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Band gap and morphology engineering of TiO₂ by silica and fluorine co-doping for efficient ultraviolet and visible photocatalysis

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Abstract:

Silicon and fluorine co-doped anatase TiO₂ (Si-F-TiO₂) photocatalysts with enhanced photocatalytic activity were successfully prepared via a facile two-step synthetic method by using SiO₂ powders and (NH₄)₂TiF₆ as the precursors. The obtained products were thoroughly characterized by various techniques, including scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscope (XPS), UV-visible diffuse reflectance spectroscopy and N₂ adsorption-desorption analysis. These characterizations reveal the effects of molar ratio of silica to titanium(R) and pH value on morphology, size and crystal structure of Si-F-TiO₂ samples. We find that the band gap of the catalyst can be engineered from 3.16 to 2.88 eV via altering the molar ratio of Si : Ti and pH value. Compared with un-doped or F-doped TiO₂, co-doped Si-F-TiO₂ samples exhibited improved photocatalytic degradation toward different dye molecules under both ultraviolet and visible light illumination. With the aid of holes and radicals trapping experiments, we proposed the photocatalytic mechanism for the examined systems. Furthermore, first-principle calculations provide theoretic insights for the enhanced photocatalytic performance of codoped Si-F-TiO₂ photocatalyst.

Key words: Titanium dioxide; hydrothermal synthesis; silicon; fluorine doping; photocatalytic

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1. Introduction

Remediation of environmental pollutants by photocatalytic reactions has attracted extensive attention over the past few decades [1-4]. TiO₂ has long been considered as the most efficient metal oxide semiconductor photocatalyst, and widely used in various fields such as dye-sensitized solar cells (DSSC) [5, 6], photocatalytic removal of harmful pollutants [7-9], water splitting and solar-to-fuel conversion [10-12]. However, due to its large band gap (3.0 eV for rutile and 3.2 eV for anatase), TiO₂ can only activate under the UV light (about 5% of solar light). Poor light-harvesting ability in the visible light region and solar-driven photocatalytic activity make it difficult in energy and environmental applications. Thus, the extension in the optical response of TiO₂ from the UV to the visible spectral range will be a crucial issue on the practical applications of the material.

Recently, great efforts have been made to modify TiO₂ and to extend its light-harvesting range from UV to the visible light region. It is well-known that doping of TiO₂ with transition-metal elements demonstrates obvious shifts in the light absorption [13-15]. However, several drawbacks exist in metal-doped TiO_2 samples: poor thermal stability, electron trapping by the metal centers, and requirement of more expensive ion-implantation facilities [16]. Another approach employed to narrow the band gap of TiO_2 is to replace lattice oxygen with anionic dopant species, such as N [17-21], F [22-26], C [27, 28], S [29], Si [30-32]. Among the nonmetal doping, Si-doping TiO₂ has been reported to be a good candidate due to its unique properties of high thermal stability, low carrier-recombination centers and narrowing the band gap of TiO₂, as Si 3p states can effectively mix with O 2p states, leading to an acceptor level above the valence band maximum [30-32]. The presence of F dopant may prevent the grain growth and inhibit the transformation of anatase to rutile phase, suggesting a positive role in TiO_2 photocatalysis [26]. Very recently, two anions codoped TiO₂ materials have attracted more attention due to their improved photocatalytic activity compared with single anion doped TiO_2 due to the synergistic effect. Fang et al. [33] reported the synthesis of N, S co-doped TiO_2 materials, showing high visible light absorption. Shi and co-workers [34] discovered that Si, N co-doped anatase TiO₂ exhibits high photocatalytic activity under visible light irradiation, and they attributed this phenomenon to the effect of Si and N doping, which leads to enhanced the lifetime of photo-generated holes and changing the unoccupied N 2p states to occupied states. Many research papers [35-37] reported the preparation of the N-F codoped anatase TiO_2 and their enhanced photocatalytic activities. Huang et al. [37] pointed that he high activity is ascribed to a synergetic effect of the doped nitrogen and fluorine atoms, that is to say, the doped N atoms improve the visible-light absorption and the doped F atoms lead to the enhancement of the surface acidity, which can increase the adsorption of the reactant and thus further enhances the photocatalytic activity. Very recently, Yang et al. [38] described the preparation of Si, F co-doped TiO₂ photocatalysts aiming to introduce new active sites and enhance the UV light absorption capacity as well as photocatalytic activity of TiO₂. The above results indicate that co-doping synthetic method is one of the most effective approaches to extend the absorption edge to visible

light range in TiO₂, for enhanced photocatalysis.

Although many efforts have been made to the synthesis of co-doped TiO₂ photocatalysts, physical and chemical origins of enhanced photocatalytic activity and better light-harvesting ability for co-doped TiO₂ remains unexplained systemically. Therefore, in order to understand the effects of co-doped elements on anatase TiO_2 materials deeply and to explore the reason of enhancement in photocatalytic performance of co-doped TiO₂, more attention should be given to systematic and detailed experimental & theoretical investigations of different elements co-doped TiO_2 photocatalytic materials. Herein this paper, we develop an effective and facile wet chemical method to synthesize Si, F co-doped TiO₂ photocatalysts by using SiO₂ as silicon source and $(NH_4)_2TiF_6$ as F source. A variety of characterization techniques were employed to evaluate the morphological features, crystal structure, size, light-harvesting ability and chemical states of the obtained Si-F co-doped TiO_2 samples. Subsequently, the photocatalytic performance of the modified TiO_2 catalysts were investigated by the degradation of typical dye molecules RhB, MO and MB under UV and visible light illumination. The influence of Si/F molar ratio (R) and pH value in the physicochemical properties and photocatalytic activity of Si, F co-doped TiO₂ samples is also thoroughly analyzed. On the basis of results and analysis, the reason for the improvement in photocatalytic activity and the role of doped Si, F elements in enhanced photocatalysis was revealed. The findings described in this paper offer new insights into the fabrication and controllable synthesis of high-performance doped TiO_2 photocatalytic materials, and demonstrate potential applications in high efficiency catalytic conversion of clean solar energy to renewable chemical fuels.

