

The long-term photocatalytic stability of Co^{2+} -modified P25- TiO_2 powders for the H_2 production from aqueous ethanol solution

Yuqi Wu, Gongxuan Lu*, Shuben Li

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, 730000 Lanzhou, PR China

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Abstract

In this paper, the long-term stability of photocatalytic activity of Co^{2+} doped P25- TiO_2 nanoparticles for hydrogen production from aqueous ethanol solution is discussed using a photoelectrochemical method in detail. It was found that after a long-term photoreaction, the photocatalytic activity of Co^{2+} ion modified P25- TiO_2 photocatalyst for hydrogen production *has decreased* by a factor of ca. 50%, and still was very *high compared* to that of pure P25- TiO_2 photocatalyst. And the steady anodic photocurrent appeared to *have* an obvious decrease after photoreaction (from 2.75×10^{-4} to 1.5×10^{-4} A), but the character of photocurrent response was still similar to photoreaction before. Moreover, the most important reason for the decrease of photocatalytic activity is the *removal* of CoO_x active species ($x > 1$) from the surface of TiO_2 photocatalyst after a long-term photoreaction. In addition, a new CoO_x intermediate species ($x < 1$, photooxidative potential at -0.36 V versus SCE) emerged on the surface of TiO_2 photocatalyst during photoreaction.

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1. Introduction

Sunlight-induced photocatalytic reactions are widely considered as one of the most promising routes to solar energy conversion. Converting solar energy to the form of chemical energy stored in a variety of chemical fuels (e.g. hydrogen fuel) presents significant advantages compared to other nonchemical routes, for example, converting solar energy to heat or to electricity, which couldn't be stored for long term.

Many proposals about generating chemical fuels from readily available raw materials by an environment-friendly method have been appeared, and production hydrogen from the photo-splitting of water using solar energy was *one of* the most promising *methods*, and *has* been widely studied. The crucial problem of this method is an appropriate choice of the suitable semiconductor material *to be used* as *photocatalysts*. Many semiconductor materials have been tested as a photocatalyst, and TiO_2 *seems* to be the most interesting material because of its physical and chemical stability, low cost, availability,

low-toxicity, and electronic *and* optical properties. However, the TiO_2 semiconductor has a large band gap ($E_g > 3.2$ eV, excited only by UV light) and limits the use of sunlight or visible light as an irradiation resource in photocatalytic reaction [1]. In addition, photogenerated electron–hole pairs can also recombine easily on pure TiO_2 surface. Therefore the photocatalytic efficiency of pure TiO_2 semiconductor is very low.

In order to overcome these drawbacks of TiO_2 semiconductor as a photocatalyst, many studies about the modification of the TiO_2 semiconductor surface for enhancing electron–hole separation and extending the light absorption range of TiO_2 semiconductor into the visible range have *appeared* [1–11]. These studies include doping of foreign ion into the TiO_2 lattice, dye photosensitization on the TiO_2 semiconductor surface, and deposition of noble metals. The results of foreign composition modifying on the TiO_2 semiconductor surface have been shown to greatly enhance the photocatalytic production of hydrogen from water.

In comparison with the extensive investigation about others, there are a few researches about Co^{2+} modified TiO_2 photocatalysts has been reported [4–7,11]. Choi et al. [6] had been reported that TiO_2 photocatalyst doped with metal ions (such as Fe^{3+} ,

* Corresponding author. Tel.: +86 9314968178; fax: +86 9314968178.
E-mail address: gxlu@ns.lzb.ac.cn (G. Lu).

