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One type of nonlinear materials, Na$_3$VO$_2$B$_6$O$_{11}$ (NVB), demonstrates 90 times higher photocatalytic efficiency than that of the commercial P25 in dechlorination of 2, 4-DCP under UV-vis light irradiation.
Efficient Photocatalytic Dechlorination of Chlorophenols over a Nonlinear Optical Material Na$_3$VO$_2$B$_6$O$_{11}$ under UV-visible Light Irradiation


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One type of nonlinear optical crystal Na$_3$VO$_2$B$_6$O$_{11}$ (NVB) with noncentrosymmetry was synthesized and shows extraordinary UV-visible light driven photocatalytic activity in dechlorination of 2,4-DCP under UV-vis ($\lambda > 320$ nm) light irradiation. The obtained dechlorination efficiency is 90 times higher than that of the commercial P25 TiO$_2$ catalyst under the same conditions. The noncentrosymmetric structure of NVB gives rise to an intrinsic large polarization effect as evidenced by Kelvin probe force microscopy, and the polarization promotes separation of photogenerated electron-hole pairs, leading to efficient cleavage of chlorophenols into phenol series fragments and dissociative Cl$^-$ anions. A possible reaction pathway for 2,4-DCP dechlorination by NVB upon UV-vis light irradiation is proposed.

Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination which could react with hydroxyl radicals to produce 1,4-benzoquinone and catechol. This work further advances the understanding of nonlinear optical materials, which opens up a new route to the design and synthesis of highly efficient photocatalysts by using nonlinear optical materials.

1. Introduction

Semiconductor materials, as a class of promising photocatalysts for organic pollutants treatment, have attracted increasing research interests in the past decades. In principle, the overall efficiency of a photocatalytic reaction is determined by all three steps: photo-excitation, charge separation and surface reactions; while in most cases, the overall efficiency is critically limited by the charge separation since about 90% of photogenerated charge carriers recombine together within very short time (\textasciitilde ps) after initial photo-excitation. To improve photocatalytic activity of a photocatalyst, many approaches have been adopted, including plasmonic photocatalysts by loading metals (Ag, Au, Cu) in semiconductor catalyst and multiple functional heterogeneous photocatalysts such as a \textit{z}-scheme to mimic the natural photosynthesis, which can provide trapping sites for the photogenerated charges and promote the charge separation, thus enhancing the quantum efficiency. In addition, some novel catalysts have also been explored, such as, carbon nitrides (g-C$_3$N$_4$), Ag$_2$PO$_4$, graphene-based, organic molecules, and so on. Despite the significant interest and considerable efforts been paid to date, the current research on photocatalysts is still far from satisfactory in terms of efficiency, stabilities and controlling carrier generation, separation and transportation.

Polar materials are featured by lacking of inversion center in crystal structure. Macroscopic polarization is generated when dipolar units are integrated (not compensated) in some direction. Materials with macroscopic polarization exhibit a variety of special properties, such as piezo-, pyroelectricity and second-order nonlinear optical activity. A spontaneous polarization with directions pointing from the bulk to the surface usually produces a positive charge on the surface (C$^+$ domain), and the polarization pointing away from the surface to the bulk will generate a negative charge (C$^-$ domain). The spontaneous polarization can be screened by free electrons and holes, and/or by ions or molecules adsorbed on the surface from forming a Stern layer. This accumulation of free electrons on the C$^+$ surface and holes on the C$^-$ surface leads to downward and upward band bending, respectively. The internal dipolar field creates charged surfaces that cause photogenerated charge carriers to move in opposite direction which separates electron-hole pairs, leading to oxidation and reduction products formation at different locations. Nonlinear optical crystals are known as non-concentric materials, however, their efficient charge separation and enhanced light absorption as a photocatalyst have rarely been reported.