2. Experimental

2.1. Materials

All reagents were of analytical purity and were used without further purification. Tetraethyl orthosilicate (TEOS), ammonium hydroxide ($NH_3 \cdot H_2O$, 20vol.%), ammonium fluotitanate ($(NH_4)_2TiF_6$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 36-38vol.%), ethanol, rhodamine B (RhB), methyl orange (MO), methylene blue (MB), benzoquinone (BQ), disodium ethylenediaminetetraacetate (Na_2 -EDTA) and dimethyl sulfoxide (DMSO) were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of SiO₂

SiO₂ powders were synthesized by a modification of the Stober method as described in previous work [39]. In a typical synthesis, ethanol (140 mL) was mixed with tetraethyl orthosilicate (TEOS) (4 mL). Then, a mixture of deionized water (28 mL) and ammonium hydroxide (4.2 mL 20vol.%) was added to the TEOS/ethanol solution at room temperature in a sealed Erlenmeyer flask at room temperature (20 °C). After the addition, the mixture was then stirred for further 24 h, the obtained white precipitates were centrifuged, washed repeatedly with ethanol and water, and then finally dried in vacuum at 60 °C for 6 h.

2.3. Preparation of Si, F-codoped TiO₂

Typically, $0.316g (NH_4)_2 TiF_6$ was firstly dispersed in 40 mL of distilled waterby sonication for 30 min. Subsequently different mass of dried SiO₂ powders (5mg, 10mg, and 20mg) were added to the reacted mixture gradually with continuous stirring for 10 min at room temperature, and pH value of the mixture was adjusted to 12 by the addition of 1 mol/L NaOH aqueous solution. Then the obtained slurry was heated to 60 °C for 6 h in a sealed round-bottom flask. Finally the resulting precipitates were collected and washed with ethanol and deionized water for several times and dried at 60°C for 8 h in air. The theoretical molar ratio of silica to titaniumis is designated as *R*, which was controlled to be 5%, 10% and 20%, respectively. For comparison, F-TiO₂ was prepared prepared using the same method without the addition of SiO₂ powders, which was defined as R=0%.

The pH values of the mixture solution were adjusted using a 1.0 M HCl or 1.0 M NaOH aqueous solution, respectively. The Si, F co-doped TiO_2 samples obtained at different pH values (pH = 4, 6, 14) are denoted as SFT-4, SFT-6 and SFT-14, respectively. The sample prepared at R=10% was also named as SFT-12.

2.4. Characterization

The X-ray diffraction patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscopy. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in an ASAP2020 surface area and porosity analyzer (Micromeritics, USA). All the samples and Evonic P25 were degassed at 180 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_{θ}) range of 0.05 ~ 0.25. Desorption isotherm was used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method with cylindrical pore size. The nitrogen adsorption volume at the relative pressure (P/P_{θ}) of 0.994 was used to determine the pore volume and average pore sizes. UV-visible diffused reflectance spectra of the samples were obtained for the dry-pressed disk samples using a UV-visible spectrophotometer (UV2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The photoluminescence emission spectra were measured using a LS-55 (Perkin Elmer) devise as the light source. XPS measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers with a monochromatic Al K α source (Physical Electronics) operated at 150 W (15 kV, 10 mA). All the binding energies were calibrated to the C1s peak at 284.8 eV of the surface adventitious carbon. All

the measurements were carried out at room temperature.

2.5. Photocurrent measurement

To investigate the transition of photogenerated electrons in Si-F codoped TiO₂ material, P25, F-TiO₂ and Si-F codoped TiO₂ material modified electrodes were prepared. The photocurrents were measured with an electrochemical analyzer (CHI660B) in a standard three-electrode system, where a platinum wire was employed as counter electrode, Ag/AgCl was used as the reference electrode and an ITO was taken as the working electrode, respectively. A 500 W Xe arc lamp ($\lambda > 420$ nm) was utilized as the light source. A 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. The modified electrode was prepared by a simple casting method as follows: 20 µL 5.0 mg/mL Si-F codoped TiO₂ aqueous solution was dropped onto the pretreated ITO and these electrodes were dried at 50°C for 8h. All above electrochemical measurements were taken at room temperature.

2.6. Photocatalytic activity measurements

The photocatalytic activities of Si-F-TiO₂ photocatalysts were evaluated by measuring the degradation rate of RhB, MO and MB solutions under ultraviolet and visible light irradiation. The optical system for the photocatalytic reaction was composed of a 300 W Hg lamp (365 nm) as the UV light source and a 350 W Xe lamp with a cut-off filter (λ >400 nm, 120 uW/cm²) as the visible light source. A low-acidity aqueous solution containing 200 mL 1×10⁻⁵ mol L⁻¹ dyes solutions and 0.2 g powders were placed in an ultrasonic bath for 30 min and then magnetically stirred in the dark for 30 min to reach the adsorption equilibrium of dyes solutions with photocatlysts, and then exposed to UV light and visible light, respectively. Commercially available TiO₂ nanoparticles (Evonic P25) with an average particle size of 25 nm were adopted as the reference with which to compare the photocatalytic activity under the same experimental conditions. UV/Vis absorption spectra were recorded at different time intervals to monitor the absorption and photocatalytic degradation of dyes solutions, and the concentration of dyes solutions left in the aqueous system was measured by observing the absorption at 553 nm for RhB, 665 nm for MB and 465 nm for MO on a UV-visible spectrophotometer (UV-1601, Shimadzu). Before measurement, the suspension was filtered with Millex Millipore filter (0.1 mm) to remove the photocatalysts.