Mo⁵⁺, Ru³⁺, Os³⁺, Re⁵⁺, V⁴⁺, Rh³⁺, Co²⁺ and so on) enhances the photoreactivity both for the photooxidation of CHCl₃ and the photoreduction of CCl₄, Iwasaki et al. [11] had been reported that doping a small amount of Co²⁺ ions into TiO₂ particles not only enhanced the photocatalytic activity of CH₃CHO photodegradation reaction under UV–vis ($\lambda > 300$ nm) light irradiation but also induced the visible light ($\lambda > 400$ nm) response, and the highest photocatalytic activities were obtained at 0.03 mol% Co for both irradiations. We have reported [12,13] that the photocatalytic hydrogen production rate from aqueous ethanol solution of the appropriate Co²⁺ ion doped P25-TiO₂ photocatalyst exceeds that of pure P25-TiO₂ photocatalyst by a factor of 10², the highest photocatalytic activities been obtained at 0.4 wt.% Co for UV irradiations. We have estimated the values of the quantum efficiencies for the reactions, and found the quantum yields of the bare P25 TiO₂ photocatalyst and Co²⁺-modified P25-TiO₂ photocatalyst for hydrogen generation were 0.014 and 1.7%, respectively.

However, for photocatalytic reactions on TiO₂, another basic problems, i.e. the stability of modified TiO₂ photocatalyst, especially about the modifying foreign composition, should be discussed and solved for improving the photocatalytic reaction efficiency. In this paper, the long-term stability of photocatalytic activity of Co²⁺ doped P25-TiO₂ nanoparticles for hydrogen production from aqueous ethanol solution is discussed using a photoelectrochemical method in detail.

2. Experimental

2.1. The preparation of 0.4 wt.% CoO_x-TiO₂ powder photocatalyst

CoO_x-TiO₂ powders were prepared by thermal decomposition method with cobaltic salts Co(NO₃)₂·6H₂O, a commercial form TiO₂ (P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m² g⁻¹; primary size ~20–50 nm, agglomerate size ~100 nm) from Degussa was used in this paper. According to the 0.4 wt.% Co, the appropriate Co(NO₃)₂·6H₂O ethanol solution was mixed with 1 g P25-TiO₂ powders, respectively, treated ultrasonically for 5 min and then heated slowly in an infrared light supply (250 W) until the mixture slurry was dried. The photocatalyst powders were calcined in air atmosphere at 673 K for 2 h.

2.2. The characterization of CoO_x-TiO₂ powder photocatalyst before and after photocatalytic reaction

The chemical composition of CoO_x-TiO₂ powders before and after photocatalytic reaction were get from the X-ray photoelectron spectroscopy (XPS) measurements using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with a Mg (K α) X-ray resources (The binding energy scale was calibrated to 284.6 eV for the main C 1s peak). Crystallographic structure was determined by X-ray diffraction using a D/max RB X-ray diffractometer with Cu K α radiation. (The accelerating voltage, applied current, scan rate, step pace and scan range were 40 kV, 30 mA, 3.5° min⁻¹, 0.0167° and 10–80°, respectively.)

2.3. The valuing experiment of long-term photocatalytic stability for hydrogen production in Co²⁺-ion-doped TiO₂ suspensions

The experiment of the stability of photocatalytic hydrogen production in Co²⁺-ion-doped TiO₂ suspensions was carried out in a 100 ml-quartz reaction flask, with a septum for sampling. The reactant mixtures (20 mg of CoO_x/TiO₂ catalyst, 60 ml aqueous ethanol solution, ethanol 20 vol.% concentration) were placed in the flask, and purged with argon gas for 40 min in order to remove the dissolved oxygen and ensure in an anaerobic condition. The reactant mixture was stirred with a magnetic stirrer and illuminated by light from the 200 W mercury lamp. A 0.5 ml gas samples was taken 24 h-periodically from the gas phase, and hydrogen volume was analyzed using a GC8800-Model gas chromatograph with a thermal-conductor detector for calculating the rates of photocatalytic hydrogen production.

2.4. Working electrode preparation and photoelectrochemical measurements of CoO_x-TiO₂ electrodes

The sketch map of photoelectrochemical cell and the preparation of working electrode was reported elsewhere [14]. In this work, the suspension of CoO_x-TiO₂ powders TiO₂ (P25) with a concentration of ca. 1.0 g dm⁻³ was dispersed ultrasonically before use. Ten drops ca. 1.0 ml of the suspension were applied onto a piece of transparent ITO conducting glass 2.0 cm × 5.0 cm, then heated slowly in an infrared light supply (250 W) until the suspension was dried and a layer of porous CoO_x-TiO₂ film formed on the conducting glass. The surface of semiconductor working electrode exposed to the electrolyte was circular-films with a geometrical surface area of ca. 1.6 cm².

