Microhydrangeas with a high ratio of low valence MnO$_x$ are capable of extremely fast degradation of organics

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**EXPERIMENTAL**

**Materials**

MnSO$_4$·H$_2$O, (NH$_4$)$_2$SO$_4$, (NH$_4$)$_2$S$_2$O$_8$, H$_2$O$_2$ (30 %), $p$-benzoquinone ($p$-BQ), tert-butanol (TBA), sulphanilic acid, acetic acid and NaNO$_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-naphthylamine was purchased from Aladdin (Shanghai, China). Hydroxylamine hydrochloride (NH$_2$OH·HCl) was purchased from Sigma-Aldrich. They were all analytical grade reagents and used without further
purification. Pure water with a resistivity of 18.2 MΩ·cm at 25 °C was used in all experiments.

**Preparation of HRLV-MOMs**

HRLV-MOMs were synthesized by a stirring hydrothermal method, where some composition are referred to literature.\(^1\),\(^2\) In brief, MnSO\(_4\)·H\(_2\)O (0.18 g) and (NH\(_4\))\(_2\)SO\(_4\) (0.35 g) were dissolved in H\(_2\)O (30 mL) at room temperature to form a homogeneous solution. (NH\(_4\))\(_2\)S\(_2\)O\(_8\) (0.24 g) was dissolved in H\(_2\)O (10 mL) and dropped into the above solution under stirring. Then, the well mixed solution was transferred into a Teflon-lined autoclave (100 mL). The autoclave was maintained at 70 °C for 9 h in a silicon oil bath with a magnetic stirrer at 200 rpm. After reaction, the autoclave was cooled down to room temperature. The precipitates were collected by centrifugation (2000 rpm, 429 g, 3 min), washed with H\(_2\)O for 3 times and then dried at 40 °C in vacuum.

**Catalysis performance of HRLV-MOMs for H\(_2\)O\(_2\) to degrade MB**

The catalytic performance of HRLV-MOMs was evaluated in the catalytic degradation of MB with H\(_2\)O\(_2\). Firstly, MB (1.0 mL, 0.5 mg·mL\(^{-1}\)), HRLV-MOMs (1.0 mL, 1.0 mg·mL\(^{-1}\)) and H\(_2\)O (6.67 mL) were mixed and continuously stirred at room temperature. Then the catalytic reaction was started by addition of H\(_2\)O\(_2\) (1.33 mL, 30 %), whose concentration (\(c_0 = 44.7 \text{ mg·mL}^{-1}\)) is referred from the work with the largest reported efficiency by pure MnO\(_x\) catalyst.\(^3\) Every a given time interval, 0.5 mL of the suspension was collected, then quickly diluted to 5 mL and immediately filtered with a syringe filter (0.22 μm). The concentration of the collected filtrate was measured at 664 nm by a UV-Vis spectrophotometer. To test the recyclability of HRLV-MOMs, the
recycled HRLV-MOMs were collected and washed with H$_2$O for 3 times for the next catalysis cycle. The degradation rate was calculated by $(A_0 - A)/A_0$ based on the Lambert-Beer’s law, where $A_0$ and $A$ are the maximum absorbance of MB at 664 nm at the reaction time $t = 0$ and $t$, respectively.

**Catalysis degradation mechanism of HRLV-MOMs**

To distinguish the effect of different radicals, TBA or $p$-BQ was added as scavenger of ·OH or O$_2^-$ radicals, respectively. It is necessary to mention that the interference by the bright yellow $p$-BQ should be removed by deducting the absorbance of the mixture of $p$-BQ, HRLV-MOMs and H$_2$O$_2$ at the same concentration in the catalytic degradation experiments.

**Quantitative calculation on ·OH radicals**

\[
\begin{align*}
\text{Cumarin} + \cdot\text{OH} &\rightarrow \text{7-hydroxyl coumarin} \\
\end{align*}
\]

(S1)

·OH radicals interact with coumarin to generate 7-hydroxyl coumarin (eqn S1), whose fluorescence emission intensity is measured at 460 nm under the excitation wavelength of 332 nm. By recording fluorescence spectra of 7-hydroxyl coumarin generated from interaction of coumarin and ·OH radicals in the catalytic degradation system (Fig. S12b), the yield of ·OH radicals can be obtained indirectly according to the working curve of 7-hydroxyl coumarin (Fig. S12c) and the stoichiometric relationship between 7-hydroxyl coumarin and ·OH radicals.

