02) was reduced in the H_2/N_2 mixture gases (500 sccm, $96\%N_2 + 4\%H_2$) for 4 h at temperatures of 600–900 °C.

2.3. Characterization

The crystal structure of the products was determined by X-ray diffraction (XRD) using an X-ray diffractometer (XRD; SmartLab 9 KW, Rigaku Industrial Corporation, Osaka, Japan) with Cu Kα irradiation (λ = 1.5406 Å) in the scanning range 10–80° with a step size of 0.01°. X-ray photo-electron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi (ESCALAB 250Xi, Thermo Scientific Inc., USA). The ultraviolet visible diffuse reflectance spectra (UV–vis DRS) of samples were tested on a Shimadazu U-4100 spectrometer (U-4100, Shimadazu Corporation, Tokyo, Japan). The photocatalytic activity of the prepared samples was evaluated by the degradation of methylene blue, which was exposed under xenon lamp (300 W), 10 cm away from the solution. Experiments were as follows: 100 mL methylene blue aqueous solution with the concentration of 10 mg/L was mixed with 50 mg magnetic catalysts in a vessel. Before the irradiation, the mixed solution was stirred in a dark condition for 60 min until an adsorption–desorption equilibrium was established. Samples of solution were extracted every 10 min from the reactor and the concentration of methylene blue was analyzed by an UV–vis spectrometer (UV-3200S, MAPADA, Shanghai, China) and calculated by a calibration curve.

3. Results and discussion

3.1. Rh^{3+} and Ta^{5+} co-doped TiO_2 catalysts crystallized at 450 °C

The XRD trials were performed on all $Ti_{0.96}Ta_{0.04-x}Rh_xO_2$ (x = 0, 0.008, 0.016, 0.02, 0.024, 0.032 and 0.04) samples crystallized at 450 °C; the results show that all samples exhibit the similar spectral features, therefore only the XRD pattern of the x = 0.02 (Ta:Rh = 1:1) sample is representatively shown in Fig. 1(d). All samples contain the anatase, rutile and brookite TiO_2 according to their standard cards in powder diffraction files (PDF), as shown in Fig. 1(a–c) in which the indices of lattice planes are given for the strong diffraction peaks of TiO_2.

According to the (110) diffraction peak of rutile TiO_2 and the (121) diffraction peak of brookite TiO_2, the crystallite size of the rutile (D_r) and brookite (D_b) TiO_2 can be calculated by using MDI Jade 5.0 software, as listed in Table 1. The (101) diffraction peak of anatase TiO_2 overlaps with the (120) and (111) diffraction peaks of brookite TiO_2, therefore the crystallite size of anatase TiO_2 cannot be obtained. With increasing the concentration of Rh (x), the position of (110) diffraction peak of rutile TiO_2 and the (121) diffraction peak of brookite TiO_2 hardly changes, indicating that the average ionic radius of Rh and Ta close to that of Ti in TiO_2.

In order to investigate the chemical state (denoted as CS below), the XPS measurements of Ta 4f, Rh 3d, Ti 2p and O 1s core levels are carried out for the 450 °C crystallized $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ (x = 0, 0.02, 0.04) samples; Fig. 2 representatively show the results of x = 0.02 sample, in which the solid line is the experimental curve, dashed lines are the fitting curves and the empty circles are the sum of fitting curves. The CS of each element and the corresponding binding energy (E_B) and the ratio of each CS are listed in Table 2.

For the x = 0.02 sample, the peaks of Ta 4f are centered at the binding energy (E_B) = 26.0 eV and 27.0 eV, corresponding to Ta^{5+} and Ta in TaO_x [26,27]. The Rh 3d XPS spectrum shows two peaks at E_B = 308.1 eV and 309.7 eV, attributable to Rh^{3+} and Rh^{4+} [28,29]. Two peaks at E_B = 458.9 eV and 460.2 eV of Ti 2p correspond to Ti in TiO_2 and TiO_x [30]. The O 1s core level XPS spectrum shows two peaks at E_B = 530.2 eV and 532.0 eV, which can be assigned to the O element in TiO_2 [31] and oxygen vacancy (O_v) [32]. For the x = 0 sample, its O 1s core level XPS spectrum, as shown in the inset of Fig. 2(d), is obviously different from that in the x = 0.02 and x = 0.04 sample; it can be well fitted by three peaks at E_B = 530.2, 532.0 and 532.5 eV, respectively. The peak at E_B = 532.5 eV can be ascribed to Ta-O [33].

In the Ta and Rh co-doped $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ sample, with increasing x, on the one hand, the doped Rh induces the variation of chemical state of other elements. For example, the chemical state Ta-O appears in the x = 0 sample, while it disappears in the x = 0.02 and x = 0.04 samples as a result of valence balance. On the other hand, the chemical state of Rh itself also changes with increasing the concentration of dopant Rh: Compared with the x = 0.02 sample, the ratio of Rh^{4+} becomes higher while the ratio of Rh^{3+} becomes lower for the x = 0.04 (100% Rh) sample.

Fig. 3(a) shows the UV–vis DRS of 450 °C crystallized $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ (x = 0, 0.02 and 0.04) and the commercial P25 TiO_2. The absorbance of P25 sharply increases at ∼400 nm, due to the electronic transition from valence band to conduction band matching the band

Table 1
The crystallite size of rutile (D_r) and brookite (D_b) TiO_2 for all 450 °C crystallized $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ samples and the crystallite size of rutile (D_r^{800}) TiO_2 of all 800 °C crystallized $Ti_{0.96}Ta_{0.04\text{-}x}Rh_xO_2$ samples.

	x = 0	x = 0.008	x = 0.016	x = 0.02	x = 0.024	x = 0.032	x = 0.04
D_r (nm)	21.5	15.6	18.8	22.8	21.1	24.7	23.3
D_b (nm)	8.4	10.3	10.2	10.1	8.7	11.5	9.2
D_r^{800} (nm)	39.3	41.7	40.2	43.5	39.1	40.2	39.8