Research Article

Enhanced Visible Light Photocatalytic Activity of V\textsubscript{2}O\textsubscript{5} Cluster Modified N-Doped TiO\textsubscript{2} for Degradation of Toluene in Air

Fan Dong, Yanjuan Sun, and Min Fu

College of Environmental and Biological Engineering, Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Technology and Business University, Chongqing 400067, China

Correspondence should be addressed to Fan Dong, dfctbu@126.com

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V\textsubscript{2}O\textsubscript{5} cluster-modified N-doped TiO\textsubscript{2} (N-TiO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5}) nanocomposites photocatalyst was prepared by a facile impregnation-calcination method. The effects of V\textsubscript{2}O\textsubscript{5} cluster loading content on visible light photocatalytic activity of the as-prepared samples were investigated for degradation of toluene in air. The results showed that the visible light activity of N-doped TiO\textsubscript{2} was significantly enhanced by loading V\textsubscript{2}O\textsubscript{5} clusters. The optimal V\textsubscript{2}O\textsubscript{5} loading content was found to be 0.5 wt.%, reaching a removal ratio of 52.4% and a rate constant of 0.027 min\textsuperscript{-1}, far exceeding that of unmodified N-doped TiO\textsubscript{2}. The enhanced activity is due to the deposition of V\textsubscript{2}O\textsubscript{5} clusters on the surface of N-doped TiO\textsubscript{2}. The conduction band (CB) potential of V\textsubscript{2}O\textsubscript{5} (0.48 eV) is lower than the CB level of N-doped TiO\textsubscript{2} (−0.19 V), which favors the photogenerated electron transfer from CB of N-doped TiO\textsubscript{2} to V\textsubscript{2}O\textsubscript{5} clusters. This function of V\textsubscript{2}O\textsubscript{5} clusters helps promote the transfer and separation of photogenerated electrons and holes. The present work not only displays a feasible route for the utilization of low cost V\textsubscript{2}O\textsubscript{5} clusters as a substitute for noble metals in enhancing the photocatalysis but also demonstrates a facile method for preparation of highly active composite photocatalyst for large-scale applications.

1. Introduction

Environmental pollution and energy crisis are the two major global challenges faced by human beings. Semiconductor photocatalysis is green technology that allows the use of sunlight for the destruction of pollutants and conversion of solar energy to hydrogen, thus providing an attractive route to potentially solve the both problems [1–3]. The widely used photocatalyst TiO\textsubscript{2} is, however, only UV active due to its relatively large band gap [4, 5]. As UV light accounts for a small fraction (4%) of the sun’s energy compared to visible light with a large fraction of 45%, the shift in the optical absorption of TiO\textsubscript{2} from the UV to the visible region is of significance for practical application of photocatalyst [6–8].

Visible light driven photocatalysis is one of the hottest topics worldwide [9–22]. Pioneered by Asahi et al. who reported that nitrogen doping can extend the optical absorption of TiO\textsubscript{2} into visible region and enhance the photocatalytic activity under visible light irradiation [9], many efforts have been devoted afterwards to developing nonmetal doped TiO\textsubscript{2} exhibiting enhanced visible light activities [10–14]. Among the various types of nonmetal doped TiO\textsubscript{2}, N-doped TiO\textsubscript{2} is the most typical and has been intensively investigated for solar energy conversion and pollutants degradation [15–18]. However, nitrogen doping intrinsically favored the formation of defects that act as recombination center, which largely limited the photoactivity of N-doped TiO\textsubscript{2} under visible light illumination [19–22].

In order to improve the visible light photocatalytic performance of N-doped TiO\textsubscript{2}, further modification has been employed, including codoping with nonmetals (C, S, F) [23–25], co-doping with metal ions (Fe, La, V) [26–28], noble metal deposition (Pt, Au) [29, 30] and metal oxide coupling (WO\textsubscript{3}, PdO, ZrO\textsubscript{2}) [31–33]. The modifications usually show promotive effects on visible light photocatalytic activity of N-doped TiO\textsubscript{2}. The activity promotion is related to phase structure, optical absorption, charge transfer, and surface properties. Recently, nanoscale clusters have been utilized to modify different types of photocatalysts [34–42]. Highly enhanced photocatalytic activities over the investigated
cluster/photocatalyst composites systems, including Ni(OH)$_2$/TiO$_2$, Cu(OH)$_2$/TiO$_2$, CuO/self-doped TiO$_2$, V$_2$O$_5$/C-doped TiO$_2$, V$_2$O$_5$/TiO$_2$, vanadium species/N-doped TiO$_2$, Fe$_2$O$_3$/WO$_3$, and CdS/graphene have been observed [34–42]. However, to our knowledge, there are few reports on the enhanced photocatalytic activity over V$_2$O$_5$ cluster-modified N-doped TiO$_2$ up to now.