Quantitative coumarin was mixed with the catalytic solution without MB to form 7-hydroxyl coumarin with ·OH radicals. 5 min later, 1.0 mL of the mixture was diluted
to 5.0 mL and filtered with a syringe filter (0.22 μm), whose fluorescence emission intensity was measured at 460 nm under the excitation wavelength of 332 nm. Fluorescence emission intensity of a series of 7-hydroxyl coumarin solutions in the concentration range of 1 to 25 mg·L⁻¹ were measured to plot a linear working curve against concentration. The final mixture was diluted 5 times and according to the working curve (Fig. S12c), the equation is given by

$$c_{\text{7-hydroxyl coumarin}} = 0.02 I_{460} \, (\mu g \cdot L^{-1})$$  \hspace{1cm} (S2)

where $c_{\text{7-hydroxyl coumarin}}$ is the mass concentration of 7-hydroxyl coumarin, $I_{460}$ is the corresponding fluorescence emission intensity at 460 nm under the excitation wavelength of 332 nm.

The stoichiometric relationship between 7-hydroxyl coumarin and ·OH radicals based on eqn (S1) is 1: 1, so the yield in the weight ratio of ·OH radicals to HRLV-MOMs can be obtained as follows,

$$\omega_{\text{OH}} = \frac{c_{\text{7-hydroxyl coumarin}} \, (mg \cdot L^{-1}) \cdot M_{\text{OH}} \, (g \cdot mol^{-1})}{M_{7\text{-hydroxyl coumarin}} \, (g \cdot mol^{-1}) \cdot c_{\text{HRLV-MOMs}} \, (mg \cdot mL^{-1})}$$

$$= \frac{0.02 I_{460} \cdot M_{\text{OH}}}{M_{7\text{-hydroxyl coumarin}} \cdot c_{\text{HRLV-MOMs}}} \, (mg \cdot g_{\text{HRLV-MOMs}}^{-1})$$  \hspace{1cm} (S3)

All the catalytic reactions were carried out with HRLV-MOMs concentration ($c_{\text{HRLV-MOMs}}$) of 0.1 mg·mL⁻¹. $M_{\text{OH}}$ and $M_{7\text{-hydroxyl coumarin}}$ is the molar mass of ·OH radicals (17.0 g·mol⁻¹) and 7-hydroxyl coumarin (162.14 g·mol⁻¹), respectively. Thus,

$$\omega_{\text{OH}} = 0.021 I_{460} \, (mg \cdot g_{\text{HRLV-MOMs}}^{-1})$$  \hspace{1cm} (S4)

The fluorescence emission intensity of 7-hydroxyl coumarin produced in the reaction of coumarin and ·OH radicals in the catalytic system was 3525 (Fig. S12b).
So, the yield of ·OH radicals in our catalytic mixture (10 mL) of HRLV-MOMs (0.1 mg·mL\(^{-1}\)) and H\(_2\)O\(_2\)\((c_0 = 44.7 \text{ mg·mL}^{-1})\) at room temperature was 74.0 mg·g\(^{-1}\)HRLV-MOMs\(^{-1}\) according to eqn (S4).

**Quantitative calculation on O\(_2^-\) radicals**

\[
\text{NH}_2\text{OH} + 2\text{O}_2^- + \text{H}^+ \rightarrow \text{NO}_2^- + \text{H}_2\text{O}_2 + \text{H}_2\text{O} \quad (S5)
\]

\[
\text{NO}_2^- + \text{H}^+ + \overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{COOH}} \rightarrow \overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{COON}} + \text{H}_2\text{O} \quad (S6)
\]

\[
\overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{COON}} + \overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{NH}_2} \rightarrow \overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{COOH}} + \overset{\text{N}}{\overset{\text{H}}{\text{C}}\text{H}_3\text{NH}_2} \quad (S7)
\]

