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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/cs400080w • Publication Date (Web): 22 May 2013 Downloaded from http://pubs.acs.org on May 30, 2013

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Enhanced photocatalytic activity of chemically bonded TiO₂/graphene composites based on the

effective interfacial charge transfer through C-Ti bond

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Abstract

Recently, graphene-based semiconductor photocatalysts have attracted more attention due to their enhanced photocatalytic activity caused by the interfacial charge transfer (IFCT). However, it is rarely involved for the effect of chemical bond on IFCT. In this work, TiO₂/graphene composites with chemical bonding interface were prepared by a facile solvothermal method using tetra-butyl ortho-titanate (TBOT) as Ti source. The chemically bonded TiO₂/graphene composites effectively enhanced their photocatalytic activity in photodegradation of formaldehyde in air, and the graphene content exhibited an obvious influence on photocatalytic activity. The prepared composite with 2.5 wt% graphene (G2.5-TiO₂) showed the highest photocatalytic activity, exceeding that of Degussa P25, as-prepared pure TiO₂ nanoparticles and the mechanically mixing TiO₂/graphene (2.5 wt%) composite by a factor of 1.5, 2.6 and 2.3, respectively. The enhancement in the photocatalytic activity was attributed to the synergetic effect between graphene and TiO₂ nanoparticles. Other than the graphene as an excellent electron acceptor and transporter, the enhanced photocatalytic activity was caused by IFCT through C-Ti bond, which markedly decreased the recombination of electron-hole pairs, and increased the number of holes participating in the photooxidation process, confirmed by XPS analysis, the gaseous phase transient photocurrent response, electrochemical impedance spectroscopy (EIS) and Photoluminescence (PL) spectra. This work about effective

IFCT through chemical bonding interface can provide new insights for directing the design of new heterogeneous photocatalysts, which can be applied in environmental protection, water splitting and photo-electrochemical conversion.

Keywords: Chemical bonding; C-Ti bond; photocatalytic activity; interfacial charge transfer; gaseous phase photocurrent

1. Introduction

In recent years, semiconductor (SC) photocatalysis has emerged as an advanced green technology for environmental pollution purification.¹ In photocatalysis, photogenerated electron and (or) hole involve mainly two process. One is driving the photocatalytic reactions, and another is recombination and generation heat, which is harmful to photocatalysis. Further studies indicate that only a small fraction of photogenerated carries can successfully transfers to the interface to initiate redox reactions. So, effective electron transfer at SC surface has been widely acclaimed to be of great importance, which is a fundamental process relevant to photocatalytic applications.

To date, titania has proven to be the most suitable photocatalyst, largely due to its strong oxidizing power, biological and chemical inertness, and low cost.² Unfortunately, the rapid recombination rate of photogenerated electron-hole pairs within TiO₂ results in its low quantum efficiency, thus limiting its practical applications.³ In the past decades, various strategies have been developed in an attempt to modify the photocatalytic process and improve the photocatalytic performance.^{2b, 4} In particular, carbon-titania hybrid materials have been receiving much attention as a new class of photocatalysts,⁵ which could potentially offer desirable efficiency for separating electron-hole pairs.

Recently, owing to the high specific surface area and superior electron mobility of graphene, numerous efforts have been paid to combine graphene with semiconductor photocatalysts to enhance the catalytic performance.⁶ It is believed that photoexcited electrons from TiO₂ transfer to nanocarbons, such as carbon nanotubes or graphene, and hinder the recombination process, thereby enhancing the oxidative reactivity.⁷ Further studies indicate that the interaction between graphene and TiO₂ can significantly determine the interfacial electron transfer properties, which is a key issue for photocatalytic activity. Dong et al.⁸ find that RGO/TiO₂ composite will significantly increase the photovoltaic response and significantly prolong the mean life time of electron-hole pairs compared with pure TiO₂, which is experimentally supported by transient photovoltage (TPV) result. Li et al^{7c} reported that chemical bonded P25-graphene composite as a high performance photocatalyst for degradation methylene blue. In Zhang and Wang's reports,⁹ P25/RGO composite with the most intensive interaction fabricated by hydrothermal method shows the highest H₂ evolution activity. However, there has been rarely reported that chemical bonding plays a critical role on the IFCT and photocatalytic performance, especially compared with mechanically mixing semiconductor/grapheme without chemical bonding interface.