B-O units, such as BO$_3$, BO$_4$, B$_2$O$_4$, and so on, have long been investigated as nonlinear optical (NLO) materials due to their rich structural chemistry. On the other hand, Vanadium appears to be one of the best alternatives to improve visible light-driven photocactivity since it plays important role in extending optical absorption region and the high separation efficiency of electron-hole pairs. Herein, we demonstrate that a simple vandate-boron semiconductor, Na$_3$VO$_2$B$_6$O$_{11}$ (NVB), a kind of NLO materials, can function as an effective photocatalyst for dechlorination...
under UV-visible light irradiation. Chlorophenols are typical hazardous organic pollutants utilized for timber and textile protection worldwide. They are listed as priority contaminants by China and the European Union. In this work, 2, 4-dichlorophenol (2, 4-DCP) was selected as a model pollutant to test the photoactivity of NVB. The dechlorination efficiency is about 90 times higher than that of the commercial P25 TiO$_2$ catalyst. To the best of our knowledge, this is the first time to report the novel NVB single crystal material as a photocatalyst for dechlorination reactions.

2. Results and discussion

2.1. Structure and Optical Absorption

Na$_3$VO$_2$B$_6$O$_{11}$ (NVB) crystallizes in the space group $P2_12_12_1$ with cell dimensions $a = 7.7359(9)$ Å, $b = 10.1884(12)$ Å, and $c = 12.5697(15)$ Å, which is made of repeated B$_6$O$_{11}$,VO$_4$ units and Na ions as shown in Fig. 1.

Fig. 1 Crystal structures of (a) B$_6$O$_{11}$ units and (b) VO$_4$ units. (c) Drawing of the structure of NVB viewed down the a axis.

The basic building units of the NVB are trigonal planar BO$_3$ and tetrahedral BO$_4$, which form an isolated B$_6$O$_{11}$ unit. The B$_6$O$_{11}$ unit is connected with VO$_4$ tetrahedron to form infinite sheets, whereas Na$^+$ cations are distributed in the extended framework. The crystal structure of NVB is confirmed by XRD analysis (Fig. 2a). The UV-vis diffuse reflectance spectrum (Fig. 2b) indicates that the NVB particles can absorb photons in wavelength up to 419 nm, and the bandgap of NVB estimated from the intercept of the tangent to the inset plot of Fig. 2b is 2.95 eV.

2.2. Photocatalytic Performance of NVB nanoparticles

Experimental runs involving in the absence of the catalyst, with P25 and NVB under different wavelength of UV-visible irradiation were performed separately to evaluate each factor influencing the enhancement of photocatalytic degradation by NVB in Fig 3. One can observe in Fig. 3a that no obvious degradation took place in the absence of catalyst under UV-visible light. This is understandable considering that 2, 4-DCP degradation by oxygen flow is negligible. To explore the photocatalytic activity of the NVB samples for real applications, the photo-dechlorination of 2, 4-DCP was tested under natural sunshine. As shown in Fig. 3a, almost 43.85% of 2, 4-DCP can be dechlorinated by sunlight (Intensity = 0.05-0.08 w/cm$^2$ at noon) within 60 min, and complete dechlorination can be achieved in 3 min under UV-visible light irradiation (Intensity = 0.15 w/cm$^2$) (Fig. 3a). During the dechlorination, a yellow color accumulated in the medium. This color is due to chloro-2-hydroxymuconic semialdehyde (CHMS), the via-meta cleavage product of 4-chlorocatechol as also claimed by Farrell$^{23}$ and Sahinkaya$^{24}$. An interesting observation is that CHMS concentration increases steadily with time course of degrading 2,4-DCP, as is also confirmed by LC-MS data and released chloride ion concentration. About 82.7% of the total chloride content is converted into Cl$^-$ anions after 30 min of irradiation (Fig. 3b). The particle size of the crystals is in the range of 80-150 nm as
measured by scanning electron microscope (SEM) (Fig. S1). Furthermore, the Brunauer-Emmett-Teller adsorption analysis shows that the specific surface area of the NVB is 1.18 m$^2$g$^{-1}$ (in the powder state). Such a small area value clearly indicates a high photo-reactivity of the present NVB samples in nature. In dark within 20 min, the adsorption reached equilibrium, and about 6% of 2, 4-DCP was adsorbed ontoNVB. Under the same conditions, about 15% of 2, 4-DCP was adsorbed onto P25 TiO$_2$. Considering that P25 TiO$_2$ has much bigger surface area (58 m$^2$g$^{-1}$), the higher adsorptive capacity of NVB would be contributed by its surface charge properties other than the surface area.