In our previous study, N-doped TiO$_2$ (N-TiO$_2$) photocatalyst was prepared by partial oxidation of TiN in air [43]. In the present study, we report the facile preparation of V$_2$O$_5$ cluster-modified N-doped TiO$_2$ nanocomposite for the first time through an impregnation-calcination method and enhanced visible light photocatalytic activity for degradation of toluene in air. The microstructure, optical, and surface properties of the resulted nanocomposites photocatalysts were investigated systematically by XRD, Raman, TEM, XPS, UV-vis DRS, and PL. Based on the characterization results, a new mechanism on the promotive effects of V$_2$O$_5$ cluster modification on the charge transfer and visible light photocatalysis of N-doped TiO$_2$ was discussed and proposed.

2. Experimental Section

2.1. Preparation of Photocatalysts. N-doped TiO$_2$ (N-TiO$_2$) was prepared by partial oxidation of TiN in air [43]. In the present study, we report the facile preparation of V$_2$O$_5$ cluster-modified N-doped TiO$_2$ nanocomposite for the first time through an impregnation-calcination method and enhanced visible light photocatalytic activity for degradation of toluene in air. The microstructure, optical, and surface properties of the resulted nanocomposites photocatalysts were investigated systematically by XRD, Raman, TEM, XPS, UV-vis DRS, and PL. Based on the characterization results, a new mechanism on the promotive effects of V$_2$O$_5$ cluster modification on the charge transfer and visible light photocatalysis of N-doped TiO$_2$ was discussed and proposed.

2.2. Characterization. The crystal phase of the samples was analyzed by X-ray diffraction with Cu Ka radiation (XRD: model D/max RA, Rigaku Co., Japan). Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Raman: RAMANLOG 6, USA) with a 514.5 nm Ar$^+$ laser as the excitation source in a backscattering geometry. The morphology and structure of the samples were examined by transmission electron microscopy (TEM: JEM-2010, Japan). X-ray photoelectron spectroscopy with Al Ka X-rays ($h\nu = 1486.6$ eV) radiation (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties of the samples. The shift of the binding energy was corrected using the C1s level at 284.8 eV as an internal standard. The UV-vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV-vis spectrophotometer (UV-vis DRS: UV-2450, Japan) equipped with an integrating sphere assembly, using BaSO$_4$ as reflectance sample. The photoluminescence spectra were measured with a fluorospectrophotometer (PL: Fluorolog-3-Tau, France) using a Xe lamp as excitation source with optical filter. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 200°C prior to measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure ($P/P_0$) range of 0.05–0.3.

2.3. Visible Light Photocatalytic Activity. The visible light photocatalytic activity was evaluated by removal of toluene in air in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A 300 W commercial Xe lamp was vertically placed outside the reactor. Four minifans were used to cool the lamp. For the visible light photocatalytic activity test, a UV cut-off filter (420 nm) was adopted to remove UV light in the light beam. Photocatalyst (0.20 g) was coated onto a dish with a diameter of 12.0 cm. The coated dish was then treated at 70°C to remove water in the suspension. The toluene gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of toluene. The initial concentration of toluene was diluted to 1.0 ppm at indoor level by the air stream supplied by compressed gas cylinder. The relative humidity (RH) level of the flow system was controlled at 50%. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 1.0 L/min by a mass flow controller. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of toluene was continuously measured by GC-FID (Shanghai, 7890II). The removal ratio ($\eta$) of toluene was calculated as 

$$\eta(\%) = \left(1 - \frac{C}{C_0}\right) \times 100\%,$$

where $C$ and $C_0$ are concentrations of toluene in the outlet steam and the feeding stream, respectively. The kinetics of photocatalytic toluene removal reaction is a pseudo first-order reaction as

$$\ln \left(\frac{C_0}{C}\right) = kt,$$

where $k$ is the initial apparent rate constant [44, 45].