3. Results and Discussion

3.1 Characterization of Si-F codoped TiO₂ samples

SEM and TEM are used to characterize the morphology and microstructure of the as-prepared samples. Fig. 1 presents typical SEM images of the Si-F co-doped TiO₂ samples prepared at different molar ratios of silicon to titanium (*R*). In the absence of silicon, the products are nonuniform octahedron-shaped particles with an average size of about 200 nm (Fig. 1a). At R = 5% and 10%, the shape and size of the products exhibit obvious changes, and a large amount of nanoparticles with size about 20 nm were obtained, as shown in Fig. 1b and Fig. 1c. When further increasing *R* value to 20%, large agglomerates and small nanoparticles were obtained, which

indicated optimal R value is important for controlling the morphology and size of the Si-F-TiO₂ particles. Fig. 1e and 1f show TEM and HRTEM images of the Si-F codoped TiO₂ samples prepared at R = 10%, respectively. It can be seen from Fig. 1e that plate-like nanoparticles with average length of 20 nm were obtained in addition with a small amount of nanoparticles, consistent with SEM results. The corresponding SAED pattern (insert in Fig. 1e) reveals the polycrystalline nature of anatase Si-F codoped TiO₂. Fig. 1f shows the corresponding HRTEM image of the sample. It shows clear lattice fringes, and the lattice spacing is ca. 0.35 nm, corresponding to the (101) planes of anatase TiO₂ single crystals. XRD patterns of Si-F codoped TiO₂ samples prepared with varying R values confirm the formation of anatase (JCPDS NO. 21-1272) in each case, as shown in Fig. 1g. No peaks from the SiO_2 crystal phase were observed for all samples, which could be attributed to its amorphous nature, or because Si as an interstitial atom is well-inserted into the crystal lattice of TiO₂. Furthermore, the XRD peak intensities of anatase steadily decrease and the widths of peaks become broader with the increasing silica content, which is consistent with the decrease in average crystallization size (Table 1) and variation in size of samples shown in SEM and TEM images. This is in good agreement with the previous report [40]. EDX analysis of Si-F codoped TiO_2 samples prepared with R = 10 % (see Fig. 1h) shows that the sample is composed of Si, Ti, F and O elements, indicating a successful incorporation of Si, F ingredients and anatase TiO₂.

XPS measurement was used to further investigate the chemical states of different elements in the modified Si-F co-doped TiO₂ samples. In particular, the chemical nature of involved dopants was investigated in details. Fig. 2a shows the XPS survey spectrum of Si-F codoped TiO₂ prepared at R =10%, in which all peaks derived from Ti, O, C, Si and F elements are evident. The C 1s peak located at 284.6 eV mainly results from the contamination of environment [22]. Fig. 2b shows the XPS spectra for the Ti 2p region of Si-F-TiO₂ samples. The Ti 2p_{3/2} and Ti 2p_{1/2} of doped TiO₂ appear at 458.8 and 464.6 eV, respectively, indicating that Ti exists in the form of Ti⁴⁺ [23]. The binding energy of Ti 2p_{3/2} for Si-doped TiO₂ is above 458.8 eV, 0.6 eV greater than that of pure TiO₂, which is 458.2 eV as reported [41]. It is an evidence for the formation of Si–O–Ti bond. The electronegativity of Si is greater than that of Ti, which results in the decrease of electron density around Ti atom. As a result, the binding energy of Ti increases. Fig. 2c shows the Si 2p XPS spectrum, in which only one peak at 103.0 eV is detected for Si 2p (Fig. 2a). The binding energy of Si 2p is smaller than that (103.4 eV) of pure SiO₂ [42]. The lower binding energy of Si 2p in the co-doped TiO₂ is ascribed to the decrease of the effective positive charge on the Si atoms. Since electron-negativity of Si is higher than that of Ti, compared with pure SiO₂, the formation of the

Si–O–Ti bonds causes a less positive charge on the Si atoms [42], which is indicative of strong interactions of silicon species with TiO₂ lattice. Meanwhile, a high-resolution XPS spectrum of O 1s is shown in Fig. 2d. The peak is predominantly fitted into three peaks, corresponding to Ti–O (530.4 eV), O–H (531.6 eV) and Si–O bonds (532.8eV), respectively. It was reported that the binding energies of O 1s in Si–O–Si and Ti–O–Ti bonds are 533.2 and 530.1 eV [42-43], respectively. An intermediate binding energy value of 532.8 eV in O 1s spectrum can be attributed to the formation of Si–O–Ti crosslinking bonds in the matrix of anatase TiO₂. This result is consistent with the XPS analysis of Si 2p, and also well in line with XPS results from previous reports on Si-doping [42]. Fig. 2e shows the high-resolution XPS spectrum of F 1s. The F 1s peak can be deconvoluted into two peaks with Gaussian distributions, implying the presence of two F species. The peak at 684.8 eV originates from surface fluoride (Ti-F) formed by ligand exchange between F anions and surface hydroxyl groups physically adsorbed on TiO₂ surface [23], while the other small peak at 686.7eV can be assigned to the substitutional F atoms that occupied oxygen sites in the TiO₂ crystal lattice and form bond of Ti–O–F [25].

Previous study showed that pH values have considerable effects on the microstructures and photocatalytic activity of titania photocatalyst [44]. Fig. 3 shows the influence of pH values on size of nanocrystalline Si-F codoped TiO₂ samples. The results indicate that the particle size of the samples is mainly dependent on the pH values of the precipitation medium. However, an optimal pH value may exist. With increasing pH values, the particle size decreased initially, followed by an increase in the particle size when the pH value is above 12. This phenomenon may be attributed to the following reasons: a lower pH value inhibits the hydrolysis of NH₄TiF, which leads to a low monomer concentration. This process slows down the nucleation process and may also have an impact on the crystal growth, resulting in the generation of samples with larger sizes. However, a higher pH value can promotes the hydrolysis of NH₄TiF, and a large amount of crystal nucleus is formed, leading to the production of samples with smaller sizes. The corresponding XRD results of Si-F codoped TiO₂ samples recorded at different pH values are shown in Fig. 2e. All diffraction peaks can be indexed to pure anatase TiO_2 . Intensities of diffraction peaks originating from anatase TiO₂ steadily decrease and the widths of peaks become broader with increasing pH values. The average crystallite size was then calculated by line broadening methods and Scherrer equation and the results are shown in Table 2. Therefore, it can be concluded that the pH value plays an important role in determining the size and morphology of TiO_2 , which can potentially be used to tune the photocatalytic activity.