**Fig. 3** (a) Photocatalytic dechlorination of 2, 4-DCP (50mg L$^{-1}$, 100 mL) in aqueous dispersions (containing the NVB catalyst, 50 mg). (b) Formation of Cl as a function of irradiation time during the photodechlorination process under UV-vis light, source light wavelength $\lambda > 320$ nm.

The pH value is a complex parameter, since it is related to the state of the material surface as well as their redox potentials, which affects the adsorption and reaction of DCP on the material. The effect of pH value on the photoreaction was investigated over NVB. The pH of point of zero charge ($\text{pH}_{\text{pzc}}$) value was measured as 4.94 for NVB. When the pH is near the $\text{pH}_{\text{pzc}}$ of the semiconductor, most of the surface hydroxyl groups are in a neutral state; nearly no surface charge exists.$^{25}$ Considering that the pKa of 2, 4-DCP is 7.85, it is in its undissociated form at the tested neutral pH values, and the surface of NVB is more favorable to the adsorption of 2, 4-DCP. As shown in Fig. S2, the sample has higher degradation activity in acidic pH than in alkaline pH solution. At pH 3 (adjusted with HCl), the NVB surface is positively charged which is more beneficial for adsorption of unionized 2, 4-DCP molecules (Fig. S2a). A similar enhancement of adsorption in acidic environment compared to neutral media was also observed in case of phenol compounds.$^{25}$

At pH 11 (adjusted with NaOH), which is above the $\text{pH}_{\text{pzc}}$ of NVB, the photocatalyst surface is negatively charged. Under such conditions water molecules can block the photocatalyst surface thus giving rise to low adsorption ability and dechlorination activity of 2,4-DCP (Fig. S2b). The NVB sample retains photocatalytic activity after four successive cycles of complete degradation 2, 4-DCP under UV-visible irradiation (Fig. S3). No peak change in the XRD patterns of NVB with the JCPDS Card (No. 52-0421) observed before and after the photodechlorination reaction (Fig. S4), indicating the stability of the NVB catalyst in the present photocatalytic reaction process.

**2.3. Calculations and Electron Transfer Mechanism**

A bond valence approach has been adopted to evaluate the local dipole moments in NVB.$^{26}$ The calculations for trigonal [BO$_3$] and tetrahedral [BO$_4$] give values of 0.277-1.482 D and 0.337-1.428 D,$^{27}$ respectively. It is noteworthy that [VO$_4$] polyhedra have a large negative charge which maintains a large dipole moment 5.548 D. A complete calculation of dipole moments for the constituted polyhedra is listed in Table S1. These B-O units possess large electron cloud overlapping, and prefer to attract holes and repel electrons. Therefore, NVB can be easily polarized, thus facilitating separation of the photogenerated electron-hole pairs. This in turn enhances the photocatalytic activity.

**Fig. 4** The total and projected DOS plots calculated for (a) NVB and (b) the different O atoms in NVB; (c) a schematic illustration showing the internal polarized field enhances the charge separation and the photocatalytic mechanism of NVB, one of the O atoms is labeled by a purple circle.

To get a deeper understanding of the high photocactivity of NVB, we have performed density functional theory (DFT) calculations. Fig. 4 presents the electronic band structure of NVB in terms of density of states (DOS). The VB has strong O 2p contributions, while the CB has V 3d contributions (Fig. 4a). There are three types of oxygen atoms in NVB: the O1 atoms belong to the bridge between VO$_4$ unit and B$_6$O$_{11}$ unit, while the O2 atoms form the VO$_4$ unit, and the O3 atoms belong to B$_6$O$_{11}$ unit. The VB top has O 2p contributions, and O1 and O3 atoms...
have similar contribution values (Fig. 4b). Therefore, photoexcitation from the VB top to the CB generates holes at the O 2p states in all O atoms, especially in O2. On the other hand, the CB bottom has V 3d primary contributions and O3 2p secondary contributions from B2O11 unit, thus the photogenerated electrons can be gathered in B2O11 unit and cease at the p-states of the V 5+ sites (Fig. 4c). As described in Fig. 4c, with a polar electric field in the crystal structure of NVB, photogenerated charges at B2O11 unit can migrate through the O1 atoms (circled in purple) to adjacent VO2 unit, and vice versa. When electrons and holes are separated at B2O11 units, electrons can move to adjacent VO2 units by means of the bridging O1 whose contribution to the CB is present, while holes can be trapped in O3 because of their vertical orientation with the direction of the internal polar field or maintained at O3. In a similar manner, the photogenerated holes at B2O11 units can move through the bridging O1 to the VO4 units and eventually be immobilized on the O2 atoms of VO4 units, while the photogenerated electrons might end up in V 3d at the CB bottom. In general, electrons and holes are gathered at B2O11 units and VO4 units, respectively, separated along the b axis. Furthermore, for the crystallographic non-centrosymmetry structure of NVB, with the ordered arrangement of the units in crystal structures, the direction of the dipole moment is along the [010] direction, an internal polar field is verified to be existed and its orientation is shown in Fig. 5a. From the crystal structure of NVB, the direction of the polar field is in accordance with that of charge transfer in VO4, the internal polar field promotes their separation along the field direction in the bc plane (Fig. 5a), which is expected to function as a driving force for the photoexcited holes and electrons to move to their respective reduction and oxidation sites. Under the action of the internal polar field, the photoinduced electron and hole would thereby transfer along opposite directions, and facilitate the charge separation, thus resulting in high photocatalytic activity.

