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Ultrasonic spray pyrolysis assembly of TiO$_2$-WO$_3$-Pt multi-heterojunction microspheres photocatalyst by highly crystallized WO$_3$ nanosheet: less is better

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Abstract: Multi-heterojunction is more promising than single-heterojunction in photocatalysis due to the availability of more interfaces between each component. However, its photocatalytic activity is highly dependent on the contact mode of individual component. In this work, we assemble TiO$_2$-WO$_3$-Pt multi-heterojunction microspheres by ultrasonic spray pyrolysis and focus on their contact mode governed photocatalytic activity. The results reveal that highly crystalline WO$_3$ nanosheets as building blocks could particularly enhance the photocatalytic activity of TiO$_2$/WO$_3$ system toward degrading gaseous acetaldehyde and isopropyl alcohol. Furthermore, loading of Pt nanoparticles on WO$_3$ nanosheets could facilitate to a more prominent enhancement of activity than that of TiO$_2$/Pt, benefiting from the two-electron reduction of oxygen at the interface of WO$_3$/Pt. Meanwhile, high crystallinity of WO$_3$ nanosheets allows a loading amount of Pt as low as 0.04 wt% in TiO$_2$-WO$_3$-Pt system, which reduces the catalyst cost in comparison with the conventional amount of 1wt%.

1. Introduction

TiO$_2$ continues to gain research interest in photocatalysis-related
Recent study reveals that its solar conversion efficiency could be further improved when TiO$_2$ meets second metal oxide in terms of type II heterojunction.$^{5,15}$ For example, Zhang et al.$^{14}$ prepared the WO$_3$/TiO$_2$ composites and 5.0% WO$_3$/TiO$_2$ composite showed far superior photoactivity as compared to pure TiO$_2$, P-25 and pure WO$_3$ in the degradation of methyl orange and 2,4-dichlorophenol in UV and visible light. Liu et al.$^{15}$ developed Bi$_2$MoO$_6$ nanosheet/TiO$_2$ nanobelt heterostructure and observed an excellent photodegradation performance under UV and visible light irradiation. Moreover, such a heterostructure possessed high photocatalytic oxygen production with a rate of 0.668 mmol h$^{-1}$ g$^{-1}$. However, among part of type II heterojunctions, conduction band of secondary oxide in type II heterojunction is lower than that of TiO$_2$ and thereby photogenerated electrons on the side of secondary oxide are difficult for onset of single-electron reduction of oxygen. As such, photo-generated electrons flowed from TiO$_2$ to foreign component across interface of heterojunction usually tend to seriously aggregate on the side of secondary metal oxide and result in unfavorable “back electron transfer” recombination.

To overcome the difficulty in initiation of oxygen reduction by photo-generated electrons, promotion of multi-electron transfer is found to be an alternative mean in order to boost the photocatalytic activity of aforementioned metal oxides.$^{16-18}$ For example, the potential of conduction band of Ag$_3$PO$_4$ cannot match the redox potentials of single-electron reduction of oxygen. However, the two-electron reduction of oxygen over Ag$_3$PO$_4$ can be initiated and result in remarkable photooxidation ability.$^{19}$ Similarly, Abe et al.$^{20}$ reported that Pt-WO$_3$ photocatalytically decomposed isopropyl alcohol with ca. 100-fold enhanced CO$_2$ generation rate, while only 4-fold enhancement was observed for Pt-(N-TiO$_2$). The reason for high activity of Pt-WO$_3$ was due to the promotion of multi-electron reduction of O$_2$ on the Pt cocatalyst rather than single-electron reduction. Hashimoto et al. grafted Cu(II) or Fe(III) species on a series of oxides, such as Ti$_{1-x}$W$_x$Ga$_{2x}$O$_2$,$^{21}$ (Sr$_{1-y}$Na$_y$)(Ti$_{1-x}$Mo$_x$)O$_3$,$^{22}$ Ti$^{3+}$ self-doped TiO$_2$ $^{23}$ and Fe doped TiO$_2$. $^{24}$ The grafted species consistently enhance photocatalytic activity toward degradation of isopropyl
alcohol induced by interfacial charge transfer (IFCT) process and thereafter consumption in multi-electron reduction of \( \text{O}_2 \) mediated by the surface clusters.