In this paper, we demonstrate that TiO₂/graphene composites with C-Ti chemical bonding interface were prepared by a facile solvothermal method using TBOT as Ti source. XPS analysis confirmed the existence of chemical C-Ti bond between

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the graphene and TiO₂ nanoparticles. What's more, chemical bonding is of great importance for the efficiency of photo-induced interfacial electron transfer. Due to the photoinduced chemical-bonded interfacial charge transfer (CB-IFCT), TiO₂/graphene nanocomposites with C-Ti bond exhibit an exceptional photocatalytic reactivity towards removing HCHO in air compared to the pure TiO₂ and the corresponding mechanical mixing sample (without chemical bonding). It is proposed that the photoinduced CB-IFCT can effectively enhance photocatalytic reactivity by decreasing the possibility of recombination of electron-hole pairs, and increasing the number of holes participating in the photooxidation process.

2. Experimental

2.1. Sample Preparation

All chemicals used in this study were analytical grade and were used without further purification. Distilled water was used in all experiments. The graphene used in all experiments were prepared based on Stride's reports.¹⁰ In a typical preparation procedure for graphene/TiO₂ nanocomposites, 0.02 mol of tetra-butyl ortho-titanate (TBOT) was dissolved into 30 mL of ethanol and then this TBOT solution was dropwisely added under magnetically stirring to 10 mL of graphene water suspension, which contains a specific amount of the graphene. The designed mass ratio of graphene to titania is 0, 0.5, 1.5, 2.5 and 3.0 wt%, and the corresponding final products are denoted as Gx-TiO₂, where x is 0, 0.5, 1.5, 2.5 and 3.0, respectively. After stirring for another 120 min, the mixed suspension was transferred to a 70 ml Teflon-lined autoclave, and maintained at 200°C for 10 h. The obtained white or black–white precipitates were collected and washed thoroughly with distilled water and absolute ethanol for several cycles, and then dried in vacuum at 80°C for 12 h to get the Gx-TiO₂ nanocomposites. For comparison, a sample with graphene loading about 2.5 wt% was also prepared by a simple mechanical mixing of G0-TiO₂ and graphene, which was noted as Mixing.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Philips X'Pert Pro X-ray diffractometer (PANalytical, Holland) with Cu K α radiation ($\lambda = 0.15418$ nm) at a scan rate (2 θ) of 0.05° s⁻¹. The accelerating voltage and the applied current were 40 kV and 80 mA, respectively. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Horiba Jobin Yvon, LabRAM HR800) in the backscattering geometry with a 488 nm laser as an excitation source. Transmission electron microscope (TEM) measurements were performed with a JEM-2100F STEM microscope working at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG Multilab 2000 spectrometer employing Mg K α radiation. UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (Lambda 35, PerkinElmer, America). BaSO₄ was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The thermogravimetric analysis differential thermal analysis (TG-DTA) was

carried out using a PerkinElmer Pyris Diamond analyzer in air at a heating rate of 10°C·min⁻¹. Photoluminescence (PL) emission spectra were acquired under excitation at 325 nm using an Edinburgh Instruments PLSP920 spectrometer.

For the EIS measurement, the as-prepared photocatalyst powders were fabricated to the film electrodes by the method as below. First, the powders and ethanol were mixed homogeneously (200 mg/mL), and the obtained paste was then spread on the conducting fluorine-doped SnO₂ glass substrate (FTO, with a sheet resistance of 15 Ω) with a glass rod. Finally, the resultant films with a *ca.* 2 µm thickness and 2 cm² active areas were calcinated at 450°C for 2 h in inert atmosphere to achieve good electronic contact between the photocatalyst and FTO glass. The EIS measurements were carried out on an IM6eX electrochemical workstation (Zahner, INC. Germany) by using three-electrode cells. EIS measurements were carried out in H₂SO₄ solution (25%) by using a three-electrode system. The resultant electrode served as the working electrode, with a platinum wire as the counter electrode and a Ag/AgCl (saturated KCl) electrode as the reference electrodes, which was performed in the presence of a 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in 0.1 M KCl solution. The impedance spectra were recorded under an AC perturbation signal of 5 mV over the frequency range of 1 MHz to 10 mHz at 0.5 V.