All photoelectrochemical measurements were carried out using a standard three-electrode system equipped with a quartz window, a saturated calomel reference electrode and a platinum wire counter-electrode. A 0.1 mol L⁻¹ Na₂SO₄ ethanol–water solution (20 vol.% ethanol, pH 6.5) was used as supporting electrolyte. A Model CHI-660 photoelectrochemical workstation was used for potentiostat controlling, bias voltages supplying and the photocurrent or photopotential recording. All potentials reported were measured against a saturated calomel electrode (SCE). The light source is 200 W high-pressure mercury-lamp, and the CoO_x-modified TiO₂ films electrode was illuminated from above to below of supporting electrolyte.

In this paper, the kinetics of photocurrent of unbiased electrode and the photo-reduction potential for hydrogen production were investigated with current–time and cyclic-voltammetry method.

3. Results and discussion

3.1. The analysis of chemical composition and crystal structure

The XRD was used to investigate the changes of phase structure of the CoO_x-modified TiO₂ powder photocatalyst before

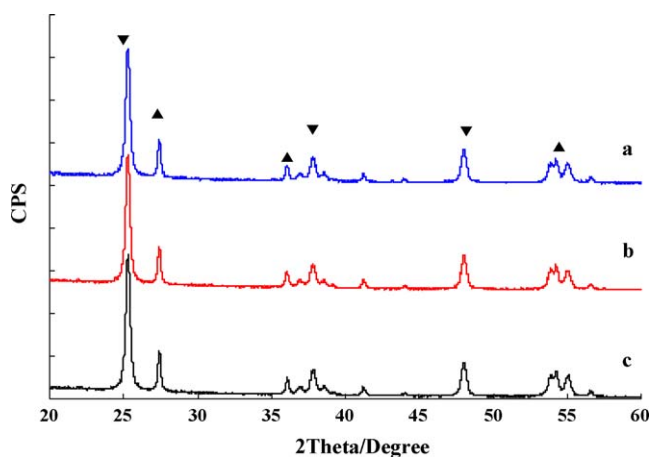


Fig. 1. XRD patterns of 0.4 wt.%Co-TiO₂: (a) after 240 h photoreaction, (b) before photoreaction, and (c) pure TiO₂ photocatalyst; (▼) Anatase and (▲) Rutile.

and after photoreaction, and XRD pattern is shown in Fig. 1. According to Fig. 1, the effect of a long-term photoreaction on the phase structure of CoO_x-modified TiO₂ powder photocatalyst comparing to the pure TiO₂ (P25) photocatalyst has not been appeared because the XRD pattern in Fig. 2a–c samples are similar. This clearly indicated that the crystal structure of the CoO_x-modified TiO₂ powder photocatalyst has no obvious changes during a long-term photoreaction.

Fig. 2 shows the Co 2p XPS of CoO_x-TiO₂ powder photocatalyst before and after a long-term photoreaction. The XPS peaks shown that after a long-term photoreaction, the relative intensity of Co 2p XPS peak (binding energy at 780.9 eV, attributed to the active composition CoO_x ($x > 1$)) of CoO_x-TiO₂ powder photocatalyst has an obvious decrease comparing to that of the samples before photoreaction. This indicated that during a long-term photoreaction, a part of the active composition CoO_x was run out and removed from the surface of TiO₂ powder photocatalyst to the suspension and thus resulted in the decrease of the photo-reactivity.