The amount of O\(_2^-\) radicals was calculated based on a colorimetric method at the wavelength of 530 nm, which corresponds to the maximum absorbance of the finally formed azo dye complex.\(^4\) Briefly, hydroxylamine (NH\(_2\)OH) reacts with O\(_2^-\) radicals from the catalytic degradation system containing HRLV-MOMs, MB and H\(_2\)O\(_2\) to produce NO\(_2^-\) (eqn S5). Then NO\(_2^-\) reacts with sulphanilic acid to form an azo compound (eqn S6), which interacts with 1-naphthylamine to generate an azo dye complex (eqn S7) with the intense absorbance at 530 nm. NH\(_2\)OH·HCl (0.21 g) was dissolved in H\(_2\)O (10 mL), then the NH\(_2\)OH solution (0.5 mL) was mixed with the catalytic solution without MB, followed by addition of a chromogenic solution (5.0 mL), the latter was obtained by mixing sulphanilic acid solution (0.4 %w/v), 1-
naphthylamine solution (0.1 %w/v) and acetic acid (25 %w/v). The mixture was stored in dark for 20 min to form reddish purple azo dye complex. A series of NaNO₂ solutions with concentration gradient were prepared and mixed with the chromogenic solution to form the azo dye complex solutions with concentration gradient. Then their absorbance at 530 nm was measured to plot a working curve of the azo dye complex against the concentration of NO₂⁻. According to the working curve and stoichiometric relationship between the azo dye complex, NO₂⁻, and O₂⁻ radicals can be quantitatively calculated.

A series of NaNO₂ solutions with concentration gradient were prepared and mixed with the chromogenic solution to form the azo dye complex solutions with concentration gradient. Then their maximum absorbance at 530 nm was measured to plot a working curve of the azo dye complex against the concentration of NO₂⁻. According to the working curve (Fig. S12e), the equation is given by

\[ c_{\text{azo dye complex}} = 29.89 \ A_{530} \ (\mu \text{mol} \cdot \text{L}^{-1}) \]  

(S8)

where \( c_{\text{azo dye complex}} \) is molar concentration of the azo dye complex, \( A_{530} \) is the corresponding absorbance at 530 nm.

The stoichiometric relationship between different species based on eqn (S6) - (S7) in the main text is as follows,

\[ c_{\text{O}_2^{-}} = 2 \ c_{\text{NO}_2^{-}} = 2 \ c_{\text{azo dye complex}} = 59.77 \ A_{530} \ (\mu \text{mol} \cdot \text{L}^{-1}) \]  

(S9)

The yield in the weight ratio of O₂⁻ radicals to HRLV-MOMs can be calculated by

\[ \omega_{\text{O}_2^{-}} = \frac{c_{\text{O}_2^{-}} \ (\mu \text{mol} \cdot \text{L}^{-1}) \cdot M_{\text{O}_2^{-}} \ (g \cdot \text{mol}^{-1})}{c_{\text{HRLV-MOMs}} \ (mg \cdot mL^{-1})} \]  

(S10)

All the catalytic reactions were carried out with HRLV-MOMs concentration \( c_{\text{HRLV-}} \).
of 0.1 mg·mL\(^{-1}\) and \(M_{O_2^-}\) is the molar mass of O\(_2^-\) radicals, 32.0 g·mol\(^{-1}\). Thus,

\[
\omega_{O_2^-} = 19.13 A_{380} (mg \cdot g_{HRLV-MOMs}^{-1})
\] (S11)

The absorbance of the azo dye complex from NO\(_2^-\) produced in the reaction of NH\(_2\)OH and O\(_2^-\) radicals in the catalytic system was 0.348 (Fig. S12f). So, the yield of O\(_2^-\) radicals in our catalytic mixture (10 mL) of HRLV-MOMs (0.1 mg·mL\(^{-1}\)) and H\(_2\)O\(_2\) (\(c_0 = 44.7\) mg·mL\(^{-1}\)) at room temperature was 6.6 mg·g\(_{HRLV-MOMs}^{-1}\) according to eqn S11.

**Characterization**

Field emission scanning electron microscopy (SEM) and elemental mapping were performed on a SU8010 (Hitachi, Japan) instrument (an accelerating voltage, 5 kV). Transmission electron microscopy (TEM) images of HRLV-MOMs were obtained with a JEM-1011 (Jeol, Japan) under an accelerating voltage of 100 kV. High resolution TEM (HRTEM) images and selected area electron diffraction (SAED) of HRLV-MOMs were obtained on a JEOL-2100F TEM (Jeol, Japan) with an acceleration voltage of 200 kV. X-ray diffraction (XRD) measurement of HRLV-MOMs was obtained by a D8 Advance X-ray diffractometer (Bruker, Germany) at 40 kV and 40 mA (Cu (K\(\alpha\) radiation, \(\lambda = 1.54184\) Å). X-ray photoelectron spectroscopy (XPS) was performed on a Phi 5300 ESCA (Perkin Elmer, USA) with the Mg (K\(\alpha\)) irradiation (X-ray energy, 1253.6 eV, spot area, 1.0×3.5 mm\(^2\)). Fourier transform infrared (FTIR) spectra of HRLV-MOMs were recorded with a Vertex-70 FTIR spectrometer (Bruker, Germany), where they were mixed with KBr and pressed into a thin platelet. Thermogravimetric analysis (TGA) of HRLV-MOMs was carried out from 25 to 800 °C in N\(_2\) at a heating
rate of 10 °C·min\(^{-1}\) with a TGA-50 thermal analyzer (SHIMADZU, Japan). Powder nitrogen (N\(_2\)) adsorption-desorption isotherms were recorded with an ASAP 2020 HD88 instrument (Micromeritics, USA). Ultraviolet-visible (UV-Vis) absorption spectra were measured with a double-beam spectrophotometer (UV-2550, Shimadzu Co., Japan). Fluorescence emission spectra were recorded with a fluorescence spectrophotometer (F-7000, HITACHI, Japan). Zeta potential of dilute HRLV-MOMs suspension was measured by a Zetasizer Nano-ZS90 (Malvern Instruments Ltd., UK) at room temperature.