For the gaseous phase photocurrent measurement under HCHO gas atmosphere, the as-prepared photocatalyst powders were fabricated to the film electrodes by the method as below. First, the powders and ethanol were mixed homogeneously (200 mg/mL), and the obtained paste was then spread on alumina thin flats (ca. 6×8 mm), which was preprinted with the Au interdigital electrode. The condition of photocurrent measurement was kept as the same as gaseous photocatalytic degradation experiments (200 ppm HCHO gas and 36 W/m² UV irradiation) and the bias voltage is 5 V.

2.3. Photocatalytic activity

Photocatalytic activity of the samples was evaluated by degrading ca. 200 ppm HCHO under irradiation of a UV (365 nm) LED light at ambient temperature with a 1 L reactor. The powder photocatalysts were coated onto a square groove (5×5 cm), and dried in an oven at 80°C for 2 h. The weight of the photocatalysts used for each experiment was kept at about 0.05 g. After the square groove coated with photocatalyst powders were placed into the reactor, the HCHO gas with concentration of ca. 200 ppm was passed through the reactor and reached adsorption-desorption equilibrium with the catalyst before light irradiation. The initial temperature was 25 ± 1 °C. Finally, a 2.8 W UV LED array lamp (1 cm above the groove) was switched on to trigger the photocatalytic reaction. The measured UV intensity was ca. 36 W/m². The analysis for the HCHO concentration and carbon dioxide in the reactor was performed on-line with a Photoacoustic Field Gas-Monitor (INNOVA Air Tech Instruments, Model 1412). Each set of experiment was followed for 60 min under UV irradiation.

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3. Results and discussion

3.1. Enhanced photocatalytic properties

To analyze the application potential of graphene/TiO₂ nanocomposites in volatile organic compounds (VOCs) gas purification, photocatalytic degradation was determined to select HCHO gas as target gas. The photocatalytic activities of the as-prepared graphene/TiO₂ nanocomposites were evaluated by the oxidation of 200 ppm HCHO gas in air. Note that, under dark conditions without light illumination, or illumination in the absence of catalyst, did not result in the photocatalytic decomposition of HCHO. Therefore, the presence of both illumination and catalyst was necessary for the efficient degradation. These results clearly indicated that the decomposition of HCHO in air was caused by photocatalytic reactions on graphene/TiO₂ composite powders under UV illumination.

The kinetics of the degradation reaction was fitted to a pseudo-first-order reaction and a much larger apparent rate constant (κ) for the hybrid was quantitatively evaluated, as Fig. 1 shows. Without graphene, the sample G0-TiO₂ shows good photocatalytic activity, and its κ reaches 11.03×10^{-3} min⁻¹. Even the loading amount of graphene (0-3.0 wt%) is low, the adding graphene exhibits a significant influence on the photocatalytic activity of the graphene/TiO₂ nanocomposites. Especially, the photocatalytic activity increases significantly with increasing loaded graphene content, and the κ reaches the highest value of 28.52×10^{-3} min⁻¹ at 2.5 wt% graphene (G2.5-TiO₂). In this regard, the photocatalytic activity exceeds that of pure TiO₂ by 2.6 times. However, further increasing the graphene content to 3.0 wt%, its κ value decreases to 23.48×10^{-3} min⁻¹. For comparison, the photocatalytic activity of P25 (Degussa, TiO₂) and Mixing was also carried out, with a respective κ value of 19.52×10^{-3} min⁻¹ and 12.2×10^{-3} min⁻¹, under the same test conditions. The highest photocatalytic activity (G2.5-TiO₂) exceeds that of P25 by 1.5 times, which means the excellent photocatalytic activity of Gx-TiO₂ composite. The Mixing sample only shows κ value slightly higher than that of G0-TiO₂ sample, which indicates that the simple mechanically adding graphene without chemical bonding interface has small effect on photocatalytic activity. Also, even the Mixing sample and G2.5-TiO₂ sample have the same graphene loading, their photocatalytic activity shows great difference, by a factor of ca. 2.3. This difference in the photocatalytic activity means that the interaction state between graphene and TiO₂ nanoparticles has vital effect on photocatalytic activity.

