Supplementary Information

Efficient Photocatalytic Dechlorination of Chlorophenols over a Nonlinear Optical Material $Na_3VO_2B_6O_{11}$ under UV-visible Light Irradiation

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Calculations of the B-O bond valences and dipole moments of the BO_n (n = 3, 4) polyhedra and the V-O bond valences and dipole moments of the VO_4 tetrahedra in NVB.

An internal polar electric field is constructed along the *bc* plane in the crystal structure of NVB and the alignment of BO_3, BO_4, VO_4, NaO_7 and NaO_8 polyhedron in an individual asymmetric polyhedra.

The bond-valence-sum V_i for each atom i is defined as

$$V_i = \sum_j S_{ij} = \sum_j \exp[\frac{R_0 - R_{ij}}{B}]$$

where B is a constant with value 0.37. R_0 and R_{ij} represent the reference and actual lengths of the bond i-j that the atom i makes with the surrounding atoms j, respectively, and S_{ij} is the corresponding bond valence. R represents the difference between the "centroids" of the positive (r+) and negative charges r-).

$$R = r^- - r^+$$

For a given B_i-Oj bond with the actual bond length R_{ij}, the nuclear charges of B and O are 5 and 8, respectively.

$$(5 - V_i) \times r^- = (8 + S_{ij}) \times (R_{ij} - r^-)$$
$$5 \times r^+ = 8(R_{ij} - r^+)$$

Then, in units of Debye, in which R is measured by Å and the charge by statcoulomb, the net bond dipole moment μ_{ij} of the B_i-O_j bond is then calculated using the expression.

$$\mu_{ij} = n_{ij} e R$$
$$n_{ij} = (5 - V_i) + (8 + S_{ij})$$

where n_{ij} is the number of electrons forming the B_i-O_j, and e the electron charge (i.e., 4.8×10^{-10} statcoulombs in cgs unit).

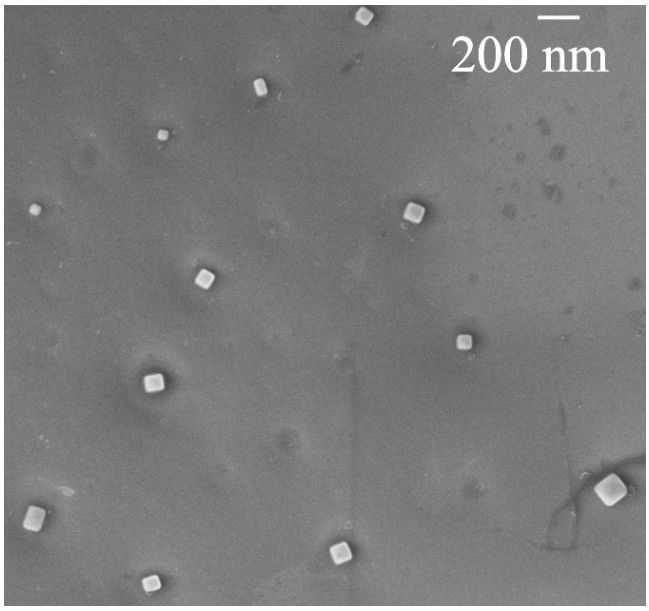

Fig. S1. SEM images of NVB samples.

