



Control over energy level match in Keggin polyoxometallate-TiO₂ microspheres for multielectron photocatalytic reactions

Han Zheng, Changhua Wang*, Xintong Zhang*, Yingying Li, He Ma, Yichun Liu

Center for Advanced Optoelectronic Functional Materials Research, and Key Laboratory for UV-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China

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ABSTRACT

Recent years have witnessed that polyoxometallate (POM) is promising to mediate electron transfer on TiO₂ for enhanced photocatalysis. Therein, significant progress is made on photooxidation process, which mainly involves single electron transfer. It still represents a major challenge to develop POM-TiO₂ composites to promote multielectron transfer, such as in CO₂ reduction. In this work, we assembled oxygen-defected TiO₂-Keggin POM microspheres by ultrasonic spray pyrolysis technique for multielectron transferred reactions including mineralization of gaseous acetaldehyde and CO₂ reduction. Comprehensive analysis including transient photovoltage, surface photovoltage, and photochromic phenomena reveal that oxygen defects could induce better energy level match and hence mediate multielectron transfer. With variation of loading amount and kind of POM, the (5 wt %) H₃PW₁₂O₄₀ (HPW)-TiO₂ displays the highest activity among composites of HPW-TiO₂, H₄SiW₁₂O₄₀ (HSiW)-TiO₂, and H₃PMo₁₂O₄₀ (HPMo)-TiO₂, which is consistent with the best energy level match between defective TiO₂ and H₃PW₁₂O₄₀. The strategy of assembly of POM-TiO₂ microspheres provides a facile and promising solution to promote multielectron reaction for environmental purification and solar-to-fuel conversion.

1. Introduction

Semiconductor photocatalysis is considered as a promising technology for solar fuels generation and environmental remediation [1–3]. With the progress of photocatalytic research, it has been witnessed that photoinduced multielectron transfer is harder than single electron transfer and remains a highly relevant challenge due to the more probable recombination of charge carriers [4–6]. For example, TiO₂ works as an efficient photocatalyst on remediation of environmental organic pollutant, by which single electron transfer pathway dominates the early stages of reaction [7–9]. Nevertheless, TiO₂ and even benchmark P25 exhibit poor mineralization by which multielectron transfer pathway dominates the last stage of reaction. Also, they enable CO₂ reduction to CO via two electron transfer but not CH₄ via eight electron transfer. In this regard, further efforts are being made on promotion of multielectron transfer to make photocatalyst more efficient in solar energy conversion.

As is well reported, grafting of cocatalyst on semiconductor oxide facilitate efficient charge separation [10–13]. Unfortunately, the charge carriers in semiconductor oxide are intrinsically scattered and tend to participate in surface redox reactions via single electron transfer. Different from the scatter nature of charge carriers in semiconductor oxide,

increasing research documented that introduced oxygen defects effectively trap photogenerated carriers and facilitate charge accumulation [14–20]. On grafting cocatalyst onto defective semiconductor oxide, the integration of exterior charge transfer and interior trapping is favored for onset of multi-electron transfer. In spite of this, it is critical to create an energy level match between energy level of trapping electrons and reduction potential of surface cocatalyst. For example, researchers have developed a series of strategies of combining cationic ion doping or self-doping with cocatalyst grafting [20–25]. By these strategies, doping of cationic ion or Ti³⁺ self-doping can produce energy level below the conduction band of TiO₂, which match well with the potential of multielectron reduction of O₂ over surface grafted M_xO nanocluster cocatalyst (Cu_xO, Fe_xO, etc.). Benefiting from the multielectron transfer, ultrahigh rate of CO₂ evolution via mineralization is achieved in degradation of gaseous isopropyl alcohol. Therefore, introduction of defect level in TiO₂ to meet energy level match with reduction potential of surface cocatalyst is a promising mean to facilitate multielectron transferred reaction.