3. Results and Discussion

3.1. Phase Structure. The XRD patterns of as-prepared samples are shown in Figure 1. The phase structure of N-TiO$_2$ and V$_2$O$_5$ cluster-modified N-TiO$_2$ samples consists of mixed phases of anatase (JCPDS file No. 21–1272) and rutile (JCPDS, file no. 77–442). In the absence of substrate N-TiO$_2$, pure orthorhombic V$_2$O$_5$ phase (JSPD file no. 72–433) was produced. No characteristic diffraction peaks of V$_2$O$_5$ are observed in N-TiO$_2$/V$_2$O$_5$ composite samples because of its lower loading content, on the other hand, also indicating that V$_2$O$_5$ clusters were well dispersed on the N-TiO$_2$ surface [34, 35]. Figure 1 also shows that V$_2$O$_5$ cluster loading has almost no influence on the phase structure of N-TiO$_2$. By using the Debye-Scherrer equation, the crystallite sizes of anatase and rutile phase are calculated to be 18.3 and 22.8 nm, respectively. The BET surface areas of N-doped TiO$_2$ are measured to be 62.8 cm$^2$/g, and V$_2$O$_5$ cluster loading is found to have little influence on the surface areas of N-doped TiO$_2$. 
3.2. Raman Analysis. Figure 2(a) shows the Raman spectra of N-doped TiO$_2$, selected V$_2$O$_5$ cluster modified N-TiO$_2$, and V$_2$O$_5$ samples. The observed characteristic Raman bands at 144, 196, 395, 515, and 638 cm$^{-1}$ for samples containing N-TiO$_2$, assigned to the $E_g$, $B_{1g}$, $A_{1g}$, $B_{2g}$, and $E_g$ vibrational modes of anatase phase TiO$_2$ [46]. The typical Raman bands of rutile phase TiO$_2$ appear at 143, 235, 447, and 612 cm$^{-1}$, which can be ascribed to the $B_{1g}$, two-phonon scattering, $E_g$, and $A_{1g}$ modes of rutile phase, respectively [47]. Raman bands of rutile phase at 143 cm$^{-1}$ are overlapped by 144 cm$^{-1}$ band of anatase phase. The inset in Figure 2(a) shows the enlarged Raman bands at 447 cm$^{-1}$ of rutile phase for samples containing N-TiO$_2$. As the content of rutile phase is low, other Raman bands of rutile phase cannot be observed directly in Figure 2(a). Raman mode of V$_2$O$_5$ is also shown in Figure 2(a) [48]. No Raman bands relevant to V$_2$O$_5$ are observed for the composite samples, which imply the absence of a separate crystalline V$_2$O$_5$ phase on the N-TiO$_2$/V$_2$O$_5$ samples, consistent with XRD results. The enlarged view of Raman bands in the range of 110–180 cm$^{-1}$ in Figure 2(b) shows that the bands at 144 cm$^{-1}$ shift to lower wave numbers as the loading content of V$_2$O$_5$ increases, suggesting the strong interaction between N-TiO$_2$ and V$_2$O$_5$ clusters.

3.3. TEM-EDS Analysis. TEM observation (Figures 3(a) and 3(b)) reveals that the N-TiO$_2$ and N-TiO$_2$/V$_2$O$_5$-0.5% sample consists of agglomerates of primary particles of 20–30 nm in diameter. For V$_2$O$_5$ modified sample, some V$_2$O$_5$ clusters with size of ca. 1–3 nm are observed and dispersed on the surface of N-TiO$_2$ (Figure 3(b) and see Figure S1 in supplementary material available on line at doi: 10.1155/2012/569716). The direct contact between V$_2$O$_5$ cluster and N-TiO$_2$ favors the formation of heterojunction between the two components. Figure 3(c) illustrates the energy-dispersive X-ray spectroscopy (EDS) spectra of N-TiO$_2$/V$_2$O$_5$-0.5% sample. The amount of vanadium content obtained from EDS (Table inset in Figure 3(c)) is in agreement with the modification content. To further reveal the dispersity of V$_2$O$_5$ clusters, elemental mapping images of O, Ti, and V are demonstrated in Figures 3(d)–3(f). It can be seen that V$_2$O$_5$ clusters are uniformly deposited on the surface of N-TiO$_2$ nanoparticles, which is also favorable for the interaction between V$_2$O$_5$ clusters and N-TiO$_2$.

3.4. XPS Analysis. XPS is used to determine the chemical composition and surface properties of catalysts. Figure 4(a) shows the binding energy ($E_b$) for the N1s region of N-TiO$_2$ and N-TiO$_2$/V$_2$O$_5$-0.5% samples. For both samples, $E_b$ of N1s at around 400 eV can be observed. This $E_b$ is a typical feature of substitutional lattice nitrogen (N$^{3-}$) for oxygen, forming N-Ti-O structure [43]. The formation of N-Ti-O bond is the natural result of partial oxidation of TiN by oxygen. The content of nitrogen doping is determined to be 0.87 at % and have little change after modification with V$_2$O$_5$ clusters according to the XPS result.