For the practical application of photocatalysts, mineralization ratio in the catalysis process and the stability of photocatalyst are two key issues. The photocatalytic process is complex, and many intermediate products are produced, especially when the initial pollutant is complicated. Some intermediate products may be more harmful to human health than the initial pollutant. So a thorough decomposition of pollutant is of much necessarity. Fortunately, the concentration of HCHO and CO_2 decreases and increases linearly, respectively, for all the prepared photocatalysts. Moreover, the

concentration of the produced carbon dioxide is about the same as that of the decomposed HCHO (shown in Fig. 2a), suggesting that HCHO is completely degraded to CO_2 by the prepared TiO₂/graphene photocatalysts.

The stability of photocatalyst is another important practical issue. The intermediate products are usually adsorbed on the surface active position of the photocatalyst. The photocatalytic activity will decrease dramatically after several cycles of usage. Fig. 2b shows the photocatalytic stability of G2.5-TiO₂ photocatalysts for five cycles of usage. The κ value kept rarely the same in the first four cycles and only decreased slightly in the fifth cycle.

The excellent mineralization efficiency and high photocatalytic stability demonstrate the good practical application potential of the prepared TiO_2 /graphene nanocomposite. The excellent photocatalytic activity of as-prepared TiO_2 /graphene nanocomposites is interesting, and detailed characterizations are carried out to reveal the photocatalysis mechanism.

3.2. Structure and morphology of TiO₂/graphene nanocomposites

Fig. 3a shows the XRD patterns for the TiO_2 /graphene nanocomposites synthesized with different contents of graphene compared to pure TiO_2 . The present peaks clearly represent the formation of anatase crystallites (JCPDS no. 01-089-4921). Otherwise, no apparent peaks for graphene were observed. The trace amount of loaded graphene with low atomic number (Z=6) can not be resolved by XRD.¹¹ However, the existence of graphene can be clearly elucidated by Raman analysis as discussed next.

The local structure of TiO₂/graphene composite is investigated by comparing its Raman spectra with those of the pure TiO₂ and graphene (Fig. 3b). The four bands located at around 141 ($E_{g(1)}$), 391 ($B_{1g(1)}$), 514 ($A_{1g} + B_{1g(2)}$) and 634 cm⁻¹ ($E_{g(2)}$) are characteristic for pure anatase TiO₂ (G0–TiO₂, Fig. 3b).¹² The two typical bands located at around 1355 (D-band) and 1595 cm⁻¹ (G-band) correspond to graphene (Fig. 3b).¹³ As for the Mixing and G2.5-TiO₂ (Fig. 3b), all the Raman bands for anatase TiO₂ and graphene are basically retained. In addition, a smaller intensity ratio of the D band to G band was found in Mixing ($I_D/I_G = 0.75$) and G2.5-TiO₂ ($I_D/I_G = 0.79$) compared with pure graphene ($I_D/I_G = 0.94$), which can be assigned to lower defects and disorder of the graphene structures.^{11a} This demonstrated that TiO₂ and graphene existed in Mixing and G2.5-TiO₂.

The SEM images of as-prepared Gx-TiO₂ nanocomposite are shown in Fig. 4. The pure TiO₂ nanoparticles (G0-TiO₂) were evenly distributed (in Fig. 4a). After adding graphene, the TiO₂ nanoparticles were located or wrapped by graphene nanosheets (in Fig. 4b-d). The external morphology and microstructures of the TiO₂/graphene nanocomposites with 2.5 wt% graphene were further studied by TEM (Fig. 5). Due to interfacial interactions and preferential heterogeneous nucleation,^{6c} numerous TiO₂ nanocrystals were densely deposited onto the graphene sheets (in Fig. 5a and b). The corresponding HRTEM image (in Fig. 5d) showed clear lattice fringes, which allowed for the identification of crystallographic spacing. The fringe spacing of ca. 3.51 Å matched that of the (101) crystallographic plane of anatase TiO₂. From the inset of Fig. 5d,

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the (-101) facet was also observed. According to the crystallographic knowledge and imaging theory of TEM, the exposed facet (010) of TiO_2 was perpendicular to these two crystal facets. In addition, the edge of the graphene can also be observed and indicated in Fig. 5d. This suggested that the exposed facet (010) of TiO_2 was attached to the surface of graphene, and thus probably forming an interface between TiO_2 and graphene. In addition, the (010) facet with more Ti atoms exhibited a higher surface energy than (101) plane,¹⁴ indicating that there probably was an interaction between Ti atoms and graphene.