Keggin type POMs have been undoubtedly recognized as electron acceptors once they meet TiO₂, due to their lower energy level of LUMO than that of conduction band of TiO₂ [26–30]. Inspired by aforementioned considerations on defective TiO₂, we anticipate that energy level

* Corresponding authors.

E-mail addresses: wangch100@nenu.edu.cn (C. Wang), xtzhang@nenu.edu.cn (X. Zhang).

match between defective TiO₂ and POM can further extend the application of POM-TiO₂ composites from single-electron-transfer dominated oxidation for environmental remediation to that of multi-electron-transfer dominated reduction for solar fuels. More interestingly, Lv et al revealed that the POM anions interact mainly with Ti-OH₂⁺ sites on the surface of TiO₂ rather than replacement of surface hydroxyl group [31]. By this way, the TiO₂ surface can be fascinatingly covered by POM without decreasing the amount of surface hydroxyl group. The preservation of surface hydroxyl group after compositing TiO₂ with POM provides a very important clue for multi-electron-transfer reaction. That is, surface hydroxyl group can be oxidized by photogenerated holes and thereafter promote the release of proton [32], multi-electron-transfer reaction can proceed more easily via proton coupled electron transfer such as oxygen reduction (e.g. 2e⁻/2H⁺ to H₂O₂, 4e⁻/4H⁺ to H₂O), CO₂ reduction (e.g. 2e⁻/2H⁺ to CO, 8e⁻/8H⁺ to CH₄) and etc.

Herein, by means of a simple ultraspray pyrolysis technique, loading of POM and introduction of oxygen vacancy in TiO₂ was achieved simultaneously and finally POM-TiO_{2-x} microspheres were produced. The kind and content of Keggin POM including HSiW, HPW and HPMo are optimized for energy level match and promotion of multielectron transfer at POM-TiO₂ interface. Model reaction including mineralization of gaseous acetaldehyde and CO₂ reduction governed by multi-electron transfer process are tested to evaluate the photocatalytic activity. The results demonstrate that the presence of oxygen vacancy is adverse to charge separation, and whereas oxygen vacancy type POM-TiO₂ become a better candidate for multielectron involved reaction due to proper energy level match induced multielectron transfer. Therein, HPW (5 wt%)-TiO₂ exhibits the highest mineralization yield and CH₄ selectivity among all samples, benefiting from best energy level match and strong interaction between TiO₂ and HPW component. This simple but effective means on the basis of energy level match can be extended to apply doped semiconductor-POM system for highly active photocatalyst as well.

2. Materials

TiO₂ powders (Degussa P25) were obtained from Nihon Aerisil Co. Keggin polyoxometallates, including H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀ and H₃PMo₁₂O₄₀, were purchased in analytical purity from Chinese National Medicine Group Chemical Reagent Co. CH₄ (0.3 vol% in N₂) and CO (50 vol% in N₂) were obtained from Beijing AP BAIF Gases Industry Co., Ltd. All chemical reagents were used as received, without further purification.

2.1. Characterization

Morphology and composition analyses were carried out on a FEI quanta 250 field emission scanning electron microscope (FESEM) and high resolution electronic micrographs were acquired using a JEOL JEM-2100 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku, D/MAX-2500 X-ray diffractometer with Cu K α radiation. The UV-visible (UV-vis) diffuse reflectance (DR) spectra of the samples were collected using a PerkinElmer UV WinLab spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Magna 560 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using a VGESCALAB MKII instrument with a Mg K α ADES source at a residual gas pressure below 10⁻⁸ Pa. Electron spin resonance (ESR) measurements were conducted on an X-band CW-EPR Bruker ELEXSYS spectrometer in the X band (9.38 GHz) at 90 K equipped with a cylindrical cavity operating at 100 kHz field modulation. Transient photovoltage spectroscopy (TPV) and surface photovoltage spectroscopy (SPV) measurements were carried out using a lab-made instrument according to the references [33–36]. Zeta potential was measured using a DLS Zeta potential analyzer (ZS90) from Malvern Instruments.