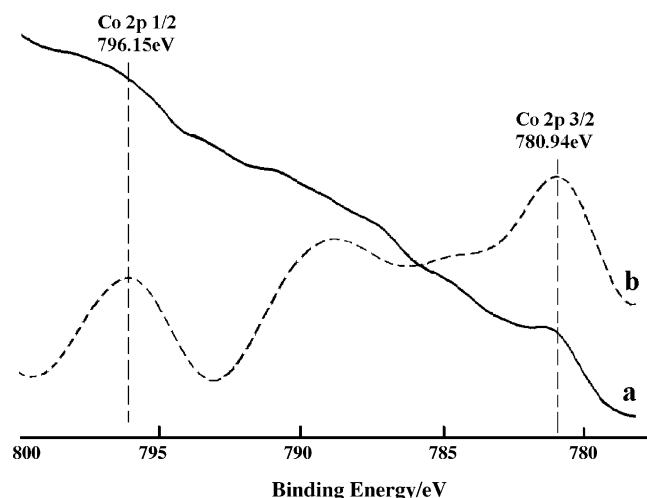


Fig. 2. The Co 2p XPS profiles of 0.4 wt.%Co-TiO₂ photocatalyst: (a) after 240 h-photoreaction and (b) before photoreaction.

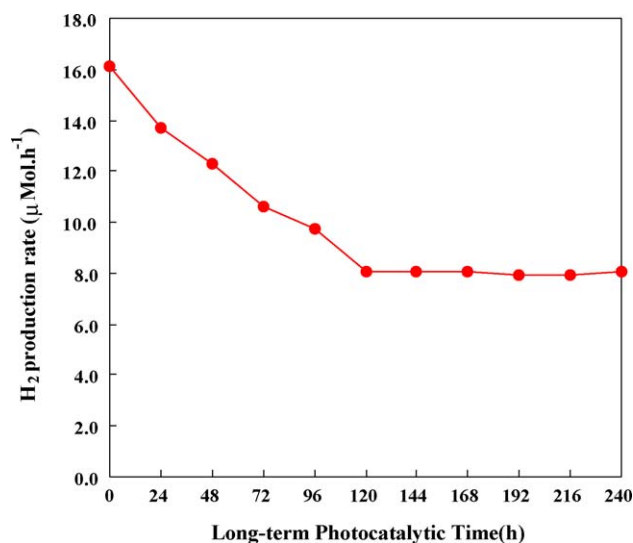


Fig. 3. The dependence of photocatalytic hydrogen production rate on the long-term reaction time.

3.2. The photocatalytic properties of hydrogen production in Co²⁺-ion-doped TiO₂ suspensions

The dependence of hydrogen production rate on the long-term photoreaction time (240 h) is showed in Fig. 3. During 240 h photoreaction, the hydrogen rate is decreasing with a linearity from 16.1 to 8.0 μmol h⁻¹, and then is remain a stable state with ca. 50% of the highest rate. Although the hydrogen generation rate of 0.4CoO_x-TiO₂ photocatalyst has been a decrease by ca. 50%, it is very higher than that of pure TiO₂ powder photocatalyst (0.13 μmol h⁻¹) in same condition.

3.3. The photoelectrochemical properties of CoO_x-modified TiO₂ films electrode

Fig. 4 shows the unbiased transient photocurrent–time curve of 0.4CoO_x-TiO₂ photoelectrodes before and after a long-term

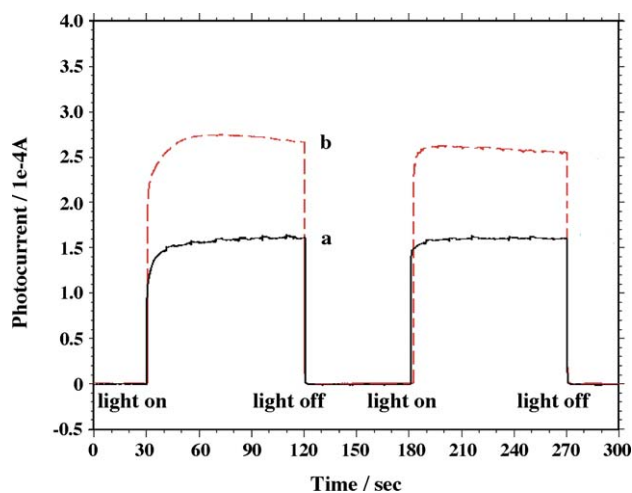


Fig. 4. Unbiased photocurrent vs. time curve for 0.4 wt.%CoO_x-TiO₂ electrodes before and after photoreaction recorded during on-off cycles of illumination by UV light. Solution: 0.1 mol l⁻¹ Na₂SO₄, 20 vol.% ethanol–water. (a) After 240 h photoreaction and (b) before photoreaction.