Nitrogen adsorption-desorption isotherms were measured to determine the specific surface

areas of Si-F codoped TiO₂ samples prepared with varying R values (Fig. 4a, Table 1). The isotherm curves of all samples exhibit a type-IV shape, in accordance to the International Union of Pure and Applied Chemistry (IUPAC) classification. At high relative pressures from 0.7 and 1.0, the isotherms exhibit distinct hysteresis loops, which show the presence of mesopores (2-50 nm). With increasing R, the value of BET surface area (S_{BET}), average pore size and pore volume increases due to decreasing of crystallite size. When R = 10%, the highest surface area of 66 m².g⁻¹ was obtained. It can be concluded that the doped Si is able to enter the lattice of $Si-F-TiO_2$, which hampers the crystal growth of TiO₂ and then leads to the decrease of particle size and an increase in specific surface area. The hysteresis loop is of type H3, which is associated with aggregates of tabular-shaped particles giving rise to slit-like pores. Quantitative details on BET surface area, pore volume and average pore size of the Si-F codoped samples prepared at different R values are presented in Table 1. Fig. 4b shows nitrogen adsorption-desorption isotherms of the Si-F codoped TiO₂ samples prepared at pH 4, 6, 12 and 14. The isotherms of all samples were of type IV (BDDT classification) at relative pressure range of 0.8 to 1.0, indicating the presence of mesopores. The variation of pH value in the reaction system exerts a significant influence on the BET surface areas of the obtained products. With increasing pH value, the S_{BET} increased. When pH = 12, the highest S_{BET} reached 66 m².g⁻¹, consistent with the smallest crystal size based on TEM image.

It is well-known that light-harvesting ability of the catalyst plays a significant role in the photosensitization activity. The high photocatalytic activity of the samples can be attributed to the higher UV–Vis light absorbance, which can be easily proved by UV–Vis diffuse reflectance spectra. Fig. 5a shows the UV-Vis spectra of the Si-F codoped TiO₂ powders with the different Si/Ti molar ratio (R). It is apparent that a red shift in the band gap absorption edge was observed with the increase of the concentration of doped-Si. The slightly red shift indicated the decrease of band gap energies for all Si-F-TiO₂ samples. The band gap energy can be estimated from Kubelka–Munk function [45]. The relationship of $(\alpha hv)^{1/2}$ versus hv curves is plotted and displayed in Fig. 5b. The extrapolated band gap energies of the as-prepared Si-F-TiO₂ samples with different R values (0, 5, 5)10 and 20 %) are about 3.16, 3.11, 2.88 and 3.03 eV, respectively. The smaller band gap energy of Si-F codoped samples means a broader spectral response range, which could contribute to an enhanced photocatalytic activity. The influences of pH values on the optical absorption characteristics of Si-F codoped TiO_2 are shown in Fig. 5c. A significant red-shift of the band gap absorption edge was observed with the increase of pH values. Especially, the codoped TiO₂ sample prepared at pH 12 exhibits the strongest optical adsorption under both UV and visible region. Using the same procedure as in Figure 5b, the relationship of $(\alpha hv)^{1/2}$ versus hv curves is plotted and displayed in Fig. 5d. The band gap energy can be extrapolating the linear absorption edge of the curve. The Eg values of doped TiO₂ samples obtained at pH = 4, 6, 12, 14 were found to be 3.21, 3.12, 2.88 and 2.98, respectively. Because the absorption wavelength range is extended greatly towards visible light and the absorption intensity increases, the formation rate of electron-hole pairs

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on the photocatalyst surface also increases greatly, which results in the photocatalyst exhibiting higher photocatalytic activity. The results are consistent with the evaluation of photocatalytic activity that we will show later.

In order to investigate the synergistic effect of Si/F codoping, theoretical analysis of the electronic structures was carried out by first-principles calculations. Anatase TiO₂ belongs to body-centered tetragonal crystal structure with I41/am d space group, and there are four Ti atoms and eight O atoms in each unit cell. $2\times2\times1$ anatase TiO₂ supercell (as shown in Fig. 6a) is constructed to study their electronic properties. For F/Si-codoped anatase TiO₂, an oxygen atom is substituted by a fluorine atom while a titanium atom is substituted by a silicon atom with a concentration of 4.17 at.% (see Fig. 6b). Table 3 lists the optimized structural parameters of pure and doped $2\times2\times1$ anatase TiO₂ supercell. The calculated lattice constants for pure TiO₂ supercell area a = b= 7.601 Å and c = 9.703 Å, which are consistent with previous calculations, indicating that our calculation methods are reasonable and the calculated results are authentic. Albeit the fact that these ways are slightly over estimate than the experiment values of a=b=7.570Å and c=9.514Å [46] owing to well-known limitation of the DFT, but will not affect the results' relative accuracy.

Fig. 6c and 6d shows the band structures of the pure TiO_2 supercell and the Si-F codoped configurations. The calculated band gap of pure anatase TiO_2 is 2.95 eV (Fig. 6c), consistent with the reported results [47]. After O atoms are partically replaced by F and Si, the Fermi level shifts from the top of the valence band to the bottom of the conduction band [30], which is a typical characteristic of the n-type doping. Especially, the band gap of the codoped TiO_2 is effectively narrowed to 2.67 eV (Fig. 6d) by introducing F, Si impurity. Furthermore, the band structure shows that an isolated impurity states lie around the Fermi level E_F . Electron transfer from these fully occupied impurity states to the conduction band minimum (CBM) will reduce the photon transition energy significantly, which should red-shift the fundamental absorption edge of Si-F doped anatase TiO_2 .

The total density of states (TDOS) and projected density of states (PDOS) for the pure anatase TiO_2 and the codoped TiO_2 structures are given in Fig. 6e and 6f. It can be clearly seen that, in pure TiO_2 (Fig. 6e), the top of the valence band is mainly composed by O 2p states and the bottom of the conduction band is dominated by Ti 3d states agreed with previous calculations [48]. In Si/F-codoped TiO₂ structure (Fig. 6f), the Fermi level is shifted to higher energy as compared to that in the pure case. At the same time, there are asymmetric density of states contributed by Ti 3d states and O 2p states around the Fermi level. These special states provides migrating steps for the electrons in the valence band to be excited into these mid-gap states, subsequently to the conduction band by visible-light absorption, which is responsible for red shifts in the absorption edge of codoped TiO₂ consistent with the other's reports which introducing the impurity level [49].