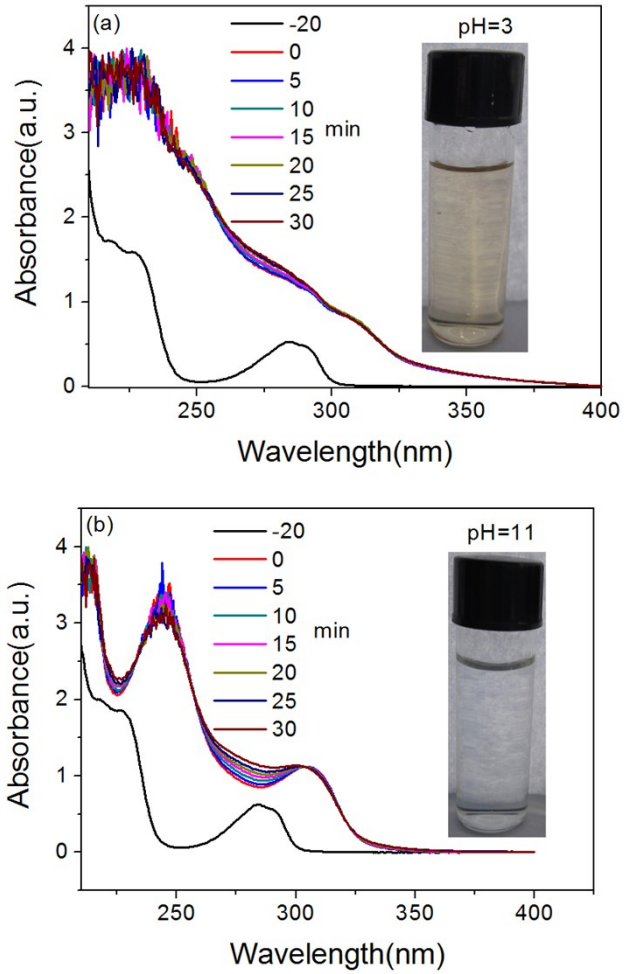

Fig. S2. The appearance and color of the 2,4-DCP solution treated by NVB powder under different pH values.

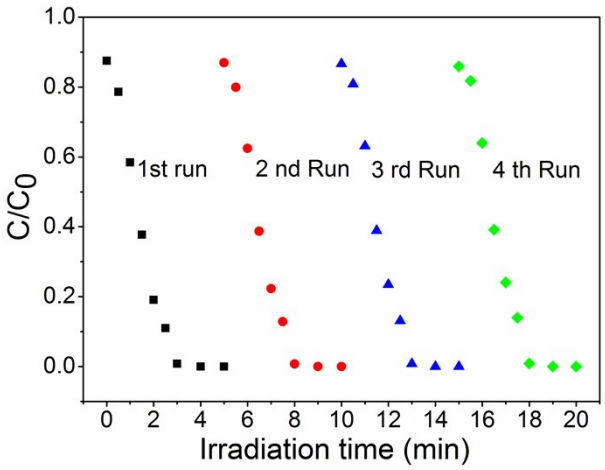

Fig. S3. Photocatalytic stability of NVB in recycling reactions under UV-vis light irradiation.

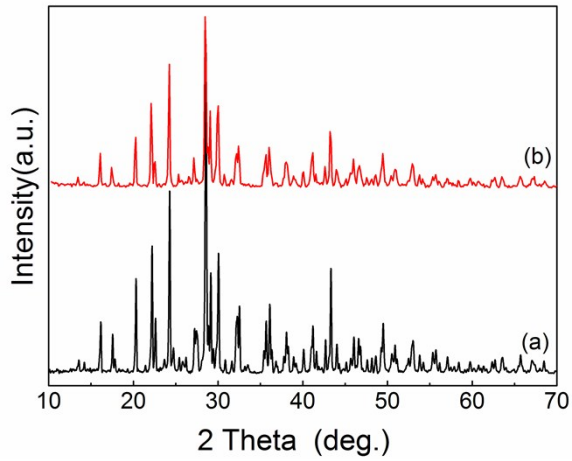

Fig. S4. XRD partern of NVB particles before (a) and after fouth cycles (b) in degradation of 2, 4-DCP under UV-vis light irradiation.

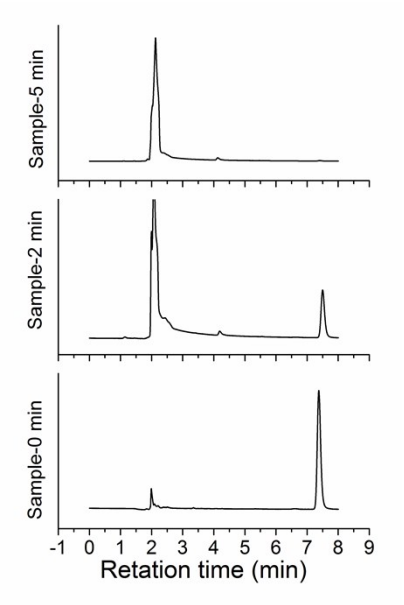

Fig. S5. HPLC chromatogram of 2,4-DCP (R_t= 7.4-7.5 min) before and after degradation 0 min (a), 2 min (b), and 5 min (f), respectively.