2.2. Preparation of TiO₂-POM composite photocatalyst

POM-TiO₂ composite microspheres were prepared using the ultrasonic spray pyrolysis method. Typically, P25 TiO₂ powder (3 g) was dispersed into 1000 ml of water with a glass beaker, and added some 0.005 M HPW aqueous solution into the beaker to form a mixed suspension. Subsequently, the suspension was atomized using an ultrasonic nebulizer, and the formed mist was passed through a quartz tube heated at 823 K. Then, powder was collected at an electrostatic collecting device connected to the end of the quartz tube. Finally, Samples of 0, 5, 10, and 20 wt% POM-loaded TiO₂ were obtained. The color of as-obtained powders changes from original white of P25 to grey or light blue, indicating that they are defective. For comparison, POM-TiO₂ composites with no defects were prepared by direct drying of the POM-TiO₂ colloid suspension at 70 °C in air and turned to no USP process. By this way, the obtained powders perfectly maintained the original white color of P25.

2.3. Photocatalytic reduction of CO₂

The photocatalytic reduction of CO₂ was carried out in a closed gas system (Beijing CEAL Light Technology Co., Ltd, China). 1.3 g NaHCO₃ was added at the bottom of reaction (350 mL) firstly. Then, 50 mg of the TiO₂-POM microspheres powder was uniformly dispersed in a sample holder with a geometric area of 1.23 cm⁻². Prior to the light irradiation, the above system was thoroughly vacuum-treated to remove the air completely, and then 5 mL 4 M H₂SO₄ was injected into the reactor to react with NaHCO₃ to achieve 1 atm CO₂ gas. After that, the reactor was irradiated from the top by a 150 W xenon lamp (Hayashi UV410) which emits light in the wavelength range of 350–700 nm. The light intensity used to irradiate the samples was determined to be 20 mW cm⁻² at 365 nm using a light intensity meter from Beijing Normal University. During the irradiation, 1 mL of gas was taken from the reaction cell for subsequent qualitative analysis by gas chromatograph (GC2014, SHIMADZU Co.), equipped with a Shin-carbon ST column and a flame ionization detector. The quantification of the production yield was based on a calibration curve. The outlet gases was determined to be CO, CH₄ and CO₂.

3. Results and discussion

3.1. USP procedure based on isoelectric point of POM-TiO₂ suspension

As reported in previous study, USP can be served as a facile and scalable methodology to fabricate porous microspheres [37–40]. Three sequential stages are involved: (1) formation of precursor droplets by the ultrasonic nebulization of a colloid solution; (2) transport of droplets flux across the heating furnace by inert gas, accompanied by solvent evaporation and pyrolysis of precursor; (3) self-assembly and aggregation of nanoparticles into porous microspheres by further annealing. Up until now, we have successfully fabricated porous microspheres by employing TiO₂ nanoparticles [41], Nb doped TiO₂ nanoparticles [42], WO₃ nanosheets and Pt nanoparticles as building blocks [43]. In this work, P25 TiO₂ nanoparticles suspended in deionized water at a 3 g L⁻¹ concentration formed a relatively stable dispersion with a zeta potential of 21.5 mV (as shown in Fig. 1), which facilitates generation of uniform precursor droplets for ultrasonic sprayed pyrolysis. Upon addition of POM into TiO₂ colloid solution, the value of zeta potential is drastically decreased and value of zero is close to isoelectric point when the weight percentage of POM is about 5 wt%, which indicates strong interaction between protonated TiO₂ and POM anion. With further increase of POM content, the zeta potential is reversed from positive to negative and become stable until the loading content is higher than 20%. It indicates that the stability of P25 colloid is deteriorated once it meets POM solution. However, the as-formed particles aggregates can be re-dispersed with the increase of POM

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