To study the interaction between graphene and TiO₂ in Gx-TiO₂, XPS analysis was utilized. Fig. 6a shows the high resolution XPS spectra of C 1s region for Mixing. The binding energy of 284.8 eV was a typical peak position for graphite carbon, which demonstrated the sp²-hybridized carbon in the graphene state.^{11a} Furthermore, the deconvoluted peaks certered at the binding energy of 285.9 eV and 289.0 eV were attributed to the C-O and C=O oxygen-containing carbonaceous bands.^{5j} C 1s spectra for the as-prepared G2.5-TiO₂ composite are shown in Fig. 6b. Two distinct peaks at 284.7 eV and 286.0 eV corresponded to graphitic carbon in grapheme and oxygenated carbons in C-O bond. Besides, an additional shoulder-peak located at 281.2 eV was found, which was usually assigned to the formation of chemical bond between carbon atom and titanium atom in the lattice of TiO₂, which resulted in formation of C-Ti bonds.¹⁵ Furthermore, lower amounts of the oxygen-containing carbonaceous bands were detected in the carbon peak of G2.5-TiO₂ as the peak area ratio of C-O bonds were decreased obviously and the peak of C=O were not observed in Fig. 6b, indicating less oxygen deficiencies. Formation of the C-Ti bond also can be examined and confirmed by analysis of the Ti (2p) core level of the XPS spectra, as shown in Fig. 6c and d. Fig. 6c shows XPS spectra for Mixing at Ti (2p) binding energy regions. The bands located at binding energies of 458.8 eV and 464.6 eV were assigned to O-Ti bond in TiO2.¹⁶ In Fig. 6d, in addition to the two characteristic peaks of TiO₂ at 458.8 eV (Ti $2p_{3/2}$) and 464.6 eV (Ti $2p_{1/2}$), two other weak peaks centered at 455.1 eV and 461.1 eV (relating to the Ti $2p_{3/2}$ and $2p_{1/2}$) were found and probably coming out of a C-Ti bond between TiO₂ and graphene in G2.5-TiO₂ composite. This demonstrated that the C-Ti chemical bond was present in G2.5-TiO₂ and absent in Mixing. In addition, the formation of C-Ti chemical bond was also confirmed by the Calculation results in Fig. S1 and 2. As can be seen that the (010) facet of TiO_2 with a higher energy surface and more Ti atoms can adsorb graphene easily and thus C-Ti chemical bond can be formed easily between the (010) facet of TiO₂ and graphene. Furthermore, the DOS of anatase (010)/graphene in Fig. S3 showed that the DOS profiles of Ti and C were coincide with each other, further suggesting the formation of the chemical bond between Ti and C atoms.

The TG-DTA analysis was carried out to further confirm the chemical bonding by carbon atom in G2.5-TiO₂ composite. Fig. 7 shows the TG-DTA curve of G2.5-TiO₂ and mechanical mixing TiO₂/graphene (with 2.5% graphene loading) composite, which were performed in air atmosphere with a heating rate of 10°C·min⁻¹. With increasing temperature, the mechanical mixing TiO₂/graphene showed a gradual mass loss until ca. 400°C and a very sharp exothermic peak at 427°C

in the DTA curve (Fig. 7b), which was attributed to the combustion of graphene layers. In the contrast, $G2.5-TiO_2$ composite exhibited a later onset of weight loss than the mechanical mixing TiO_2 /graphene composite, and showed an obvious exothermic peak centered at 533°C (Fig. 7a). This suggested that the thermal stability of the nanocomposite samples was enhanced, with the graphene nanosheets being stabilized by the deposited TiO_2 nanoparticles due to the strong chemical coupling between them.¹⁷ Likewise, this result proved that there was a C-Ti bond in G2.5-TiO₂ composite, in line with the above results.