![SEM images](image1)

**Fig. S1** (a) SEM images of monodisperse HRLV-MOMs and corresponding elemental mapping images of the (b) Mn and (c) O element.

![XPS and TGA curves](image2)

**Fig. S2** (a) XPS survey spectrum, (b) TGA curves of HRLV-MOMs.

The weight loss of about 1.0 wt% is due to the adsorbed water on the surface of HRLV-MOMs below 160 °C while the weight loss of 2.2 wt% from 160 to 350 °C is
ascribed to the desorption of the crystal water existing in nanosheets of HRLV-MOMs. The weight loss between 380 and 600 °C is due to the reduction of MnO_2 to Mn_2O_3 accompanied by evolution of oxygen. The weight loss between 700 and 800 °C corresponds to the transformation from Mn_2O_3 to Mn_3O_4 accompanied by oxygen release as Mn_3O_4 is in stable state at high temperature.

![Visible absorption spectra](image)

**Fig. S3** Visible absorption spectra of (a) crystal violet (c_0 = 0.05 mg·mL\(^{-1}\)) with the maximum absorbance at 590 nm and (b) ethyl violet (c_0 = 0.05 mg·mL\(^{-1}\)) with the maximum absorbance at 596 nm over time in the presence of HRLV-MOMs (0.1 mg·mL\(^{-1}\)) and H_2O_2 (c_0 = 44.7 mg·mL\(^{-1}\)).
Fig. S4 Catalytic degradation efficiency comparison of different morphologies of MnO₅ for MB degradation by the main radicals ·OH or the radicals SO₄⁻ and O₂⁻. The insets are adapted from references with copyright from Elsevier, Wiley-VCH, American Chemical Society and The Royal Society of Chemistry, respectively.
**Fig. S5** The recyclability of the HRLV-MOMs (0.1 mg·mL\(^{-1}\)) using successive catalytic degradation of MB (\(c_0 = 0.05\) mg·mL\(^{-1}\)) with H\(_2\)O\(_2\) (\(c_0 = 44.7\) mg·mL\(^{-1}\)). The insets are the SEM image and XRD pattern of the HRLV-MOMs after 10 cycles of catalysis.

![Graph of Efficiency vs. Cycle](image)

**Fig. S6** Linear fitting of experimental data by first-order kinetic model.

![Linear fitting graph](image)

**Fig. S7** Visible absorption spectra of MB (\(c_0 = 0.05\) mg·mL\(^{-1}\)) over time in the presence of HRLV-MOMs (0.1 mg·mL\(^{-1}\)) and H\(_2\)O\(_2\) (\(c_0 = 44.7\) mg·mL\(^{-1}\)) in N\(_2\)-saturated...
solution.

When the catalytic degradation experiment is carried out in N₂-saturated solution (Fig. 3c in the main text and Fig. S7), the efficiency decreases remarkably, which indicates that dissolved O₂ also contributes to high catalytic performances. Dissolved O₂ can interact with the electrons (e⁻) in negatively charged HRLV-MOMs with Zeta potential of -17.6 mV to generate O₂⁻ radicals,¹² which contribute to MB degradation.

![Figure S8](image)

**Fig. S8** (a) UV-Vis absorption spectra of MB ($c_0 = 0.05$ mg·mL⁻¹) over time with interference of p-BQ (5.4 mg·mL⁻¹) containing HRLV-MOMs (0.1 mg·mL⁻¹) and H₂O₂ ($c_0 = 44.7$ mg·mL⁻¹). (b) UV-Vis absorption spectra of the mixture of HRLV-MOMs (0.1 mg·mL⁻¹), H₂O₂ ($c_0 = 44.7$ mg·mL⁻¹) and p-BQ ($c_0 = 5.4$ mg·mL⁻¹).