On the basis of above considerations, integration of advantages of type II heterojunction (wide light absorption range and improved charge separation) and cocatalyst (multi-electron induced surface reaction) into multi-heterojunction becomes a very promising way to access to high solar conversion efficiency. With regard to multi-heterojunction, contact mode between individual components is highly critical. For instance, Hoffmann et al. observed high hydrogen production rate about \((6-9) \times 10^{-3} \text{ mol h}^{-1} \text{ g}^{-1}\) over \(\text{CdS}/(\text{Pt-TiO}_2)\), which is higher by a factor of 3-30 than that of \(\text{Pt-}(\text{CdS/TiO}_2)\).\(^{25}\) Wang et al. showed a synergistic enhancement of \(\text{H}_2\) evolution over the \(\text{Pt/SnO}_x/\text{TiO}_2\) heterostructures formed by anchoring Pt NPs at SnO\(_x\) sites, whereas the rate of \(\text{H}_2\) evolution over \(\text{Pt/TiO}_2/\text{SnO}_x\) counterparts prepared by grafting SnO\(_x\) species on Pt/TiO\(_2\) was significantly decreased.\(^{26}\) Pap et al.\(^{27}\) obtained TiO\(_2/\text{WO}_3/\)noble metal (Au or Pt) composites by means of selective photodeposition of noble metal on desired surface of TiO\(_2\) or WO\(_3\). Major differences were observed in photocatalytic activity toward degradation of oxalic acid and production of hydrogen over catalysts wherein only the position of the noble metal was changed.

We have fabricated \((\text{WO}_3/\text{Pt})/\text{TiO}_2\) multi-heterojunction photocatalyst based on WO\(_3\) nanorods and Pt and TiO\(_2\) nanoparticles.\(^{28}\) The photocatalytic performance of the multi-heterojunction under visible light was found dependent on the location of the loaded Pt nanoparticles. Pt surface loading on WO\(_3\), as opposed to loading on the TiO\(_2\) surface, was more beneficial in maximizing the photocatalytic activity. Therefore, contact mode of chosen building blocks should not be overlooked and multiheterojunction should be smartly designed for photocatalysis.

Inspired by these reports, in this work, we continue to focus on multi-heterojunction assembled from TiO\(_2\), WO\(_3\) and Pt as well as their contact mode dependent photocatalytic activities. Furthermore, ultrasonic spray pyrolysis technique is employed to assemble multi-heterojunction due to fact that production of porous microspheres where light trapping via multiple scattering at air-solid interface is favored. Highly crystallized WO\(_3\) nanosheets are chosen as building blocks for the
sake of not only good contact with TiO₂ and Pt nanoparticles but also minimization of defects at the interface. Structural features and photocatalytic activities of as-assembled multi-heterojunction will be systematically discussed.

2. Experimental Section

2.1 Materials and Characterization

2.1.1 Materials

TiO₂ powders (Degussa P25) were obtained from Nihon Aerisol Co. H₂PtCl₆ • 6H₂O was purchased from Aladdin in analytical grade purity. Acetaldehyde (2 vol% in N₂) and CO₂ (2 vol% in N₂) were obtained from Beijing Chemical Co. Bi₂O₃, WO₃ powders were purchased in analytical purity from Chinese National Medicine Group Chemical Reagent Co. All chemical reagents were used as received, without further purification.

2.1.2 Preparation of WO₃ nanosheets

WO₃ nanosheets were synthesized by stoichiometric amounts of Bi₂O₃ and WO₃ to 800 °C for 16 h. The obtained powders were ground and then treated with 6M HCl solution for 3 days at room temperature to promote the proton exchange. The obtained light yellow suspension was centrifuged, washed thoroughly with deionized water to remove the residual acid, and finally dried at 80 °C in air overnight. The obtained powders(0.4 g) was immersed into 100 ml tetramethylammonium hydroxide aqueous solution (0.0028 M) for 8 days with continues stirring. As a result, a colloidal suspension with a light green appearance was obtained successfully, as references ²⁹. After centrifugation and drying at 80 °C, the obtained products were WO₃ nanosheets.