The optical properties of the as-prepared TiO₂/graphene nanocomposites were measured by UV-vis diffuse reflectance spectra (in Fig. S4a). All of these samples displayed the typical absorption with an intense transition in the UV region of the spectra, which was assigned to the intrinsic band gap absorption of TiO₂ due to the electron transitions from the valence band to conduction band $(O_{2p} \rightarrow Ti_{3d})$.¹⁸ The TiO₂/graphene nanocomposites exhibited increasing absorption in the visible region after adding graphene. In line with the previous reports,^{7c} a red shift to higher wavelength in the absorption edge of Gx-TiO₂ composites has been observed, indicating a narrowing of the band gap of Gx-TiO₂. However, it was difficult to determine the value for such a red shift. A plot of the transformed Kubelka-Munk function dependent on the energy of light is shown in Fig. S4b. The roughly estimated band gaps were 2.91, 2.94, 3.00, 2.94 and 3.02 eV for G3.0-TiO₂, G2.5-TiO₂, G1.5-TiO₂, G0.5-TiO₂ and pure TiO₂, respectively. This red shift could be attributed to the chemical bonding between TiO₂ and the specific sites of GO,^{7c} which was consistent with the DOS result in Fig. S3. In addition, there was an obvious decease in UV-light absorption for Gx-TiO₂ compared with G0-TiO₂, which was in a good agreement with the previous reports.⁹

3.3. Mechanism of enhanced photocatalytic activity

Based on the above characterization results, the mechanism of enhanced photocatalytic activity could be mainly attributed to chemically bond interfacial contact between TiO₂ and graphene. Charge carrier transfer plays a pivotal role in photocatalytic processes, for once electron-hole pairs are generated by light excitation, most of them recombine generating heat and only a small fraction can successfully transfer to the interface to initiate redox reactions. It is reported that the factors affecting the efficiency of the electron transfer property includes the nanoparticles surface,¹⁹ size ²⁰ and morphology.²¹ As for graphene-based photocatalysts, the enhanced carrier transfer property is mainly contributed by the enhanced special charge transportation properties of graphene.^{7c, 22} Also, the interaction extent between graphene and semiconductor nanoparticles determines the electron transportation, which further determines the photocatalytic activity.⁹ Our previous work about graphene/BiOCl photocatalyst reveals that the formation of C-Bi bond contributes much for the photocatalytic performance.^{11a} Herein, we propose an effective chemical-bonded interfacial charge transfer (CB-IFCT) to explain the enhanced photocatalytic activity of TiO₂/graphene composite.^{11a, 23}

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This is ascribed that mechanical mixing process is not able to create effective interfacial contact between TiO_2 and grapheme, while TiO_2 /graphene composite with chemical bonding causes an intimate interaction between TiO_2 nanoparticles and graphene nanosheets (illustrated in Fig. 8a).^{22a, 24} In this regard, the graphene loading with intimate chemical bonding can efficiently facilitate the interfacial electron transfer and electron-hole separation. TiO_2 has a high potential of conduction band bottom (2.81 eV vs. NHE, normal hydrogen electrode),²⁵ so the free electrons have powerful reducibility. Oxygen molecules adsorbed on the TiO_2 surface could react with free electrons. Thereby, a depletion layer is created with low conductivity near the surface.²⁶ Within TiO_2 material, the CB electrons have to travel through the grain boundaries (GB). Thus, when potential barrier is formed at the GB regions, the mobility of electron carriers could be limited.²⁷ In other words, the electrons transfer from one TiO_2 grain to the neighbored one should get through the potential barrier. So, if TiO_2 and graphene are chemically coupled, they can decrease the potential barrier at the GB regions. The chemical binding could provide a good spatial condition for charge transport from TiO_2 to graphene via the interfaces. However, the mechanical mixing could not provide intimate spatial condition for charge transport.

For the TiO₂ materials, the reported energy level ²⁵ of valence band (VB) and conduction band (CB) is 2.81 V and -0.39 V vs. NHE (normal hydrogen electrode), respectively. The calculated Fermi energy level of graphene is -0.08 V vs. NHE.²⁸ So, the photo-generated electron on the CB of TiO₂ is energetically feasible to transfer to graphene (as showed in Fig. 8b). As the Fermi energy of graphene is much lower than the CB of TiO₂, the graphene can act as a sink for the photogenerated electrons. The excited electrons can be stored in the huge π - π network of graphene nanosheets in the composites, which can retard the electron-hole recombination on TiO₂. This process facilitates effective interface charge separation and hinders carrier recombination.