Figure 4(b) shows the XPS spectra for O1s region. It can be seen that the O1s region can be fitted into three peaks for both samples, which can be attributed to Ti-O (529.9 eV), -OH hydroxyl groups (531.3 eV), and chemisorbed H$_2$O (532.7 eV), respectively [44]. Further observation in Figure 4(b) indicates that the molar ratio of oxygen in hydroxyl groups to all kinds of oxygen contributions increases after V$_2$O$_5$ cluster modification.

Figure 4(c) shows the $E_b$ for Ti 2p$_{3/2}$ for both samples. It can be seen that Ti2p peak at 458.85 eV of N-TiO$_2$/V$_2$O$_5$-0.5% sample shifted positively by 0.25 eV in comparison with that of the Ti2p peak in N-TiO$_2$ sample (458.60 eV). The shifting of $E_b$ can be ascribed to the interaction between host N-TiO$_2$ and guest V$_2$O$_5$ clusters, as also confirmed by Raman spectra [20].

Figure 4(d) shows the $E_b$ for V2p$_{3/2}$ for both samples. The V 2p$_{3/2}$ peak of V$_2$O$_5$ cluster samples can be fitted into two peaks, located at 517.3 and 516.2 eV. These two $E_b$ can be assigned to $V^{5+}$ and $V^{4+}$, respectively [49]. The variation of vanadium oxidation state is frequently observed in catalysts. In XPS measurement, N-TiO$_2$ can be exited by the high energy of X-rays ($h\nu = 1486.6$ eV) to produced electrons in conduction band (CB). The $V^{5+}$ then accepts the CB electrons to produce $V^{4+}$. These results also confirm that the electrons transfer from the CB of N-TiO$_2$ to V$_2$O$_5$ clusters on the surface and the partial reduction of $V^{5+}$ to $V^{4+}$ [37].

3.5. UV-Vis DRS. Figure 5(a) shows UV-vis DRS of N-doped TiO$_2$, N-TiO$_2$/V$_2$O$_5$, and V$_2$O$_5$ samples and P25. Compared with undoped TiO$_2$ P25, optical absorption of N-doped TiO$_2$ shifts into visible light region (400–550 nm) as the localized N doping level was formed in the band gap. When the amount of vanadium loaded was less than 0.20 wt.%, there was no obvious change in visible light absorption compared with N-TiO$_2$. The optical absorption in visible region was significantly increased when the content of vanadium loaded was higher than 0.50 wt.%. Pure V$_2$O$_5$ exhibits broad visible light absorption. The enhanced absorption of V$_2$O$_5$ cluster-modified N-TiO$_2$ nanocomposite can be ascribed to d-d transition of vanadium species.

Bandgap ($E_g$) energies can be estimated from UV-vis DRS spectra. Semiconductors are classified to be indirect or
The relation between absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) can be written as $\alpha h\nu = B_d (h\nu - E_g)^n$ for allowed transitions ($n = 2$ for indirect transition, $n = 1/2$ direct transition), where $B_d$ is the absorption constants. Plot of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2}$ versus $h\nu$ from the spectra data of N-TiO$_2$ and V$_2$O$_5$ in Figure 5(a) presented in Figure 5(b) [44, 45]. The $E_g$ estimated from the intercept of the tangents to the plots is 2.75 and 2.24 eV for N-TiO$_2$ and V$_2$O$_5$, respectively. The estimated $E_g$ for V$_2$O$_5$ is consistent with previous report [50]. It is generally recognized that nitrogen doping could reduce the bandgap of TiO$_2$ by uplifting the position of valence band (VB) while keeping the position of CB unchanged [15–18].