2.1.3 Preparation of WO₃/Pt hybrids

The WO₃ nanosheet sample (100 mg) was added into 10 ml water and ultrasonically dispersed for 10 min, and then, aqueous H₂PtCl₆ solution (256µl , 0.1 M) and 1.1 mL methanol was added. The solution was stirred continuously under UV light (340-420 nm) irradiation for 2 h.³⁰ The as-obtained Pt-loaded WO₃ nanosheets were centrifuged and dried at 343 K at ambient condition. The stoichiometric ratio of Pt on WO₃ is 1 wt%.
2.1.4 Preparation of TiO$_2$-WO$_3$-Pt multi-heterojunction

TiO$_2$-WO$_3$-Pt microspheres were prepared by the ultrasonic spray pyrolysis method. Typically, P25 TiO$_2$ powders (3 g) and pre-synthesized WO$_3$-Pt composite (0.12 g) were dispersed into 1000 ml of water to form a mixture suspension. Subsequently, the suspension was atomized by an ultrasonic nebulizer, and the formed mist was passed through a quartz tube heated at 1073 K. Then, powders were collected at an electrostatic collecting device connected to the end of the quartz tube. Finally, the as-obtained powders were annealed at 773 K for 30 min under ambient conditions.

2.1.5 Characterization

X-ray diffraction (XRD) characterization was carried out on a Rigaku D/max-2500 X-ray diffractometer. Photoluminescence (PL) spectra were recorded on a Jobin-Yvon HR800 instrument with an Ar$^+$ laser source of 325 nm wavelength in a macroscopic configuration. Morphology and composition analyses were carried out on a FEI quanta 250 field emission scanning electron microscopy (FESEM) and a high resolution electronic micrographs were acquired using a JEOL JEM-2100 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. UV-Vis diffusion reflectance (DR) spectra were recorded on a Lambda 900 UV–vis–NIR spectrophotometer, using BaSO$_4$ as reference.

2.1.6 Photocatalytic Test

Photocatalytic properties of samples were investigated by measuring the photodegradation of gaseous acetaldehyde and isopropanol under solar light irradiation. 0.05 g microsphere powders were uniformly spread in a sample holder with a geometric area of 0.25 cm$^2$, which was placed on the bottom of a 500 mL cylinder-type Pyrex glass vessel. The glass vessel was flushed with O$_2$ (20%)/N$_2$ gas to remove carbon dioxide from the system, and the relative humidity of atmosphere inside the vessel was controlled to 45% by passing the O$_2$/N$_2$ gas through chilled water. 5 mL acetaldehyde was introduced into the reaction vessel using a
Pressure-Lock syringe to reach a concentration of 200 ppmv. After keeping dark for 30 min, the glass vessel was irradiated from top by a 150 W xenon lamp (Hayashi UV410) which emit light of wavelength range of 350-700 nm. The light intensity irradiated on the samples was determined to be 1 mW/cm² at 365 nm by light intensity meter from Beijing Normal University. The degradation of acetaldehyde and the generation of carbon dioxide were monitored using a gas chromatograph (SP-2100A, BFRL Co.), equipped with a 2 m Porapak-Q column and a flame ionization detector. Isopropanol and acetone were monitored on gas chromatograph (GC2014C, SHIMADZU Co.), equipped with a WonderCap Wax column and a flame ionization detector.

3. Results and Discussion

In our work, firstly, we synthesize highly crystalline WO₃ nanosheet, employ photochemical method to load platinum (Pt) on the WO₃ nanosheet to form a noble metal-semiconductor heterostructure. The reason to choose highly crystalline WO₃ nanosheets instead of traditional WO₃ nanoparticles is that highly crystalline WO₃ nanosheet has few defects and inhibits recombination of electrons and holes. In addition, lamellar material has more reaction sites which are helpful for forming a good contact between Pt nanoparticles and WO₃ nanosheets. Subsequently, we combine pure TiO₂ (P25) with Pt loaded WO₃ nanosheets to form multi-heterojunction microspheres with ordered contact by a ultrasonic spray pyrolysis method. The multi-heterojunction microspheres microspheres have follow advantages: (1) porous microspheres are facile for adsorption of organic compounds and improve the photocatalytic activity due to their large surface areas. (2) The multiple heterogeneous structure photocatalyst with ordering contact mode can migrate the photogenerated electron and holes and suppress recombination more effectively than pure TiO₂ and TiO₂-WO₃ binary-heterogeneous structure. (3) Only rarely little platinum nanoparticles (0.04%, relative to the amount of TiO₂) are loaded in the multiple heterostructure photocatalyst, which not only results in activity enhancement but also save cost in comparison with traditional value of 1%.
3.1 Structure and morphology