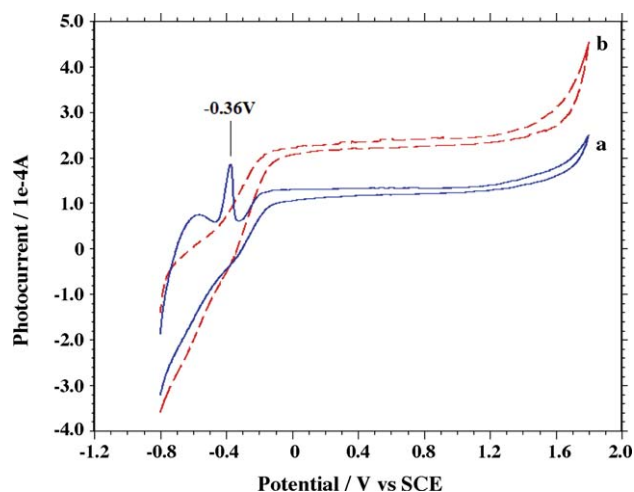


Fig. 5. The cyclic voltammograms curves for 0.4 wt.% CoO_x - TiO_2 electrodes before and after photoreaction with illumination using UV light. Solution: $0.1 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$, 20 vol.% ethanol-water. Scan rate, 50 mV s^{-1} . (a) After 240 h photoreaction and (b) before photoreaction.

photoreaction. It can be seen that the steady anodic photocurrent appeared to be an obvious decrease after photoreaction (from 2.75×10^{-4} to 1.5×10^{-4} A). The photo-response rapidly appeared at the beginning of UV illumination, and then converted to a steady anodic photocurrent, followed by a rapid decrease of photocurrent when the UV light was switched off. That is to say, before and after photoreaction, the character of photocurrent response was still similar. This indicated that the remaining parts of CoO_x active species on the surface of the TiO_2 are still remaining a good photoreaction for hydrogen production from aqueous ethanol solution.

Fig. 5 shows the cyclic voltammograms curve for 0.4 CoO_x - TiO_2 photoelectrodes before and after a long-term photoreaction. The photo-potential for hydrogen production from aqueous ethanol solution was determined from the CV curve. It can be seen from Fig. 5 that the hydrogen producing photo-potential of 0.4 CoO_x - TiO_2 photoelectrodes after a long-term photoreaction was about the same as that before photoreaction (ca. -0.2 V versus SCE). In addition, after photoreaction, a new reductive species peak was appeared at -0.36 V (versus SCE), and it probably was the nonstoichiometric intermediate of CoO_x active species produced during photoreaction process. The detailed producing process will be discussed in the next section.

3.4. Supposal and presumption of the emerging and removal process about CoO_x active species

In order to investigate the changes of the photocatalytic activity for the hydrogen production over CoO_x - TiO_2 photocatalyst after a long-term photoreaction in detail, we have presumed and described the emerging and removal process of the CoO_x active species ($x > 1$) and the new CoO_x intermediate species ($x < 1$) on the surface of P25- TiO_2 semiconductor particles. The sketch map is shown in Fig. 6.

It is well known that P25- TiO_2 semiconductor particles have a higher-defect surface with microporosity structure for the pho-

