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Spatial separation of Pt and IrO_2 cocatalysts on SiC surface for enhanced photocatalysis

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ABSTRACT

The spatially separated Pt and IrO_2 deposition on micro-SiC surface was synthesized via an *in-situ* photodepositing method. The interaction between Pt and SiC resulted in this spatial isolation, which then suppresses the photo-excited electron-hole recombination on SiC surface by the synthetic effect between two cocatalysts. Due to this mechanism, the hydrogen evolution over Pt/SiC/IrO_2 achieves 130 times higher photocatalytic activity than that of pure SiC in the presence sacrifice reagent. The degradation rate of RhB was also increased by double times.

1. Introduction

SiC is a representative metal-free photocatalyst and is considered to be promising photocatalysis reactions, because of its suitable band gap, abundant source, as well as environmental-friendly properties [1–6]. Moreover, Micro-sized SiC is desired to be practical applications duo to its low-cost. However, the micro-sized SiC do not exhibit satisfying photocatalytic action due to its fast recombination of excited electron-hole pairs and lack of active sites on surface. Recent studies have shown that surface modification by cocatalysts (such as Ag and graphene.), especially noble metals, is beneficial to charge separation and surface catalytic reactions [7–9]. Spatially separated of the electron and hole capture cocatalysts can greatly inhibit the surface charge recombination [10]. Unfortunately, these two cocatalysts were easily deposited on the same location and did not separated on the semiconductor surface when they were prepared by an impregnation or hydrothermal method. It is hard to fully realize the high and stable performance for these cocatalysts [11]. Therefore, it is necessary to control the reduction and oxidation cocatalyst on the different sites.

Our previous work has been investigated that the Pt could be selectively deposited on the Si sites of micro-SiC surface forming the Pt-Si bond. The Pt-loaded SiC was found to show 40 times higher activity than that of unloaded SiC [12]. Based on this finding, we herein successfully deposit Pt and IrO_2 nanoparticle in spatially-separated feature on micro-SiC (6H) surface using an in-situ photodeposition method. The spatial separation of two cocatalysts remarkably suppresses electron-hole recombination on SiC surface. Due to the synergetic effect, hydrogen production is drastically enhanced from 12 to 2337 $\mu L \cdot h^{-1} \cdot g^{-1}$ over Pt/SiC/IrO_2, which is the highest photocatalytic activity for the micro-SiC catalysts as far as we know. The degradation rate of RhB was also increased by double times than that of pure SiC.

2. Experimental

All chemicals were analytical grade and used as received without further purification. Green SiC particles (99.9%) were purchased from Shanghai ST-nano Science & Technology Co. Ltd. China. SiC powder was pre-treated as previous work [12]. The particle size of obtained SiC was roughly estimated to be 5 μm (Fig. S1).

The Pt/SiC/IrO_2 was synthesized by two-step procedures. Firstly, SiC/IrO_2 was obtained by impregnation method, in which we used Na_2IrCl_6 $6H_2O$ as precursors of IrO_2. Briefly, 0.5 g of SiC powder was impregnated in an aqueous solution containing 1.5 mL Na_2IrCl_6

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(corresponding to 0.1 wt% IrO_2). The solution was then evaporated by water bath at 80 °C, followed by calcinations at 450 °C in air for 3 h. Secondly, the loading of Pt (0.5 wt% Pt) on SiC/IrO_2 was performed using the *in-situ* photodepositon method, as noted in Supporting Information (SI). For comparison, $Pt/SiC/IrO_2$ (IM) was prepared by typical impregnation method.

The samples were characterized by a variety of characterization techniques. The characterization details and photocatalysis conditions can be found in Supporting Information (SI).

3. Results and discussion

The morphology of $Pt/SiC/IrO_2$ and SiC/IrO_2 was characterized by SEM (Fig. 1a and b). Both two cocatalysts show a nanoparticle modality. The dark dot is Pt nanoparticles while the light one is IrO_2. It demonstrates that the location of Pt is different from that of IrO_2. The high resolution TEM images of $Pt/SiC/IrO_2$ are shown in Fig. 1c and d. The particle size of Pt is 1–2 nm, while the IrO_2 is slightly larger (3–4 nm). The value of 0.197 and 0.225 nm corresponds to the lattice spacing of {200} facet of Pt and {200} facet of IrO_2, respectively. The element mappings further confirmed the different locations between Pt and IrO_2 (shown in Fig. 1e, f, g, h). Therefore, the spatially separated Pt and IrO_2 was successfully deposited on SiC surface.