![XRD and TEM images of WO₃ nanosheets](image)

Fig. 1: Structural characterization of WO₃ nanosheets: (a) XRD pattern; (b) TEM image; (c) SAED pattern.

XRD and HRTEM analysis are performed to characterize pre-synthesized WO₃ nanosheets. As shown in Fig.1a, all diffraction patterns can be well indexed to orthorhombic phase (JCPDS No.20-1324). TEM image in Fig. 1b shows that the products are nanosheets with side length of ca. 400 nm. In HRTEM image (Fig. 1c) of a WO₃ crystallite, interplanar distances corresponding to d(020) (0.384 nm measured; 0.3783 nm theoretical) and d(002) (0.392 nm measured, 0.3894 nm theoretical) are separated by a 89.6° ± 0.5° measured angle (90° theoretical). Corresponding selected area diffraction pattern shows a typical orthorhombic symmetry consisting of clear spots with strong diffraction, indicating the high crystallinity of WO₃ nanosheet. The clear spots can be labeled with planes of (002), (200) and (220) of orthorhombic WO₃, respectively.

SEM images of different samples synthesized by ultrasonic spray pyrolysis are shown in Fig. 2. As can be seen in Fig. 2a, pristine TiO₂ samples display the morphology of polydispersed microspheres with diameters from 0.5 to 2 μm. The surface of the spheres is not smooth, suggesting that the resulting microspheres are formed by the aggregation of nanoparticles driven by the drying of mist droplets. Similar phenomenon has been observed in ultrasonic spray pyrolysis prepared microspheres such as TiO₂, Fe₂O₃, ZnS and SiO₂. On the contrary, pure WO₃ samples in Fig. 2d show broken and hollow spheres with smooth surface, probably resulting from the difficult agglomeration of the primary large-sized nanosheets. After incorporating WO₃ nanosheets or WO₃/Pt hybrids with TiO₂ nanoparticles, porous
microspheres can be well maintained as shown in Fig. 2b and c. The edges of WO$_3$ nanosheets can not be distinguished in the microspheres, mainly due to their tendency of curling or wrapping in TiO$_2$ nanoparticles.

Fig.2: SEM images of (a) pristine TiO$_2$, (b) TiO$_2$/WO$_3$, (c) TiO$_2$-WO$_3$-Pt and (d) WO$_3$ samples

Fig.3: (a) XRD patterns of pure TiO$_2$, typical TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt samples; (b and c) XRD patterns of different TiO$_2$-WO$_3$-Pt multi-heterojunctions and enlargement of the region between 20-35 degrees.
Fig. 3 depicts XRD patterns for the samples prepared by ultrasonic spray pyrolysis. For pure TiO$_2$, diffraction peaks (Fig. 3a) at $2\theta = 25.22^\circ$, 37.78$^\circ$, 47.94$^\circ$, 54.96$^\circ$, and 62.69$^\circ$ can be respectively indexed to the (101), (004), (200), (211), and (204) planes of anatase (JCPDS No. 21-1271). In addition, diffraction peaks attributed to rutile are found, as shown by the appearance of its (110) reflection at $\sim 27.4^\circ$ of 2$\theta$ (JCPDS No. 21-1276). There is no any other characteristic peak in the XRD patterns, which confirms that other new phases are not formed during the preparation processes. Hence, the crystalline structure of pure TiO$_2$ is the mixture of anatase and rutile phase.