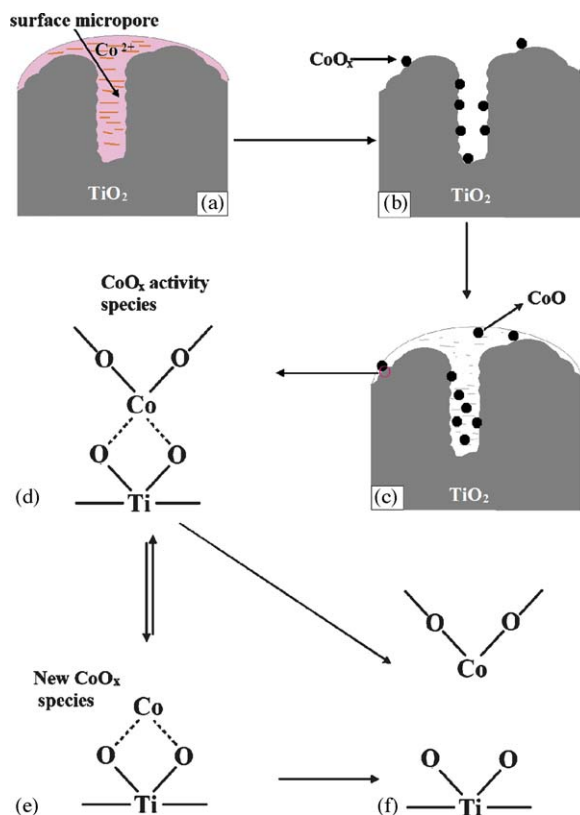


Fig. 6. The sketch map of Supposal and presumption of the emerging and removal process about CoO_x active specie: (a) TiO_2 semiconductor particle impregnated with the Co^{2+} ion solution; (b) the CoO_x active species ($x > 1$) were emerging on the surface of TiO_2 semiconductor particle after heating treatment; (c) the process of the CoO_x active species removed from the surface of TiO_2 semiconductor particle; (d) the existence form of CoO_x active species on the surface of TiO_2 semiconductor particle; (e) the new CoO_x intermediate species ($x < 1$) during a photoreaction; (f) the surface of TiO_2 semiconductor particle after the CoO_x active species removal.

photoreaction. When a TiO_2 semiconductor particle impregnated with the Co^{2+} ion solution (Fig. 6a), the surface micropore were filled by Co^{2+} ion solution. After the evaporating and thermal decomposition process (heated slowly in a 250 W-infrared light supply for drying the mixture slurry and then calcined in air atmosphere at 673 K), the CoO_x active species ($x > 1$) were emerging on the surface of TiO_2 semiconductor particle (shown in Fig. 6b and d). The majority of CoO_x active species ($x > 1$) were existed in the surface micropore of TiO_2 because the Co^{2+} ion solution impregnating into the surface micropore would evaporate finally.

During a long-term photocatalytic reaction of TiO_2 suspension, partial CoO_x active species ($x > 1$) probably would change into the new interaction form (shown in Fig. 6e) or remove from the surface of TiO_2 semiconductor particle into the suspension (shown in Fig. 6c and f). The removed partial CoO_x species could not collect with centrifuge or filtration for the charactering because of the very small particles. The interaction form shown in Fig. 6e probably is the new CoO_x intermediate species ($x < 1$, photooxidative potential at -0.36 V versus SCE, shown in Fig. 5). Moreover, the amount of the new CoO_x intermediate species ($x < 1$) is too small to find its XPS band in Fig. 2. Of

course, the process from Fig. 6d to the Fig. 6f and e is the removal process and result of CoO_x active species ($x > 1$), and it is also the most important reason of the decrease of photocatalytic generating hydrogen reactivity of CoO_x - TiO_2 photocatalyst after a long-term photoreaction.

4. Conclusions

Based on the discussion above, some conclusion can be made for the long-term stability of photocatalytic activity of Co^{2+} ion modified P25- TiO_2 semiconductor photocatalyst for hydrogen generation from aqueous ethanol solution.

After a long-term photoreaction, the photocatalytic properties of Co^{2+} ion modified P25- TiO_2 photocatalyst for hydrogen production have a decrease by a factor of ca. 50%, and still be very higher than that of pure P25- TiO_2 photocatalyst.

The steady anodic photocurrent appeared to be an obvious decrease after photoreaction (from 2.75×10^{-4} to 1.5×10^{-4} A), but the character of photocurrent response was still similar before and after photoreaction.

The most important reason for the decrease of photocatalytic properties is the removal of CoO_x active species ($x > 1$) from the surface of TiO_2 photocatalyst after a long-term photoreaction.

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