The photocatalytic degradation of organic dyes or toxic pollutants has been widely used to evaluate the activity of photocatalysts, which is of great significance in environmental pollutant

remediation. The photocatalytic activity of Si-F codoped TiO₂ samples were evaluated by monitoring the degradation of RhB in aqueous solution under UV irradiation. Fig. 7a shows the influence of Si/Ti molar ratio (R) on the photocatalytic activity. It is obvious that the photocatalytic performance of either the F-doped or Si-F co-doped TiO₂ is better than that of P25. Significantly, the photocatalytic activities of Si-F codoped TiO_2 samples is enhanced with the increase of R value because of better light absorption, narrower band gap and higher BET surface area. On the other hand, the significant enhancement could also be due to the synergistic effect between Si and F atoms. Co-doping could suppress the recombination of electron-hole pairs, thereby improving the photocatalytic performance. The highest photocatalytic activity of Si-F co-doped TiO₂ obtained from R = 10% is attributed to its largest specific surface area and smaller crystal size: the former favors dye adsorption and the latter promotes faster charge separation of photo-induced electron-hole pairs as well as better charge transport. However, when R further increases to 20%, a decrease was observed in the photocataytic activity due to the generation of TiO₂ samples with a smaller BET surface area. In addition, previous results [50] indicated that, when excessive Si was doped into TiO_2 , the produced Si-O-Ti would act as an insulator and inhibit the transfer of photoinduced electron-hole pairs, causing the deterioration of photocatalytic activity. It was found that the degradation of RhB over Si-F codoped TiO₂ with different Si/Ti molar ratios obeyed pseudo-first-order kinetics, which allows quantification of photocatalytic activity using the apparent rate constants (K.min⁻¹), as presented in Fig.7e. It can be clearly seen that the photocatalytic activity of Si-F codoped TiO₂ is enhanced rapidly with the increase of Si content. The highest degradation rate of RhB was obtained at R of 10%, and then decreased.

The photocatalytic properties of Si-F codoped TiO₂ samples prepared at different pH values were further evaluated by comparing the degradation efficiency of RhB under UV irradiation. The change of RhB concentration vs. illumination time is shown in Fig. 7b. When the pH value was 4, 6, 12, 14, the degradation percentage of RhB was estimated to be 31.8 %, 63.9 %, 97.1 %, 89.3 %, respectively. In particular, the degradation percentage of RhB over codoped TiO₂ sample prepared at pH 12 could reach 97.1% under UV light illumination for 30 min. Fig. 7f shows the dependence of the apparent rate constants (K.min⁻¹) on pH values of the starting solutions and it indicates that they follow the Langmuir-Hinshelwood first-order kinetic behavior. At pH 12, the K reached the highest value and its value was 0.1166, which might be attributed to the fact that the samples had larger specific surface areas, narrower band gap and smaller crystallite size, etc. With further increasing the initial pH values, the K decreased drastically. This was due to the crystalline growth and drastic decrease in specific surface areas (as shown in Table 2) [51].

As a comparison, photodegradation of RhB with Si-F codoped TiO_2 samples obtained at various *R* values and pH values under visible light irradiation are shown in Fig. 7c and Fig. 7d. It is evident that the photocatalytic activity of Si-F codoped TiO_2 under visible light irradiation was enhanced rapidly with the increase of Si content. The highest degradation percentage of RhB was

obtained at R of 10 %, and then decreased, which is similar to the results on the photocatalytic properties under UV light irradiation. The photocatalytic properties of the codoped TiO₂ samples prepared at different pH values under visible light irradiation is also similar to that under UV light irradiation. The degradation percentage of RhB over Si-F-TiO₂ sample prepared at pH 12 could reach the highest value under visible light. It was found that the degradation of RhB over Si-F codoped TiO₂ with different Si/Ti ratios and pH values under visible light irradiation obeyed pseudo-first-order kinetics. The corresponding the apparent rate constants (K.min⁻¹) are presented in Figure 7g and 7h.

Note that RhB as model pollutant may be photo-excited by visible light irradiation [52, 53]. To exclude the possible influence from dye used on the evaluation of catalytic performance of materials, we further performed the photodegradation tests for different dyes, including rhodamine B (RhB), methyl blue (MB) and methyl orange (MO) under the same condition. Fig. 8a-c shows the absorbance variation of RhB, MB and MO solutions under visible-light at different irradiation time, respectively. The absorption peak of RhB, MB and MO remarkably fade away during the illumination period and almost disappears after 120 min, 90 min and 105 min. The degradation percentage of RhB, MB and MO reaches 83.4 %, 93.9 % and 87.2 % after irradiated 90 min, respectively. The color change photographs of MO, MB and RhB solutions at the degradation process are shown in Fig. 8d. All the results as mentioned above demonstrate Si-F codoped TiO₂ obtained at pH = 12 and R = 10 % is an excellent semiconducting photocatalytic material, which possesses a unique universal advantage to degrade several dyes such as MO, MB and RhB. Band gaps and photocatalytic performance of doped TiO₂ materials reported by other researchers [16, 17,18, 38, 54, 55] are summarized in Table 4 and Table 5 for comparisons. To the best of our knowledge, the as-obtained Si, F co-doped samples demonstrate better photodegradation activity than Si or F-doped TiO₂, as well as N, F co-doped TiO₂ materials toward RhB.

In order to provide stronger evidence for the proposed photocatalytic mechanism, the transient photocurrent responses of P25, F-TiO₂ and Si-F TiO₂ electrodes were recorded over several on–off cycles under visible-light irradiation. As shown in Fig. 9a, under visible-light irradiation, an apparent photocurrent response is observed for all three electrodes. It can be seen that there is a fast and uniform photocurrent response to each switch-on and switch-off event in all of the electrodes, which is indicative of good reproducibility of all three samples. It is notable that pure P25 shows a very low photocurrent density, which is direct evidence for the low quantum efficiency. However, the Si-F codoped TiO₂ shows much higher photocurrent intensity than that of F-TiO₂ and P25. It is well-known that the photocurrent is mainly determined by the efficiency of the separation of photogenerated electron/hole pairs within the photoelectrode; holes are transferred at the photocatalyst/electrolyte interface, while electrons are transported to the back contact. The recorded higher photocurrent response of Si-F codoped TiO₂ implies an efficient suppression in electron/hole recombinations, leading to the enhancement in photocatalytic activity.