To evaluate the built-in electric field induced photocatalytic activity of NVB, the dechlorination of 2, 4-DCP was further carried out in aqueous dispersions under different wavelengths of light irradiation after the adsorption of 2, 4-DCP onto the NVB (Fig. 3). When irradiated at wavelengths $\lambda > 254$ nm, the rate of 2, 4-DCP dechlorination on NVB is nearly 90 times faster than that on P25 TiO2. Under irradiation of photons with wavelengths $\lambda > 320$ nm from a Xenon lamp, in the first 10 minutes no significant dechlorination occurs on P25 TiO2, which hardly absorbs photons in these wavelengths range; while NVB exhibits almost the same photocatalytic activity as that at $\lambda > 254$ nm. These results indicate that the enhanced dechlorination of 2, 4-DCP is due to the internal dipolar field of NVB nano-particles which facilitate the excited electron-hole separation. Upon irradiation with photoenergy above the bandgap, electron-hole pairs are formed, which causes a restructuring of the conduction and valance band bending. The resultant electrons and holes then migrate to their most energetically favored corresponding positions in the system, where they can accumulate, decay to the ground state, or take part in a chemical reaction (Fig. 5b). Therefore, internal electric field is critical to the enhanced activity of NVB.

2.4. Internal Electric Field Effect

The internal electric field effect was also studied with a nanoscale resolution by atomic force microscopy (AFM) in conjunction with Kelvin probe force microscopy (KPFM). In particular, KPFM allows quantitative mapping of the electronic properties of nanostructures, i.e., determination of the surface potential of nano-objects.25 Fig. 6a and 6c shows an AFM topography image of NVB nanoparticles, and Fig. 6b and 6d show surface potential images of NVB particles in the dark and under irradiation. The surface potential image has been separated into darker and brighter regions. The contrast is due to the differences in surface potential for the domains of respective donor rich and acceptor rich of the material.

In order to quantitatively determine surface potential differences, the different potential value for Fig. 6b and 6d of the NVB was analyze in Fig. 6e. Upon irradiation with a Xenon lamp light, the surface potential of the NVB becomes more positive and the average value increases by about 14.09 mV. This overall increase in surface potential is due to the filling of electrons in the conduction band during the light excitation process. And the cross section profiles with the same area circled in a white square frame in Figs. 6b and 6d is shown in Fig. 6f, from which the surface potential difference between different faces due to the charge separation is deduced to be ~30 mV. The difference is attributed to the light response for different domains of the material, and after light irradiation the charge separation is driven by the internal electric fields. This result provides direct evidence that the presence of the internal field provides a driving force for the separation of photogenerated electrons and holes.29 These properties strongly depend on that the crystal form for NVB is a non-centric crystal. Thus, the KPFM results demonstrate that the excellent electron-hole separation of NVB can be significantly improved through the enhancement in charge injection and extraction.

