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Poly(4-vinylphenol) as a new stable and metal-free sensitizer of titania for visible light photocatalysis through ligand-to-metal charge transfer process

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ABSTRACT

In this study, poly (4-vinylphenol) (denoted as PVP) was firstly used as a stable and low-cost sensitizer of titania for visible light photocatalysis. The PVP thin-layer was readily grafted on TiO₂ (PVP/TiO₂) through surface complexation between the multiple hydroxyl groups of PVP and the surface titanol groups (Ti-OH), via simple dispersion of PVP and TiO₂ powders in organic solvent. We have demonstrated that the PVP layer sensitizes TiO₂ under visible light through the ligand-to-metal charge transfer (LMCT) mechanism. The PVP/TiO₂ (with platinum as co-catalyst) composite exhibited a visible light activity of H₂ production in the presence of suitable electron donors, whereas phenol-complexed TiO₂ (compared as a control) did not generate H₂ in the identical condition. Furthermore, PVP/TiO₂ exhibited efficient photocatalytic degradation of organic pollutant (4-cholorophenol) under visible light irradiation. In addition, the photoelectrochemical measurements for PVP/TiO₂-coated electrodes (PVP/TiO₂/FTO) supported the visible light-induced LMCT process on PVP/TiO₂, which involves the direct electron transfer from the highest occupied molecular orbital (HOMO) of PVP to the conduction band of TiO₂ as the origin of the visible light photocatalytic activity.

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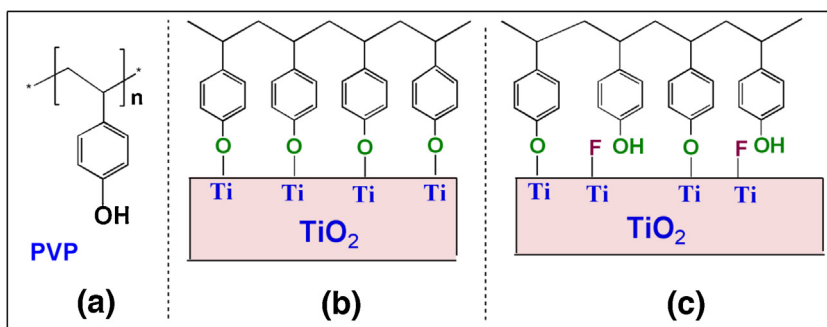
1. Introduction

Titania as a popular photofunctional material for environmental remediation [1], artificial photosynthesis [1,2] and solar cells [3] has been widely studied due to its suitable band positions, low-cost, non-toxicity and excellent (photo) chemical stability. However, it suffers from the poor performance under visible light because its wide band-gap (anatase 3.2 eV and rutile 3.0 eV) does not allow the efficient absorption of visible photons [4]. The most popular strategies to overcome this problem are the doping of foreign elements [5–7] (metals or non-metals) and sensitization by dyes, semiconductor quantum dots or conjugated polymers [8–10]. In the case of doping, the newly formed dopant energy levels can also serve as recombination centers, which will reduce the charge-transfer efficiency [11]. Although non-metal (such as N, S, P, B and C) doping has been frequently studied, the optical absorption of non-metal doped TiO₂ in the visible region is still insufficient [12]. In addition, doping foreign elements into the lattice of TiO₂ usually requires

the high temperature annealing or hydrothermal treatment, which is an energy and time consuming process. On the other hand, the most critical problem for the dye sensitization is the instability of dye sensitizers subjected to the dye degradation in aquatic environment [13]. The most popular sensitizers (e.g., ruthenium bipyridyl derivatives) are usually grafted onto the surface of TiO₂ through carboxylate linkages that are intrinsically vulnerable to hydrolytic cleavage. Furthermore, most efficient sensitizers reported are limited to the bipyridyl complexes containing noble and rare metals (e.g., Ru, Ir) [14]. The synthesis of earth-abundant metals-based or metal-free organic dyes is under investigation for dye-sensitized solar energy conversion [15].

Another type of sensitization is based on the ligand to metal charge transfer (LMCT) between surface adsorbate and semiconductor, through which the electron is photoexcited directly from the ground state adsorbate (without involving the excited state of the adsorbate) to semiconductor conduction band (CB) [16]. Therefore, considering that a wide variety of organic or inorganic compounds can form surface complexes with TiO₂ and introduce a new absorption band in the visible light region, this LMCT sensitization is quite flexible and useful for solar energy utilization. Many examples of LMCT-complex formation on TiO₂

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Scheme 1. (a) Structure of poly(4-vinylphenol) (PVP), (b) Schematic illustration of PVP complexed on TiO_2 (PVP/ TiO_2); (c) PVP complexed on surface fluorinated TiO_2 (PVP/F- TiO_2).

surface for inorganic and organic adsorbates have been reported. For example, chromate-sensitized TiO_2 system was investigated for the oxidation of 4-chlorophenol in aqueous phase and volatile organic pollutants in gas phase under visible light [17,18]. Aromatic *s*-triazine containing melon and melon units produced during annealing urea and TiO_2 at 400°C could form complexes with TiO_2 as a visible light photosensitizer [19]. The charge transfer efficiency decreased from catechol to resorcinol and quinol in the dihydroxyphenol- TiO_2 system judging from their UV-vis absorption spectra [20]. Other similar LMCT complexes on TiO_2 surface have been observed with those organic compounds with phenolic or carboxylic groups [21–24]. Various types of the LMCT sensitizers were recently reviewed [25].