For the WO$_3$-TiO$_2$-Pt composites, no diffraction peaks of WO$_3$ can be found until the content of WO$_3$ reaches 20 wt% (Fig. 3b and c), resulting from either the low amount or high dispersity of WO$_3$ component on TiO$_2$. In curve Fig. 3b and c, as-detected diffraction peaks located at 23.70$^\circ$ and 28.77$^\circ$ can be attributed to orthorhombic phase of WO$_3$ (JCPDS No. 20-1324). No diffraction peaks of noble metal Pt are detected in all TiO$_2$-WO$_3$-Pt samples, which is mainly due to the ultra-small size of Pt nanoparticles and their quite low amount.

The structure of the as-prepared heterojunctions was further studied by TEM and HRTEM. Fig. 4a shows the HRTEM for platinum loaded WO$_3$ nanosheet samples. It is shown that Pt nanoparticles have a close contact to WO$_3$ nanosheet and WO$_3$/Pt heterostructure is well formed. In typical TEM image of WO$_3$-TiO$_2$-Pt microspheres shown in Fig. 4b, uniform distribution of pores in microspheres is once again observed, confirming above observation in SEM images. HRTEM image (Fig. 4c) clearly shows an interface between WO$_3$ and TiO$_2$. The fringe spacing of 3.545 Å and 2.63 Å can be indexed to (101) plane of anatase TiO$_2$, and (220) plane of orthorhombic WO$_3$, respectively.

Fig. 4: (a) HRTEM image of WO$_3$-Pt heterojunction, (b,c) TEM and HRTEM images of TiO$_2$-WO$_3$-Pt multi-heterojunction microspheres.
3.2 Optical properties

Fig. 5 depicts the typical diffuse reflectance spectra of pure-TiO$_2$, TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt. All spectra are dominated by the edge due to the O$^2$-Ti$^{4+}$ charge transition in anatase TiO$_2$ at 300-380 nm, which is comparable to the excitation of electrons from the valence band to the conduction band. UV-vis spectra performed in the diffuse reflectance mode (R) are transformed to the Kubelka-Munk function F(R) to separate the extent of light absorption from scattering. The value of band gap is obtained from the plot of the Kubelka–Munk function (F(R)E)$^{1/2}$ versus the energy of the absorbed light E. Accordingly, the band gap (E$_g$) for pure TiO$_2$ is calculated to be ca. 3.07 eV, which fall within the range of mixed phases of anatase and rutile. Different from previously reported TiO$_2$-WO$_3$ composites, no red-shift of the absorption edge of TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt in comparison with pristine TiO$_2$ is observed, mainly resulting from the low content of WO$_3$ and its high dispersion in the composite. Hence, it can be deduced that as-incorporated WO$_3$ components in multi-heterojunction have no influence on the absorption properties of TiO$_2$. In other words, in spite of narrower band gap of WO$_3$ than that of TiO$_2$, the photocatalytic activity of either TiO$_2$-WO$_3$ or TiO$_2$-WO$_3$-Pt may not be influenced by means of improvement of absorption property.

![Fig.5: UV-Vis-DRS spectra of different samples](image)

Photoluminescence (PL) spectroscopy has been useful in the field of photocatalysis. Information such as surface oxygen vacancies and defects, as well
as the efficiency of charge carrier trapping, immigration and transfer can be obtained. For pure TiO$_2$, as illustrated in Fig. 6, it exhibits a broad emission band in the visible light region. It is believed that the peaks result from the electronic transition mediated by the defect levels such as oxygen vacancies in the band gap.\textsuperscript{40} After incorporating with WO$_3$ nanosheets, the intensity of TiO$_2$ is significantly decreased. Considering that the PL emission is the result from the free charge carrier recombination, the lower PL intensity indicate that the TiO$_2$-WO$_3$ photocatalyst has a lower recombination rate of photo-generated electrons and holes,\textsuperscript{41} which is due to the fact that the electrons and holes are separated by the charge transfer at the heterojunction interfaces of WO$_3$ nanosheets and TiO$_2$ nanoparticles. More importantly, TiO$_2$-WO$_3$-Pt multi-heterojunction shows drastic quenching of PL intensity, suggesting a markedly enhanced charge separation co-promoted by WO$_3$/Pt and WO$_3$/TiO$_2$ heterojunction. This result confirms significant participations of WO$_3$ nanosheets and WO$_3$/Pt heterojunction in the decrease of recombination of photo-generated electron-hole pairs.