Fig. 5 (a) Ball-and-stick diagram of NVB structure (orange arrows indicate the direction of the dipole moments for NVB units). (b) Schematic illustration of a polar structured NVB photocatalyst.
2.5. Enhancement of PC and PEC activity

In order to further confirm that the photon-to-electron conversion efficiency of the NVB particles is affected by the non-centric structure, the photoelectron chemical (PEC) measurements of the NVB photoanodes have been conducted. The transient photocurrent responses of P25 TiO$_2$ and NVB electrodes were recorded via several on-off cycles of irradiation.

It can be seen from Fig. 7a that a prompt generation of photocurrents occurs with good reproducibility when sample NVB is irradiated by UV-visible light. While the light is off, the photocurrent for sample NVB decreases instantaneously. This indicates that under light irradiation, most of the photoexcited electrons at the NVB surface due to internal electric field are transported towards the desired reactions. When the bias potential is 0 V, the anodic photo-current of NVB is about 3.2 times of that of P25 TiO$_2$ in the simulated UV-vis light irradiation. As the bias potential increases, the photocurrents are enhanced by 1.3, 1.7 and 1.9 times at 0.033, 0.067 and 0.134 V compared to 0 V, respectively, for NVB electrode as shown in Fig. 7b. This suggests any photocurrent enhancement observed for NVB is more significant at lower potentials which contributes to its catalytic ability towards organic pollutants degradation.

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Photoelectrochemical impedance spectroscopy (PEIS) analysis was employed to investigate the charge transfer at the semiconductor interface. A Nyquist plot for NVB and P25 TiO$_2$ measured at 0.067 V vs. Ag/AgCl under different wavelength irradiations are shown in Fig. 8. With wavelength $\lambda>320$ nm light irradiation, the impedance arcs of the two electrodes are large, indicating that the electrons going through the electrode and electrolyte interface are few. However, arcs obtained from NVB have much smaller radius than from P25 TiO$_2$, which indicates that NVB has a more effective separation of photogenerated electron-hole pairs resulting in faster interfacial charge transfer. Under UV-vis light irradiation (1300 nm), the arc radius on the EIS Nyquist plot of NVB is also smaller than that of P25 TiO$_2$. It can be deduced that UV-vis light irradiation facilitates photogenerated holes transfer from the valence band of NVB to the solution, reducing the recombination of photogenerated electron-hole pairs and improving the photocurrent density. The efficiency of NVB is higher compared to that of P25 TiO$_2$ electrodes. This could be attributed to the improved electrode-electrolyte interfacial area due to the presence of polarity in NVB arisen from its noncentric symmetry structure.
2.6. Possible Reaction Mechanism for DCP Photodechlorination

As reported by Cheng et al., the reaction pathway for 2,4-DCP dechlorination could involve adsorption, dechlorination, and cleavage of the benzene ring and several intermediates including 2-chlorophenol, 4-chlorophenol, phenol, and chlorocatechol. To elucidate the reaction pathways of DCP by NVB, LC-MS was used to identify the intermediates and end products. Degradation intermediates including 2-chlorohydroquinone, 4-chlorophenol and catechol were identified, while 1,4-benzoquinone and catechol were detected as the end products during the course of 2,4-DCP photodechlorination (see Supplementary Information Fig. S5 and Table S2 for details). Therefore, a possible reaction pathway for 2,4-DCP dechlorination by NVB upon UV-visible light irradiation is proposed (Fig. S6). As shown in Fig. S6, 2,4-DCP can react with photogenerated hydroxyl radicals to form 2-chlorohydroquinone and then to 1,4-benzoquinone. In addition, 2,4-DCP can undergo reductive dechlorination to generate 4-chlorophenol first and then reacts with hydroxyl radicals, leading to the formation of catechol and phenol. Although 2,4-DCP cannot be completely mineralized by NVB, the degradation intermediates as well as end products are less toxic than that of 2,4-DCP and can be readily biodegraded into harmless compounds by microorganisms under both aerobic and anaerobic conditions.

The enhanced photo-dechlorination of chlorinated compounds by NVB is illustrated in Scheme 1. The NVB photocatalysts can be photo-exited by UV-visible (λ > 320 nm) light irradiation to generate electron-hole pairs, while the strong built-in electric field in NVB structure inhibits the recombination of holes with electrons, leading to the enhancement of the oxidizing capability of NVB. This process would significantly accelerate the simultaneous photodechlorination rates of chlorinated compounds.