LMCT complexes that are mostly anchored on the semiconductor surface through one or two functional groups are often weak, which results in the low stability and weak visible light absorbance. To enhance the complexation, a surface adsorbate consisting of multiple LMCT-forming units can be employed since stronger LMCT complexes are formed through the multiple anchoring bonds. For example, we have reported polyhydroxyl fullerol ($\text{C}_{60}(\text{OH})_x$) and phenolic resin sensitized TiO_2 as new LMCT-type visible light photocatalysts [26,27]. Herein, we report another LMCT-type sensitization of TiO_2 using low-cost poly (4-vinylphenol) (PVP) as the sensitizer for solar energy utilization. A thin coating of PVP onto TiO_2 was readily formed by dispersing PVP and TiO_2 powders in acetone solvent. The PVP exhibits some advantages as the sensitizer of TiO_2 in terms of (1) insolubility in water; (2) rapid and strong complexation; (3) low-cost and non-toxic nature; (4) improved stability. Compared to the common surface complexes constructed via the single or multiple chemical linkages such as fullerol and phenolic resin, PVP ($M_w \sim 11,000$) is expected to form much stronger complexation because it contains more than one hundred hydroxyl groups on one PVP molecule. Therefore, the electron coupling between the surface adsorbate and TiO_2 , an important factor influencing the charge transfer efficiency, could be significantly enhanced. In this work, the LMCT-sensitization mediated photocatalytic production of hydrogen, degradation of organic pollutant (4-chlorophenol) and photocurrent generation were tested with PVP-complexed TiO_2 . The promising performance of PVP-sensitized TiO_2 under visible light allows us to develop novel sensitizers employing low-cost polymeric materials based on the LMCT process.

2. Experimental

2.1. Materials

TiO_2 powder (Degussa P25), a mixture of anatase and rutile (8:2) with a BET surface area of ca. $50\text{ m}^2\text{ g}^{-1}$ and primary particle size of 20–30 nm, was used as a base material. Other chemicals include

phenol (Aldrich, 99.5% redistilled), poly(4-vinylphenol) (Aldrich, average $M_w \sim 11,000$), sodium fluoride (Aldrich, >99%), and poly ethylene glycol (Aldrich, $M_w \sim 2000$).

2.2. PVP complexation on TiO_2 surface (PVP/ TiO_2)

Bare TiO_2 , surface fluorinated TiO_2 (F- TiO_2), and surface platinumized TiO_2 for the H_2 production were used as parent materials for PVP grafting. Surface fluorinated TiO_2 (F- TiO_2) was prepared by adding 10 mM NaF to an aqueous TiO_2 suspension according to our previous report [28]. Platinumized TiO_2 with a typical Pt loading of 0.1 wt% was prepared by the common photodeposition method using chloroplatinic acid (H_2PtCl_6) as a precursor.

In the surface complexation process, typically 0.3 g TiO_2 powder was dispersed in 200 ml acetone and sonicated for 15 min, then a certain amount of PVP (PVP/ $\text{TiO}_2 = 0.5\text{ wt}\%$, $2.0\text{ wt}\%$, $5.0\text{ wt}\%$, $10.0\text{ wt}\%$, $20.0\text{ wt}\%$) was added, the suspension was immediately changed to yellow color within 5 s. The suspension was stirred at 50°C in an oil bath for 2 h to get uniform dispersion of PVP. The acetone solvent was removed under elevated temperature (80°C) and the final powder was dried under vacuum at room temperature. After drying, the brownish powder of PVP/ TiO_2 was obtained. The PVP-grafted TiO_2 samples were denoted according to the loading content of PVP (e.g., 10.0 wt% designed as 10%PVP/ TiO_2). For comparison, 10.0 wt% phenol complexed TiO_2 (10%phenol/ TiO_2) and F- TiO_2 (10%PVP/F- TiO_2) samples were also prepared by the same way. The representative structures of various surface complexed TiO_2 samples are shown in Scheme 1. For the H_2 production, PVP-grafted Pt/ TiO_2 samples with different ratios were also prepared by the same way.

2.3. Photocatalytic activity tests

For the hydrogen generation test, the sample powder was dispersed in D.I. water ($[\text{TiO}_2] = 0.5\text{ g L}^{-1}$) with electron donors (triethylamine (TEA), *N,N*-dimethylethylamine (DMEA) and *N,N*-diisopropylethylamine (DPEA)). A 300-W Xe arc lamp (Oriel) was used as a light source. Light passed through a 10 cm^{-1} IR water filter and a UV-cutoff filter ($\geq 420\text{ nm}$), and then the filtered light was focused onto a 55 ml Pyrex glass reactor (ca. 25 ml headspace) which was sealed with a rubber septum. The incident light intensity ($420\text{ nm} \leq \lambda \leq 645\text{ nm}$) was determined to be about 200 mW/cm^2 . The suspension was deaerated by Ar purging 30 min before irradiation. The amount of H_2 was monitored using a HP6890A GC equipped with a thermal conductivity detector. For the degradation of 4-chlorophenol (4-CP) test, sample powder (bare TiO_2 and PVP/ TiO_2) was dispersed in distilled water ($[\text{TiO}_2] = 1\text{ g L}^{-1}$). An aliquot of the 4-CP stock solution was subsequently added to the suspension to give a desired concentration of $20\ \mu\text{M}$, and then the visible light ($\geq 420\text{ nm}$) was irradiated to the Pyrex reactor after

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