![Fig. 6: PL spectra of different samples](image)

### 3.3 Photocatalytic Performance

The photocatalytic test was investigated against degradation of acetaldehyde under solar light with intensity of 1 mw/cm$^2$ at 365 nm. For comparison, TiO$_2$-Pt (the same method of photochemical Pt loading, the quantity of Pt is 0.04 wt % relative to the entire photocatalyst microspheres) were also fabricated by ultrasonic spray pyrolysis method. Fig. 7a,b shows typical plots of decrease of acetaldehyde and
increase of CO$_2$ concentration as a function of irradiation time on different photocatalysts. According to the Langmuir-Hinshelwood kinetics model, the apparent rate for acetaldehyde degradation can be expressed as:

$$\ln(C_0/C) = kt,$$

where $C$ is the concentration of acetaldehyde during photocatalytic reaction, $t$ is the reaction time, and $C_0$ is the initial concentration of acetaldehyde. The apparent first order rate constant, $k$, are given by the slope of $\ln(C_0/C)$ versus $t$, and the results are 0.01422, 0.01325, 0.02491 and 0.0379 min$^{-1}$ for TiO$_2$, TiO$_2$-Pt, TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt microspheres, respectively (Fig.7c). For TiO$_2$-WO$_3$ photocatalyst, it is more efficient in degradation of acetaldehyde than that of pure TiO$_2$, which agrees well with previous TiO$_2$-WO$_3$ system. Notably, loading of Pt nanoparticles on the surface of P25 hardly exhibits improvement of activity in terms of either decrease rate of acetaldehyde or evolution rate of CO$_2$. Different from most study of TiO$_2$/Pt photocatalyst, our results suggest a poor improvement of the photocatalytic activity of TiO$_2$ after Pt loading, which is mainly due to the very few amount of Pt loading as low as 0.04%. Interestingly, when the same amount of Pt is loaded on WO$_3$, as-obtained TiO$_2$-WO$_3$-Pt multi-heterojunction displays a dramatic decrease of acetaldehyde and increase of CO$_2$ concentration at initial 60 min. About 90% of acetaldehyde was oxidized into CO$_2$ after 60 min, showing the most excellent photocatalytic activity of TiO$_2$-WO$_3$-Pt multi-heterojunction. Herein, it should be noted that Pt loading percentage in previous Pt/metal oxide composite photocatalyst is
usually 1% in most reported results. In our case, the significant enhancement of activity induced by incorporation of less amount of Pt of 0.04% in multi-heterojunction can be explained as following: Pt nanoparticles are in-situ photodeposited on the surface of WO$_3$ nanosheets. As demonstrated in aforementioned XRD and HRTEM results, WO$_3$ nanosheets are highly crystallized. Under UV light irradiation, high crystallization of WO$_3$ nanosheets can ensure easy immigration of photo-excited electrons from crystal inner to surface, less trapping of electrons by surface defects states and inhibition of recombination of electrons and holes. As such, H$_2$PtCl$_6$ is effectively photoreduced by electrons on the surface of WO$_3$ nanosheets and hence Pt nanoparticles are uniformly deposited on WO$_3$ surface without aggregation. Therefore, WO$_3$/Pt interface with high amount and good quality are produced, even if the Pt loading amount is lower than conventional value of 1%. Benefiting from the electrons flowing from WO$_3$ to Pt and onset of multi-electron reduced of oxygen, the photocatalytic performance of multi-heterojunction is obviously boosted.