3. Experimental

3.1. Synthesis of the NVB nanoparticles

Nanoparticles of NVB were synthesized by a high temperature solid-state reaction method. Stoichiometric amounts of Na₂CO₃ (Tianjin Benchmark Chemical Reagent Co., Ltd., 99.8%), V₂O₅,
The size of the sample loop was 20 mL. The wavelength of chloride ions (Cl\(^{-}\)) was 282 nm. To determine the concentration, liquid chromatography-mass spectrometry (LC-MS, Agilent, Germany) equipped with an analytical column (4 mm × 250 mm) and a guard column (4 mm × 50 mm) was used throughout the experiment. The detector was set at 282 nm. To determine the concentration of chlorophenol, a 500 W Mercury lamp was used for the working electrode in a frequency range of 100 kHz to 0.01 Hz with an AC signal amplitude of 5 mV at open circuit potential in different aqueous electrolytes.

Fluorescence spectra of 2-hydroxyterephthalic acid were measured on a Hitachi fluorescence spectrophotometer F-7000. The OH radical trapping experiments were carried out using the following procedure: terephthalic acid (TA) (16.6 mg) was first dissolved in 200 mL of dilute NaOH solution (2×10\(^{-3}\) M), followed by addition of 100 mg of photocatalysts, and stirred for 30 min in dark. The suspension was irradiated by a 300 W xenon lamp at wavelengths in the range of 320-780 nm for 30 min. The fluorescence emission spectrum of the solution was measured every 5 min during irradiation. At a defined time interval, the concentration of solution in the system was analyzed by PL (excited at 312 nm).

### 3.3. Characterization

Phase identification was performed on a Bruker D8 ADVANCE X-ray diffractometer equipped with a diffracted-beam monochromator set for Cu Kα radiation (\(\lambda = 1.5418 \text{ Å}\)). The size of the sample loop was 20 mL. The wavelength of chloride ions (Cl\(^{-}\)) was 282 nm. To determine the concentration, liquid chromatography-mass spectrometry (LC-MS, Agilent, Germany) equipped with an analytical column (4 mm × 250 mm) and a guard column (4 mm × 50 mm) was used throughout the experiment. The detector was set at 282 nm. To determine the concentration of chlorophenol, a 500 W Mercury lamp was used for the working electrode in a frequency range of 100 kHz to 0.01 Hz with an AC signal amplitude of 5 mV at open circuit potential in different aqueous electrolytes.

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### 3.4. Computational details

The first-principles calculations were performed in the framework of functional theory with the projector augmented wave (PAW) pseudopotential method using Vienna ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) in the scheme of the Perdew-Burke-Emzerhof (PBE) was used for the exchange-correlation functional. The electronic wave functions were expanded into a basis set of plane waves with a kinetic energy cutoff of 400 eV, and a Monkhorst-Pack k-point mesh of 3×2×2 was used for geometry optimization and electronic property calculations, which was found to be sufficient to reach convergence for bulk supercell calculations. The PAW potentials with the valence states 2s and 2p for B and O, 3s and 2p for Na, 3p, 4s, and 3d for V, were employed. Both the atomic positions and cell parameters were optimized until the residual forces experienced by each ion converged to be smaller than 0.02 eV/Å, and the convergence threshold for self-consistence-field iteration was set at 10\(^{-5}\) eV. The experimental atomic positions were employed as the starting points of relaxation, and subsequent calculations were conducted using the relaxed atomic positions.

### 4. Conclusion

In summary, one type of nonlinear optical crystal Na\(_2\)VO\(_3\)B\(_3\)O\(_7\) (NVB) with noncentrosymmetry was synthesized by a high temperature solid state method. As-synthesized NVB shows...
extraordinary UV-visible light driven photocatalytic activity, giving high efficiency in dechlorination of 2,4-DCP under UV-vis (λ > 320 nm) light irradiation. The obtained dechlorination efficiency is 90 times higher than that of the commercial P25 TiO2 catalyst under the same conditions. The strong built-in electric field in NVB structure can effectively separate and transfer photo-induced charge carriers. A possible reaction pathway for 2,4-DCP dechlorination by NVB upon UV-vis light irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathway for 2,4-DCP dechlorination, and 2,4-DCP irradiation is proposed. Hydrodechlorination was found to be the major reaction pathwa...