It is well known that photoluminescence (PL) analysis is a very useful technique to disclose the migration, transfer and separation efficiency of the photoexcited charge carriers in a photocatalytic material because PL emission of photocatalyst mainly results from the charge carrier recombination. Usually, the lower the PL intensity is, the better the separation efficiency of photoinduced electron-hole pairs would be, and thus the higher the photocatalytic performance would be. Fig. 9b presents the PL spectra of P25, F-TiO₂ and Si-F codoped TiO₂. It is clear that the PL spectra of pure TiO₂ photocatalyst exhibits a strong emission peak around 460 nm, which could be related to the recombination of the photoexcited electron-hole of TiO₂. From Figure 9b, it can be clearly seen that the PL intensities of Si-F codoped TiO₂ are lower than those of pure P25 and F-TiO₂, indicating that, compared with pure P25 and F-TiO₂, the photoinduced electron-hole recombination of Si-F codoped Si-F codoped TiO₂ demonstrate enhanced photocatalytic performance towards the remediation of dye molecules.

To further reveal the photocatalytic mechanism of Si-F codoped TiO₂ in details, the effects of different scavengers on the decolorization of dye molecules were investigated to shed light on the predominant reactive oxygen species in the photocatalytic process (Fig. 10). In this study, benzoquinone (BQ) [56], disodium ethylenediaminetetraacetate (Na₂-EDTA) [57] and dimethyl sulfoxide (DMSO) [58] were employed to act as scavengers for superoxide radicals, photoexcited holes and hydroxyl radicals in both UV and visible-light-driven photocatalytic systems. As shown in Fig. 10, the degradation efficiency of MO, MB, RhB under UV and visible light irradiation decreases significantly when DMSO was used as the scavenger for hydroxyl radicals. In contrast, the addition of Na₂-EDTA and BQ showed a limited impact on the photodegradation of RhB, MO and MB, implying that holes and superoxide radicals may not play predominant role in the improved photodegradation performance.

On the basis of the above results, the photocatalytic mechanism for Si-F codoped TiO₂ samples is tentatively proposed and schematically illustrated in Fig. 11, showing possible reactions that can occur in photocatalysis process. When the semiconductor is excited under light irradiation with greater energy than its band gap energy, it will cause the formation of the hole–electron pair in the semiconductor. Subsequently, the VB holes are trapped as the surface-bound •OH by oxidation of either the surface -OH groups, the surface H₂O molecules, or both. The photogenerated electrons at the photocatalyst surface are first trapped by the present molecular oxygen to yield the superoxide radical anion, $\cdot O^{2-}$, which is then converted into $\cdot OOH$ by protonation; $\cdot OOH$ is then converted into H₂O₂ through the addition of more electrons, the latter fragmenting into $\cdot OH$. Hole (h⁺) and electron (e⁻) can react with the dye molecule in favor of its degradation directly and following mineralization.

RSC Advances

It is notable that, despite of high visible light photoactivity of doped TiO₂, the photocatalytic activity is lower than the corresponding one under UV light. The mechanism has been intensively investigated by D. Dionysiou et al [35]. They declared that TiO₂ photocatalysis under UV light irradiation leads to the generation of reactive oxygen species, in which HO• produced by h_{vb}^+ oxidation of adsorbed hydroxyl groups is generally considered to be responsible for the degradation of organic pollutants. However, visible light photocatalytic activity in doped TiO₂ is predominantly due to the formation of reactive oxygen species via the reduction of molecular oxygen by conduction band electrons, and possibly singlet oxygen by oxidation of superoxide by holes in the foreign atom induced midgap state. On the other hand, under visible light, the direct formation of HO• from hv is not thermodynamically plausible for doped-TiO₂ photocatalysis. Doped-TiO₂ photocatalysis can however lead to the formation of HO• indirectly from $\cdot O^{2-}$, which can contribute to the oxidation of organic compounds [59, 60].

The synergistic effects of co-doping with Si and F are the main reasons for the enhanced activity of doped TiO₂. One of possible explanations is that Si as an interstitial atom is forced to enter the crystal lattice of TiO₂ to establish a Si–O–Ti bond during the synthesis process [58]. As a transfer bridge, photogenerated electrons can easily move to the surface via the Si-O-Ti bond. This process can facilitate the transfer of photogenerated electrons and the improvement in quantum yield leading to an increase in the photocatalytic activity. Besides, the Si doping decreases the particle size of TiO₂ (Fig. 1) and increases the specific surface areas, which promotes the adsorption of reactant molecules and the escaping to the surface of catalysts of more electrons/holes. Furthermore, the doped Si could generate a positive charge difference and the impurity cation (Si) acted as a Lewis site, which can generate more hydroxyl groups to balance the positive charge. Therefore, more holes could be quickly sacrificed by the hydroxyl groups to produce •OH. The adsorbed •OH eventually degraded RhB, MB and MO into nontoxic compounds such as carbon dioxide, water, and inorganic substrate. Both the holes transfer and sacrifice prevented the electrons and holes from being recombined, which remarkably promotes the efficiency of the photocatalytic degradation. However, if excessive Si was doped into TiO₂, the produced Si-O-Ti bonds would act as insulators and inhibit the move of photo-induced electron-hole pairs and consequently affect negatively the photocatalytic performance. On the other hand, the insulating SiO₂ could not be activated by visible light irradiation. As a result, excessive SiO_2 existing on the surface of TiO_2 could reduce its visible light photocatalytic performance. There may be another reason for this descent, that is, excessive silica prevented TiO_2 from contacting dyes molecules. Previous studies [23, 24] also indicated that F doping could enrich the surface hydroxyl groups over TiO₂ and effectively suppress the

recombination of the photogenereated electrons and holes. In photocatalytic degradation process, surface hydroxyl groups over the catalyst can capture the photogenerated holes and transform to hydroxyl radicals, which are the main reactive species for the decomposition of organic molecules. The co-doping with Si and F improved the photocatalytic efficiency of TiO_2 through narrowed bandgap, promoted separation of photo-generated electrons and holes, and enhanced photocatalytic oxidizing species.

4. Conclusion

In summary, the silicon and fluorine codoped TiO_2 phtocatlysts were successfully synthesized through an effective and simple two-step method using SiO_2 as silicon source, $(NH_4)_2TiF_6$ as fluorine source. The as-prepared Si-F codoped TiO_2 samples exhibited universal high-efficient degradation ability for methyl orange (MO), methyl blue (MB) and Rhodamine B (RhB) under the irradiation of UV and visible light. The Si-F codoped TiO_2 sample prepared with Si to Ti molar ratios of 10 % and pH of 12 exhibits the highest photoactivity either under visible light or under UV irradiation among all samples including undoped, single-doped and codoped samples. The improved photocatalytic activity can be attributed to the modified textural, surface, and electronic structures of the Si-F codoped TiO_2 photocatalyst. Collectively, the present study not only presents a very efficient codoped TiO_2 photocatalyst but also derives significant insight into the synergistic effects of codoping of Si and F by which the enhanced photocatalytic behavior may be understood.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (51275213, 51302112), Dr. X. Yang and Dr. H. Tang gratefully acknowledges financial support from Six Talents Peak Project of Jiangsu Province (2015-XCL-026) and the Specialized Research Fund for Cultivating Academic Leader of Jiangsu University, China and a Project Funded by Priority Academic Program Development of Jiangsu Higher Education Institutions.