The electron transfer between TiO_2 and graphene nanosheets can be expressed as:

$$TiO_2 + h\gamma \rightarrow e^-(CB, TiO_2) + h^+(VB, TiO_2)$$
(1)
graphene + e⁻(CB, TiO_2) $\rightarrow e^-(graphene) + TiO_2$ (2)

On the other hand, the adsorbed HCHO molecule could directly transfer electron with chemical bonded TiO_2 /graphene composite. DFT calculation results show that,²⁹ for HCHO molecule, the highest occupied molecular orbital (HOMO) is 2.5 eV below the Fermi level and the lowest unoccupied molecular orbital (LUMO) is 0.6 eV above the Fermi level. So, as Fig. 8b illustrated, the electron located at the LUMO of HCHO can transfer to graphene, and the holes stayed in the VB of TiO_2 are reacted with the absorbed HCHO, as expressed as follows:

graphene +
$$e^{-}$$
 (LUMO, HCHO) $\rightarrow e^{-}$ (graphene) + HCHO (3)

$$H_2O + h^+ (VB, TiO_2) \rightarrow \cdot OH + H^+$$
(4)

$$HCHO (ad) + OH \rightarrow CO_2 + H_2O$$
(5)

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The key of improving the oxidation efficiency for the $Gx-TiO_2$ composite is attributed to IFCT effect, which decreases the possibility of recombination of electron-hole pairs, increases the number of holes participating in the photooxidation process and thus enhances the photocatalytic activity. The IFCT effect is experimentally supported by EIS, gaseous phase photocurrent and PL test results.

In the previous studies, EIS analysis is commonly used to confirm the above proposition.^{22a, 30} Fig. 9a shows the EIS Nynquist plots of the as-prepared and the mechanical mixing $TiO_2/graphene$ nanocomposites UV irradiation. The arc radius on EIS Nynquist plot of G2.5-TiO₂ is the smallest of the three samples; and that of the Mixing sample is only smaller than G0-TiO₂ sample. In EIS Nynquist plot, the smaller the semicircle size indicates an effective separation of photogenerated electron-hole pairs and fast interfacial charge transfer to the electron donor or acceptor.³¹ Since the radius of the arc on the EIS spectra reflects the reaction rate occurring at the surface, suggesting that a more effective separation of photogenerated electron-hole pairs and a faster interfacial charge transfer occur on G2.5-TiO₂ photocatalyst under this condition. This result clearly indicates that the chemical combination of TiO₂ and graphene could effectively enhance the separation of photogenerated electron-hole pairs.

The EIS test is carried out under liquid conditions, which is not clearly the same as gaseous degradation experiments. To further support the above proposition, the transient gaseous phase photocurrent responses are recorded for photoelectrodes consisting of pure TiO₂, mechanical mixing and chemical bonding TiO₂/graphene nanocomposites under the same conditions as the photocatalytic reaction, i.e., 200 ppm HCHO gas in air and UV LED irradiation. Fig. 9b shows the I-t curves for the three samples with UV-irradiation. It is suggested that the photocurrent is mainly determined by the separation efficiency of photo-generated electron-hole pairs within the photocatalyst. The photocurrent of the chemical bonding composite (G2.5-TiO₂) is enhanced ca. 15.3 times than that of pure TiO₂ (G0-TiO₂), which indicates that the separation efficiency of photoinduced electrons and holes is improved through the electronic interaction between graphene nanosheets and TiO₂ nanoparticles. Also, the photocurrent of the chemical bonding composite (G2.5-TiO₂) is enhanced ca.