![Graphs](image)

**Fig. 8:** (a) Degradation curves of isopropanol over different samples, (b) reaction kinetic curves over different samples, (c) CO$_2$ evolution curves over different samples, (d) concentration curves of acetone intermediate over different samples.
Meanwhile, isopropanol was also employed as substance to further verify above photocatalytic results.\textsuperscript{42,43} It is well known that the photocatalytic decomposition of isopropanol proceeds via formation of acetone as an intermediate followed by further decomposition of acetone to the final products CO$_2$ and H$_2$O. Fig. 8 shows time courses of the concentration of products generated from 2-propanol over TiO$_2$, TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt under solar light irradiation. For bare TiO$_2$, either generation rate of acetone intermediate or evolution rate of CO$_2$ is slower than that of TiO$_2$-WO$_3$ and TiO$_2$-WO$_3$-Pt samples, suggesting the less efficiency of TiO$_2$ in degradation of isopropanol (Fig. 8a-d). For TiO$_2$-WO$_3$ and TiO$_2$, the higher amount of acetone intermediate and lower evolution rate of CO$_2$ at the late stage indicate their insufficient oxidation ability. For TiO$_2$-WO$_3$-Pt multi-heterojunction, it shows a comparable generation rate of acetone to that of TiO$_2$-WO$_3$ at the initial 40 mins, and whereas a slower rate to that of TiO$_2$-WO$_3$ at the last 40 mins (Fig. 8d). Importantly, TiO$_2$-WO$_3$-Pt multi-heterojunction displays higher evolution rate of CO$_2$ than that of TiO$_2$ and TiO$_2$-WO$_3$ during the whole photocatalytic reaction (Fig. 8c). In this regard, it can be deduced that TiO$_2$-WO$_3$-Pt multi-heterojunction is highly active for both oxidation of isopropanol to acetone and further mineralization of acetone to CO$_2$. Therefore, in combination with the photocatalytic results of degradation of acetaldehyde and isopropanol, it is safe to conclude that TiO$_2$-WO$_3$-Pt multi-heterojunction sample displays superior photocatalytic activity to that of pure TiO$_2$ and TiO$_2$-WO$_3$.

Mechanism for the enhancement of photocatalytic activity of the TiO$_2$-WO$_3$-Pt can be explained by Scheme 1. Since the conduction band edge of WO$_3$ is lower than that of TiO$_2$, photo-generated electrons can be transferred to and accumulated in the conduction band of WO$_3$. Furthermore, owing to the high-crystallinity of WO$_3$ nanosheet, high quality of WO$_3$-TiO$_2$ and WO$_3$-Pt interface is obtained and recombination of photo-generated electrons and holes induced by defects can be avoided.\textsuperscript{44} Accumulated electrons then quickly transfer to the surface of platinum nanoparticles and hence separation of electrons and holes can be promoted. Besides that, photo-generated electrons injected into Pt nanoparticles act as electron pools to
initiate multi-electron reductions of the oxygen molecules, which further strengthen the photooxidation ability of organic substances.

Scheme 1: Mechanism for the enhancement of photocatalytic activity of the TiO$_2$-WO$_3$-Pt multi-heterojunction.

4. Conclusions

TiO$_2$-WO$_3$-Pt multiple heterostructure porous microspheres was successfully prepared via a facile ultrasonic spray pyrolysis method. Multi-heterojunction assembled via preloading Pt nanoparticles on highly crystallized WO$_3$ nanosheets is found more active than that via nonselective deposition of Pt nanoparticles. The photocatalyst activity of TiO$_2$-WO$_3$-Pt multi-heterojunction (0.04 wt% of Pt) is 2.86 times higher than TiO$_2$-Pt heterostructure composite with the same loading amount of Pt. Furthermore, the improvement of photocatalytic performance can be confirmed by 2.66 times and 1.52 times higher in acetaldehyde degradation, and also 1.8 times and 1.03 times higher in isopropanol degradation, than that of TiO$_2$ and TiO$_2$-WO$_3$ composite, respectively. The as-assembled porous TiO$_2$-WO$_3$-Pt microspheres multi-heterojunction photocatalyst has a good application prospect on gas-phase photocatalytic degradation system. The method of selection of highly crystallized WO$_3$ nanosheets providing brilliant availability to noble metal nanoparticles for separation of photoexcited electron-hole is a good inspiration for synthesis of other multiple heterostructure photocatalyst.
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In spite of the less amount of Pt (0.04 wt%), the activity of TiO$_2$-WO$_3$-Pt multi-heterojunction is still 2.66 times and 1.52 times higher in acetaldehyde degradation than that of TiO$_2$ and TiO$_2$-WO$_3$ composite, respectively.