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Figure and Caption

Published on 28 June 2016. Downloaded by University of Sussex on 28/06/2016 15:01:33

Fig. 1 SEM images of Si-F codoped TiO₂ samples (pH=12): (a) R = 0%, (b) R = 5%, (c) R = 10%, (d) R = 20%, (e) TEM (insert in Fig. e is the corresponding SAED pattern) and (f) HRTEM images of the Si-F codoped TiO₂ samples obtained at R = 10% and pH=12, (g) XRD pattern of Si-F codoped TiO₂ samples obtained at different *R* values (*R* is denoted the ratio of Si/Ti) and (h) EDS spectrum of the Si-F codoped TiO₂ samples obtained at R=10%, pH=12.

Fig. 2 XPS spectra of Si-F codoped TiO_2 sample (R=10%, pH=12): survey XPS spectrum (a), high resolution XPS spectra of Ti2p (b), Si2p (c) ,O1s (d) and F1s (e).

Fig. 3 TEM images of (a) pH = 4, (b) pH = 6, (c) pH = 12, (d) pH = 14, and (e) XRD patterns of Si-F codoped TiO₂ (obtained at R=10%) obtained at different pH values.

Fig. 4 Nitrogen adsorption–desorption isotherms of Si-F codoped TiO_2 samples obtained at (a) different *R* (Si/Ti molar ratio) values (pH=12) and (b) different pH values (R=10%).

Fig. 5 UV-visible absorption spectrum and plot of $(ahv)^{1/2}$ versus energy hv for the band gap energy of Si-F codoped TiO₂ samples obtained at different *R* values (a,b) and different pH values (c,d).

Fig. 6 Supercell models of pure anatase $TiO_2(a)$ and Si-F codoped $TiO_2(b)$; band structures plots of pure anatase $TiO_2(c)$ and Si-F codoped $TiO_2(d)$; the calculated TDOS and PDOS of pure anatase $TiO_2(e)$ and Si-F codoped $TiO_2(f)$.

Fig. 7 (a-d) Photocatalytic degradation of RhB and (e-h) The corresponding comparison of apparent rate constants (Kapp) in the presence of different photocatalysts under UV and visible-light irradiation. a, b, e & f are under UV light, while c, d, g & h are under visible light. a, c, e, & g are changing in R and b, d, f & h are changing in pH.

Fig. 8 Absorbance variation of RhB (a), MB (b) and MO (c) solutions of Si-F codoped TiO_2 (R=10%, pH=12) under visible-light and the color change photographs of MO, MB and RhB solutions at different irradiation time (d).

Fig. 9 (a) The transient photocurrent responses and (b) Photoluminescence spectra of P25, F-TiO₂ (R=0%, pH=12) and Si-F codoped TiO₂ (R=10%, pH=12).

Fig. 10 Photocatalytic curves of RhB(a, b), MO(c, d) and MB(e, f) degradation over Si-F codoped TiO_2 (R=10%, pH=12) added radical scavengers under UV and visible light irradiation.

Fig. 11 Schematic diagram of a possible mechanism of the degradation of the dyes on the semiconductor photocatalyst surface under light irradiation.

Table 1 Crystalline size, Band gap, Surface area, average pore size and pore volume of Si-F co-doped TiO_2 prepared at different atomic ratios of silica to titanium (R).

Table 2 Crystalline size, Band gap, Surface area, average pore size and pore volume of SFT prepared at pH 4, 6, 12and 14.

Table 3 The optimized structural parameters of pure and doped $2 \times 2 \times 1$ TiO₂ supercell in F/Si-codoped configuration, Bond₁ and Bond₂ with "*" represents the bond length of Ti-F while the value with "#" represents that of Si-O.

Table 4 Comparison of the photocatalytic activity with other doped TiO_2 photocatalysts under visible light irradiation.

Table 5 Comparison of the photocatalytic activity with other doped TiO₂ photocatalysts under UV light irradiation.



Fig. 1. SEM images of Si-F codoped TiO₂ samples (pH=12): (a) R = 0%, (b) R = 5%, (c) R = 10%, (d) R = 20%, (e) TEM (insert in Fig. e is the corresponding SAED pattern) and (f) HRTEM images of the Si-F codoped TiO₂ samples obtained at R =10% and pH=12, (g) XRD pattern of Si-F codoped TiO₂ samples obtained at different *R* values (*R* is denoted the ratio of Si/Ti) and (h) EDS spectrum of the Si-F codoped TiO₂ samples obtained at *R*=10%, and *R*=10%, pH=12.



Fig. 2. XPS spectra of Si-F codoped TiO₂ sample (R=10%, pH=12): survey XPS spectrum (a), high resolution XPS spectra of Ti2p (b), Si2p (c) ,O1s (d) and F1s (e).



Fig. 3. TEM images of (a) pH = 4, (b) pH = 6, (c) pH = 12, (d) pH = 14, and (e) XRD patterns of Si-F codoped TiO₂ (obtained at R=10%) obtained at different pH values.



Fig. 4. Nitrogen adsorption–desorption isotherms of Si-F codoped TiO₂ samples obtained at (a) different *R* (Si/Ti molar ratio) values (pH=12) and (b) different pH values (R=10%).



Fig. 5. UV-visible absorption spectrum and plot of $(ahv)^{1/2}$ versus energy hv for the band gap energy of Si-F codoped TiO₂ samples obtained at different *R* values (a,b) and different pH values (c,d).



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Fig. 7. (a-d) Photocatalytic degradation of RhB and (e-h) The corresponding comparison of apparent rate constants (Kapp) in the presence of different photocatalysts under UV and visible-light irradiation. a, b, e & f are under UV light, while c, d, g & h are under visible light. a, c, e, & g are changing in R and b, d, f & h are changing in pH.