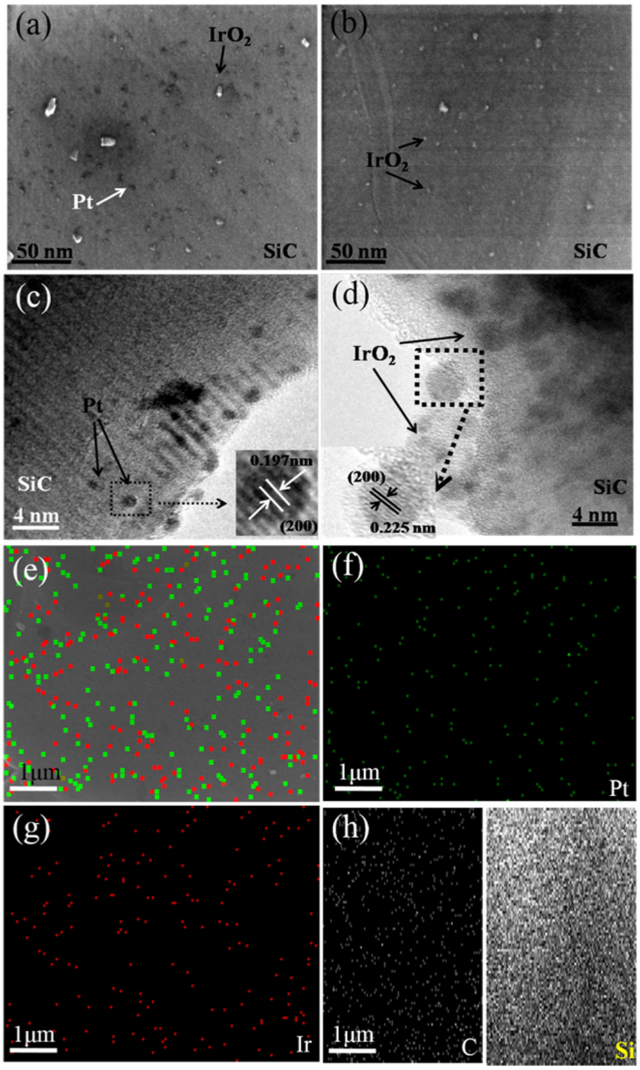

Fig. 1. SEM images of $Pt/SiC/IrO_2$ (a) and SiC/IrO_2 (b); HRTEM images of $Pt/SiC/IrO_2$ (c) and (d); Element mapping for $Pt/SiC/IrO_2$ (e), the red and green spots in (e) are represented as the distribution of Ir and Pt elements, respectively; (f), (g), and (h) are represented for platinum, iridium, carbon and silicon.

The chemical properties of the loading noble metal were characterized using the XPS technique. The peak center at 282.6 eV corresponds to the C-Si bond in SiC, while the value of 284.8 eV can be assigned to the element C (Fig. 2a). An XPS signal of Si 2p observed at a binding energy around 100.8 eV can be assigned to the Si-C bond in SiC (Fig. 2b). The peak at 101.8 eV can be assigned to SiO_x-C_y, which resulted from the surface adsorption O_2 of the SiC sample [4]. The new peak centred at 98.3 eV corresponds to the Si-Pt bond that proved by our previous work [12]. The peak at 72.4 eV can be assigned to Pt $4f_{7/2}$ (Fig. 2c). The binding energy of Ir $4f_{7/2}$ is 62.35 eV and corresponds to the value of Ir^{4+} (Fig. 2d), which means the metal oxide IrO_2 on SiC surface. Our previous work had calculated that the conduction band (CB) of SiC was consisted of a Si 3*p* orbital [12]. For a photodeposition process, IrO_2 act as hole capture. When sample was illuminated, the excited electrons transferred to the CB of SiC and then reduce the $PtCl_6^{2-}$ to Pt. Thus, the Pt atom can be deposited around the Si atom. That means the Pt was loaded at the electron-rich site in this reaction process. It is proposed that this mechanism resulted in the spatially separated between Pt and IrO_2 on SiC surface.

The characteristic peaks of SiC by XRD (Fig. 3a) correspond to hexagonal crystallinity (ICDD-PDF No. 29-1128). No characteristic peak for IrO_2 and Pt could be observed due to the low loading amount. A comparison of UV–Vis absorption spectra (Fig. 3b) indicate all of the samples displayed the similar absorbance edge, which indicates that the loaded metal nanoparticles did not have an obvious effect on absorbed position.

The synergetic effect between the spatially separated Pt and IrO_2 may lead to a significant charge separation, which is beneficial for the effective use of excited electrons and holes. In order to confirm their effects, the PL spectra of the composites were measured (Fig. 3c). In particular, the $Pt/SiC/IrO_2$ sample exhibits the lowest emission intensity, which represents the lowest recombination of electron-hole pairs. Furthermore, the time-resolved fluorescence emission decay spectra (Fig. 3d) demonstrates that the average decay lifetime of carriers in $Pt/SiC/IrO_2$ was 3.79 ns, which was relatively longer than that of Pt/SiC (3.59 ns) and pure SiC (3.41 ns). This suggested that the lifetime of charge carriers was lengthened, which was favorable for improving photocatalytic activity.

Using sacrificial water reduction (Fig. 4a), the hydrogen production for $Pt/SiC/IrO_2$ was robustly increased to 70.1 μL in 3 h (equal to 2337 $\mu L \cdot h^{-1} \cdot g^{-1}$), which was 1.7 times higher than that of Pt loading only. For the degradation of RhB (Fig. 4b), after 240 min illumination, the RhB was completely degraded over $Pt/SiC/IrO_2$ while only 60% RhB was degraded over pure SiC. The photocatalytic mechanism was illustrated in Fig. 4c. The Pt cocatalyst worked as an electron collector while IrO_2 worked as a hole capture. Therefore, the spatial separation between Pt and IrO_2 became the trap for excited electron and hole, respectively, which suppressed the electron-hole recombination on SiC surface. Thus, the synergetic effect between Pt and IrO_2 promoted the photoactivity of the SiC photocatalyst.

4. Conclusions

In summary, the spatially separated Pt and IrO_2 on micro-SiC was synthesized. Their synergetic effect suppressed the electron-hole recombination on SiC surface and lengthened the lifetime of charge carriers by 11%, thus promoted the photoactivity of the ternary photocatalyst. This finding may contribute to a starting point for designing and assembling an efficient photocatalyst based on SiC material in solar energy conversion applications.