PL emission spectra resulting from the recombination of photoinduced charge transportation are powerful demonstrations of enhanced charge transportation and separation properties.^{11a} PL signals for G0-TiO₂, Mixing and G2.5-TiO₂ under excitation at 325 nm are given in Fig. 10. The lowest PL intensity for G2.5-TiO₂ indicates the lowest recombination rate of photoinduced electron-hole pairs, consistant with the photocatalytic activity of the sample. In addition, Mixing also exhibits a slightly lower PL intensity than G0-TiO₂, but its intensity is much higher than that of G2.5-TiO₂. This is mainly attributed to the less defects in G2.5-TiO₂, confirmed by the above Raman and XPS results. More importantly, this PL result

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demonstrates that only the TiO₂/graphene composite with chemical bonding interface can effectively facilitate the charge transportation and separation, in a good agreement with the results of EIS and gaseous phase photocurrent.

4. Conclusion

In conclusion, TiO_2 /graphene nanocomposites with high photocatalytic activity were synthesized by a facile solvothermal approach at 200°C for 10 h. The anatase TiO_2 nanocrystals were densely supported on graphene nanosheets with close interfacial contacts. Further characterization results indicate that the TiO_2 nanocrystals were chemical bonding with the graphene nanosheets, which is confirmed by the formation of C-Ti bond in XPS. The chemical bonding nanocomposite (G2.5-TiO₂) exhibits 2.6 times enhancement of photocatalytic activity than pure TiO_2 . Based on the EIS, gaseous phase photocurrent and PL test results, this enhancement can be explained by the IFCT effect, which could provide a good spatial condition for charge transport from TiO_2 to graphene via the interfaces, decrease the possibility of recombination of electron-hole pairs, and thus lead to a higher photocatalytic activity.

Acknowledgements

This work was supported by the National Basic Research Program of China (Grant Nos. 2009CB939702 and 2009CB939705), Nature Science Foundation of China (No. 50772040 and 50927201). The authors are also grateful to Analytical and Testing Center of Huazhong University of Science and Technology.

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Captions for figures:

Figure 1. The photocatalytic activity (κ) of Gx-TiO₂ composites (x=0, 0.5, 1.5, 2.5 and 3.0), P25 and Mixing samples.

Figure 2. (a) The degradation curves of HCHO and increasement of CO₂ by Gx-TiO₂ composite (x=0, 0.5, 1.5, 2.5 and 3.0);

(b) the stability test of G2.5-TiO₂ photocatalyst.

Figure 3. (a) XRD patterns of TiO₂/graphene nanocomposites; (b) Raman spectra of G2.5-TiO₂, Mixing, G0-TiO₂ and pure grapheme.

Figure 4. SEM images of $Gx-TiO_2$ nanocomposite, where x=0 (a), 0.5 (b), 1.5 (c) and 2.5(d).

Figure 5. (a, b) TEM and (c, d) HRTEM images of G2.5-TiO₂ nanocomposite.

Figure 6. The C 1s (a, b) and Ti 2p (c, d) XPS spectra of mechanical mixing (a, c) and chemical bonded (b, d) TiO₂/graphene nanocomposites, respectively.

Figure 7. The TG-DTA curves of chemical bonded (a) and mechanical mixing (b) TiO₂/graphene nanocomposites, respectively.

Figure 8. Schematic illustrations for effective IFCT effect for TiO₂/graphene composites.

Figure 9. (a) EIS spectra and (b) gaseous phase photocurrent curves of G0-TiO₂, G2.5-TiO₂ and the mechanical mixing composite samples.

Figure 10. PL emission spectra of G0-TiO₂, Mixing and G2.5-TiO₂.



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Fig. 10 PL emission spectra of G0-TiO₂, Mixing and G2.5-TiO₂.

Herein, we have employed a facile solvothermal method to prepare $TiO_2/graphene$ composites with chemical bonding interface, which was confirmed by XPS analysis and TG-DTA analysis. The chemically bonded $TiO_2/graphene$ composites effectively enhanced their photocatalytic activity in photodegradation of formaldehyde. The prepared composite with 2.5 wt% graphene showed the highest photocatalytic activity, exceeding that of P25, pure TiO_2 and the mechanically mixing $TiO_2/graphene$ by a factor of 1.5, 2.6 and 2.3, respectively. The enhanced photocatalytic activity is caused by IFCT through the chemical bond, which markedly decreased the recombination of electron-hole pairs, and increased the number of holes participating in the photooxidation process. The explanation was further confirmed by gaseous phase transient photocurrent response, EIS and PL.