Fig. 8. Absorbance variation of RhB (a), MB (b) and MO (c) solutions of Si-F codoped TiO₂ (R=10%, pH=12) under visible-light and the color change photographs of MO, MB and RhB solutions at different irradiation time (d).



Fig. 9. (a) The transient photocurrent responses and (b) Photoluminescence spectra of P25, F-TiO₂ (R=0%, pH=12) and Si-F codoped TiO₂ (R=10%, pH=12).



Fig. 10. Photocatalytic curves of RhB(a, b), MO(c, d) and MB(e, f) degradation over Si-F codoped TiO₂ (R=10%, pH=12) added radical scavengers under UV and visible light irradiation.



Fig. 11. Schematic diagram of a possible mechanism of the degradation of the dyes on the semiconductor photocatalyst surface under light irradiation.

Table 1

_							
_	Samples	Crystallinesize	Bandgap ^b (eV) S_{BET}^{c}		Pore size ^d	Pore	
		^a (nm)		(m^2/g)	(nm)	volume ^e (cm ³ /g)	
	R=0%	51.3	3.16	18.523	12.578	0.035	
	R=5%	40.1	3.11	25.196	10.857	0.074	
	R=10%	13.4	2.88	61.666	3.806	0.326	
	R=20%	20.9	3.03	42.664	3.838	0.216	

Crystalline size, Band gap, Surface area, average pore size and pore volume of Si-F co-doped TiO_2 prepared at different atomic ratios of silica to titanium (R).

^aCalculated by XRD using the Scherrer equation.

^b Band gap energy was estimated from Kubelka-Munk function.

^cBET surface area estimated from the adsorption data in the relative pressure (P/P_0) range of 0.05~0.30.

^dAverage pore diameter determined from the adsorption data of the isotherms using BJH method.

^eTotal pore volume taken from the nitrogen adsorption volume at a relative pressure (P/P_0) of 0.98.

Table 2

Crystalline size, Band gap, Surface area, average pore size and pore volume of SFT prepared at pH 4, 6, 12and 14.

Samples Crystallinesize		Bandgap ^b (eV)	$\mathbf{S}_{\mathrm{BET}}^{\mathbf{c}}$	Pore size ^d	Pore
	^a (nm)		(m ² /g)	(nm)	volume ^e (cm ³ /g)
SFT-4	43.2	3.21	16.466	12.538	0.031
SFT-6 SFT-12	38.1	3.12	32.261	8.264	0.193
SFT-14	13.4	2.88	61.666	3.806	0.326
	17.1	2.98	46.923	3.836	0.223

^aCalculated by XRD using the Scherrer equation.

^b Band gap energy was estimated from Kubelka-Munk function.

^cBET surface area estimated from the adsorption data in the relative pressure (P/P_0) range of 0.05~0.30.

^dAverage pore diameter determined from the adsorption data of the isotherms using BJH method.

^eTotal pore volume taken from the nitrogen adsorption volume at a relative pressure (P/P_0) of 0.98.

Table 3

The optimized structural parameters of pure and doped $2 \times 2 \times 1$ TiO₂ supercell in F/Si-codoped configuration, Bond₁ and Bond₂ with "*" represents the bond length of Ti-F while the value with "#" represents that of Si-O.

Configurations	a(Å)	b(Å)	c(Å)	c/a	$Bond_1$	Bond ₂	Bond ₃	$V(Å^3)$
TiO ₂	7.601	7.601	9.703	1.277	1.947	1.947	2.004	560.606
F-doped	7.644	7.635	9.643	1.262	2.042	2.042	2.243	562.775
Si-doped	7.560	7.560	9.662	1.278	1.846	1.846	1.782	552.180
C:/E	7500	7.572	9.746	1.288	1.955*	1.955*	2.799	558.361
SI/F-codoped	/.366	00 /.5/2			1.730#	1.730#		

Table 4

Comparison of the photocatalytic activity with other doped ${\rm TiO}_2$ photocatalysts under visible light irradiation

Catalyst	Dye and decomposition	Irradiation	Initial	Light	Bandgap	Reference
	rate (%)	time (mm)	of catalyst and	source	$(\mathbf{c}\mathbf{v})$	
	fute (70)		dye			
F-doped	RhB, 24%	300 min	1 g/L,	320 W	3.05	[17]
			10 mg/L	Xe lamp		
F-doped	RB, 69%	150 min	0.5 g/L,	160 W	3.02	[54]
			12 mg/L	tungsten		
				halogen		
		00 ·	1 (7	lamp	0.14	
F-doped	RhB, 30%	90 min	l g/L,	350 W	3.16	This work
			4.8 mg/L	Xe lamp		
0.1		100	1 /7	500 M		[1.6]
S1-doped	MB, 69%	180 min	l g/L,	500 W	-	[16]
			20 mg/L	Xe lamp		
Si-doped	RhB. 25%	150 min	1 g/L	300 W	_	[55]
21 avp14	,,		30 mg/L	Xe lamp		[]
			6	1		
N/F-cod	MB, 47%	60 min	2 g/L,	320 W	-	[18]
oped			24 mg/L	Xe lamp		
Si/F-cod	RhB, 83%	90 min	1 g/L,	350 W	2.88	This work
oped			4.8 mg/L	Xe lamp		

Catalyst	Dye and	Irradiation	Initial	Light	Bandgap	Reference
	decomposition	time (min)	concentration	source	(eV)	
	rate (%)		of catalyst and			
_			dye			
F-doped	RhB, 95%	60 min	1 g/L,	UV-LED	3.05	[17]
			10 mg/L			
F-doped	RhB, 70%	30 min	1 g/L,	300 W	3.16	This work
			4.8 mg/L	Hg lamp		
Si-dope	MO, 80%	60 min	1.2 g/L,	400 W	3.31	[38]
d			20 mg/L	Hg lamp		
Si/F-cod	MO, 99%	60 min	1.2 g/L,	400 W	3.26	[38]
oped			20 mg/L	Hg lamp		
Si/F-cod	RhB, 97%	30 min	1 g/L,	300 W	2.88	This work
oped			4.8 mg/L	Hg lamp		

Table 5 Comparison of the photocatalytic activity with other doped TiO_2 photocatalysts under UV light irradiation