The interfering peaks (Fig. S8a) of added bright yellow p-BQ can be deducted from the catalytic spectraby deducing the spectra of p-BQ, H₂O₂ and HRLV-MOMs with the same concentration of catalytic experiments (Fig. S8b). The final spectra are shown in Fig. S11.
**Fig. S9** The catalytic degradation efficiency against time with different addition of (a) TBA and (b) $p$-BQ with MB ($c_0 = 0.05 \text{ mg·mL}^{-1}$), HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0 = 44.7 \text{ mg·mL}^{-1}$). The corresponding visible absorption spectra are shown in Fig. S10 and S11.

**Fig. S10** Visible absorption spectra of MB ($c_0 = 0.05 \text{ mg·mL}^{-1}$) over time with different concentration of TBA in the mixture containing HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0 = 44.7 \text{ mg·mL}^{-1}$). (a) 1.0, (b) 2.0, (c) 2.5, (d) 3.0, (e) 3.5 and (f) 4.0 mol·L$^{-1}$. 
Fig. S11  Visible absorption spectra of MB ($c_0 = 0.05 \text{ mg}\cdot\text{mL}^{-1}$) over time with different concentration of $p$-BQ in the mixture containing HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0 = 44.7 \text{ mg}\cdot\text{mL}^{-1}$). (a) 50, (b) 60, (c) 70, (d) 80, (e) 90 and (f) 100 mmol·L$^{-1}$.

By increasing the concentration of the scavengers, the optimal addition of TBA and $p$-BQ are obtained. The $c/c_0$ becomes the maximum when TBA increases to 4.0 mol·L$^{-1}$ (Fig. S9a and S10) and $p$-BQ increases to 100 mmol·L$^{-1}$ (Fig. S9b and S11).
Fig. S12 (a) Catalytic degradation of MB with or without scavengers (TBA for ·OH radicals and p-BQ for O$_2$·$^-$ radicals). (b) The fluorescence emission intensity of 7-hydroxyl coumarin produced in the reactions of coumarin and ·OH radicals in the catalytic degradation system, (c) the working curve of the fluorescence emission intensity of 7-hydroxyl coumarin against its concentration for quantitatively measurement of ·OH radicals. (d) The fluorescence emission intensity of 7-hydroxyl coumarin produced from the reaction of coumarin (0.3 mg·mL$^{-1}$) and ·OH radicals at different time in the catalytic degradation system. (e) The linear working curve of the absorbance of the azo dye complex against the concentration of NO$_2^-$ for quantitatively measurement of O$_2$·$^-$ radicals. (f) Visible absorption spectra of an azo dye complex relating to NO$_2^-$ produced in the reactions of NH$_2$OH and O$_2$·$^-$ radicals in the catalytic degradation system containing HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0 = 44.7$ mg·mL$^{-1}$). The corresponding fluorescence spectra of (a), (c), (d) and (e) are shown in Fig. S10f, S11f, S13c, S13d and S14, respectively.
Fig. S13 Fluorescence spectra of 7-hydroxyl coumarin (a) produced from the reaction of ·OH radicals with different concentration of coumarin in the concentration range of 0.1 to 1.0 mg·mL$^{-1}$ corresponding to (b) fitting curve of fluorescence emission intensity at 460 nm against the concentration of coumarin in catalytic degradation process. (c) Fluorescence spectra of 7-hydroxyl coumarin with concentration gradient and (d) against time during catalytic degradation process. The catalytic degradation system contains HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0 = 44.7$ mg·mL$^{-1}$).

The concentration of added coumarin in the catalytic degradation system is optimized (Fig. S13a) because inadequate coumarin is not enough to interact with ·OH radicals generated from the catalytic degradation system while excess coumarin would lead to fluorescence quenching.$^{24}$ When 0.3 mg·mL$^{-1}$ of coumarin is added to the catalytic degradation system, the fluorescence emission is the most intense (Fig. S13b).
Fig. S14 Visible absorption spectra of the azo dye complex against concentrations in the catalytic degradation system containing HRLV-MOMs (0.1 mg·mL$^{-1}$) and H$_2$O$_2$ ($c_0$ = 44.7 mg·mL$^{-1}$) for quantitative measurement of O$_2$·$^-$ radicals.

References