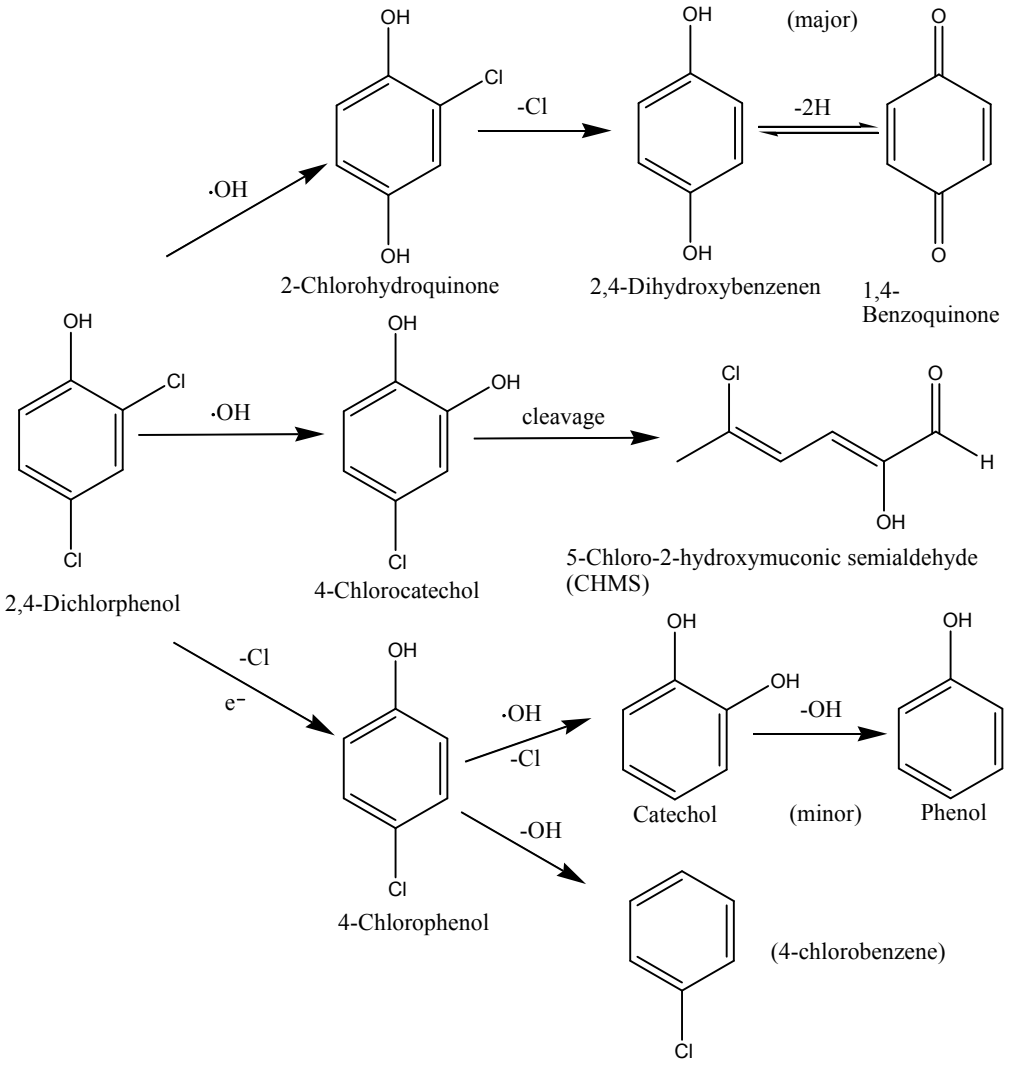

Fig. S6. The reaction pathway for 2,4-DCP photo-dechlorination at NVB upon irradiation of UV-visible-light under anoxic conditions.

Table 1. Dipole Moments of NaO_n (n = 7 or 8), BO_n(n=3 or 4), and VO_4 polyhedra in NVB crystal.

Polyhedral unit	B(1) O_4	B(2)O_3	B(3)O_3	B(4)O_3	B(5) O_4
Polyhedral dipole moment (Debye)	0.337	1.384	0.277	1.482	1.349
Polyhedral unit	B(6) O_4	VO_4	Na(2)O_8	Na(3)O_8	Na(4)O_7
Polyhedral dipole moment (Debye)	1.428	5.548	2.728	4.006	3.696

Table S2. LC-MS spectral data of main photodegraded products of 2, 4- DCP.

Retention time (min)	Mw (m/z)	Assignment
6.49	144.5	2-chlorohydroquinone
6.25	128.5	4-chlorophenol
4.66	112.21	4-chlorobenzene
2.09	107.25	1,4-Benzoquinone