3.6. PL Spectra. Photoluminescence (PL) emission spectra have been widely used to investigate the efficiency of charge carrier trapping, migration, and transfer in order to understand the fate of electron/hole pairs in semiconductors since PL emission results from the recombination of photogenerated charge carriers. Figure 6 shows the room-temperature PL spectra of selected V$_2$O$_5$ cluster-modified N-TiO$_2$ samples under the excitation of 300 nm light and 425 nm light. As the PL emission reflects the recombination rate of excited electrons and holes, a lower PL intensity indicates decreased charge recombination rate and enhanced charge separation rate [17–20]. It can be seen from Figure 6 that the PL intensity of V$_2$O$_5$ cluster modified N-TiO$_2$ is lower than that of N-TiO$_2$. As the loading content of V$_2$O$_5$ increases, the PL intensity decreases correspondingly. This result indicates that V$_2$O$_5$ loaded on N-TiO$_2$ surface (Inset in Figure 2(a)) can effectively enhance the separation of electron/hole pairs. This also implies that N-TiO$_2$/V$_2$O$_5$ has a lower recombination rate of electron/hole pairs under both UV and visible light irradiation. This is ascribed to the fact that the electrons are excited from the VB to the CB of N-TiO$_2$ and then migrate to V$_2$O$_5$ clusters, which prevents the direct recombination of electrons and holes, as also confirmed by XPS result on V2p (Figure 4(d)).

3.7. Photocatalytic Activity and Proposed Mechanism. To elucidate the effects of V$_2$O$_5$ cluster modification on the photoactivity of N-doped TiO$_2$, visible light photocatalytic degradation of gaseous toluene at indoor level was performed. Figure 7 shows the visible light photocatalytic degradation curves (Figure 7(a)) and apparent reaction rate constant $k$ (Figure 7(b)) of SiO$_2$/V$_2$O$_5$, N-TiO$_2$, and N-TiO$_2$/V$_2$O$_5$ samples with different loading content of V$_2$O$_5$. SiO$_2$/V$_2$O$_5$ exhibits negligible activity, which implies that V$_2$O$_5$ alone is not active under visible light probably due to the rapid recombination between CB electrons and VB holes. N-doped TiO$_2$ shows decent visible light activity toward toluene degradation with removal ratio $\eta$ of 27.5% and $k$ of 0.009 min$^{-1}$. With the loading of V$_2$O$_5$ clusters in range of 0.01~1.0 wt.%, N-TiO$_2$/V$_2$O$_5$ samples exhibit significantly enhanced visible light photocatalytic activity than that of unmodified N-TiO$_2$. After loading only 0.01 wt.% of V$_2$O$_5$ on N-TiO$_2$, the visible light activity of N-TiO$_2$/V$_2$O$_5$-0.01% is markedly enhanced with a $\eta$ of 39.7% and $k$ of 0.0165 min$^{-1}$. With further increasing V$_2$O$_5$ loading from 0.01 wt.% to 0.5 wt.%, the visible light activity on N-TiO$_2$/V$_2$O$_5$ is further increased and achieves a maximum $\eta$ of 52.4% and $k$ of 0.027 min$^{-1}$. When the V$_2$O$_5$ loading content is higher than 0.5 wt.%, a further increase in V$_2$O$_5$ loading leads to an obvious reduction of the photocatalytic activity. This is probably due to the following reasons: (i) deposition of excessive V$_2$O$_5$ clusters resulted in the decrease (or shield) of the V$_2$O$_5$ surface active sites; (ii) disappearance of surface effect due to the increase of particle size [34, 35].

From what has been observed and discussed above, several conclusions can be drawn: (1) V$_2$O$_5$ is inactive for photocatalytic degradation of toluene under visible light irradiation although the band gap of V$_2$O$_5$ is suitable for visible light excitation. (2) After V$_2$O$_5$ cluster modification, the visible light activities of N-TiO$_2$/V$_2$O$_5$ samples are highly
Figure 3: TEM image of N-doped TiO$_2$ sample (a), TEM image (b), EDS (c) and elemental mapping image (d, e, f) of of N-TiO$_2$/V$_2$O$_5$-0.5% sample.

enhanced. (3) The content of V$_2$O$_5$ cluster significantly influences visible light activity of N-TiO$_2$. Obviously, the enhanced separation of electrons and holes pairs on N-TiO$_2$/V$_2$O$_5$ nanocomposite due to the CB electron migration from N-TiO$_2$ to V$_2$O$_5$ cluster is directly responsible for the highly enhanced visible light photocatalytic activity.

Here comes a fundamental issue. What is the driven force for CB electron of N-TiO$_2$ to migrate to V$_2$O$_5$ clusters? The
Figure 4: XPS spectra for N-doped TiO$_2$ and N-TiO$_2$/V$_2$O$_5$-0.5% samples of N1s (a), O1s (b), Ti2p, (c) and V2p (d).

Figure 5: UV-vis DRS of N-doped TiO$_2$, N-TiO$_2$/V$_2$O$_5$, V$_2$O$_5$ samples and P25 (a). Plot of $(\alpha h \nu)^2$ versus photon energy of V$_2$O$_5$ (direct semiconductor) (b), inset in (b) shows the plot of $(\alpha h \nu)^{1/2}$ versus photon energy of N-TiO$_2$ (indirect semiconductor).
Figure 6: PL spectra of N-TiO₂ and selected V₂O₅ cluster modified N-TiO₂ samples under the excitation of 300 nm light (a) and 425 nm light (b).

Figure 7: Visible light photocatalytic degradation curves (a) and comparison of the apparent rate constant (k) of as-prepared samples (b), (1) SiO₂/V₂O₅ sample, (2) N-TiO₂, (3)–(7) V₂O₅ cluster modified N-TiO₂ samples.

The schematic enhanced charge transfer and separation in the V₂O₅ cluster modified N-doped TiO₂ system are illustrated in Figure 8. Under visible light irradiation, electrons can be excited to the CB of N-TiO₂, leaving holes in the VB (1). These holes will react with OH⁻ on the catalyst surface to form •OH radicals (2). Because the potential of V₂O₅ (E⁰_CB = −0.48 eV) is lower than the CB level of N-TiO₂ (E⁰_CB = −0.19 V), the photogenerated CB electrons in N-TiO₂ can transfer rapidly to V₂O₅ clusters and then effectively reduce

band edge positions of CB and VB of semiconductor can be determined with the following approach. The CB edge (E⁰_CB) of a semiconductor at the point of zero charge (pH_ZPC) can be predicted by the equation E⁰_CB = X − E_C − 1/2E_g [35, 50], where X is the absolute electronegativity of the semiconductor (for V₂O₅, X is 6.10 eV [51]; for P25 TiO₂, X is 5.81 eV [51]; X is unknown for N-doped TiO₂). E_C is the energy of free electrons on the hydrogen scale (≈4.5 eV). E_g is the band gap energy of the semiconductor. The calculated positions of CB and VB of V₂O₅ and P25 are listed in Table 1. It is well known that nonmetal doping does not change the CB position of TiO₂. The VB position of N-doped TiO₂ can be determined based on the calculated CB position of undoped TiO₂ P25 and E_g of N-doped TiO₂, as also shown in Table 1.
Table 1: Absolute electronegativity, calculated conduction band (CB) edge, calculated valence band (VB) position, and bandgap energy for P25, V2O5, and N-doped TiO2 at the point of zero charge.

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Absolute electronegativity (X) (eV)</th>
<th>Calculated CB position (eV)</th>
<th>Calculated VB position (eV)</th>
<th>Band gap energy $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>5.81</td>
<td>−0.19</td>
<td>2.81</td>
<td>3.0</td>
</tr>
<tr>
<td>V2O5</td>
<td>6.10</td>
<td>0.48</td>
<td>2.72</td>
<td>2.24</td>
</tr>
<tr>
<td>N-doped TiO2</td>
<td>—</td>
<td>−0.19</td>
<td>2.56</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Figure 8: Schematic illustration for the enhanced charge transfer and separation in the V2O5 cluster modified N-doped TiO2 system under visible light irradiation.

The effect of V2O5 cluster modification on the charge transfer and separation of other semiconductor is, to some extent, similar to that of the role of noble metals in photocatalysis [45, 52–54]. The present work not only displays a feasible route for the utilization of low cost V2O5 clusters as a substitute for noble metals in enhancing the photocatalysis but also demonstrates a facile method for preparation of highly active composite photocatalysts for environmental application.

4. Conclusion

In order to enhance the visible light photocatalytic activity of N-doped TiO2 for practical environmental application, a facile impregnation-calcination method is developed for the preparation of highly active V2O5 cluster modified N-doped TiO2 nanocomposites photocatalyst for degradation of toluene in air. The V2O5 clusters can act as electron mediator to effectively inhibit the recombination of photogenerated electron/hole pairs. The optimal V2O5 loading content is determined to be 0.5 wt.%, and the corresponding toluene removal ratio is 52.4%, which largely exceeds that of unmodified N-doped TiO2. The CB potential of V2O5 (0.48 eV) is lower than the CB level of N-doped TiO2 (−0.19 V), which is the driven force for the electron transfer from CB of N-doped TiO2 to V2O5 clusters, thus greatly promoting the visible light activity of N-doped TiO2. This work not only provides a feasible route for utilizing low-cost V2O5 clusters as a substitute for noble metals in enhancing the visible light photocatalysis but also demonstrates a facile method for preparation of highly active composites photocatalyst for large scale application.

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