

Supplementary Material (ESI) for RSC Advances
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Supplementary Information

Natural montmorillonite nanosheet colloid-catalyzed hydrogen peroxide
ultra-weak chemiluminescence

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Experimental

Chemicals and Solutions

All chemicals were of analytical reagent grade and were used without further purification. NaOH, NaIO₄, NaHSO₃ were purchased from Beijing Chemical Reagent Company (Beijing, China). 1,4-Diazabicyclo[2.2.2]octane (DABCO) and 2,2,6,6-tetramethyl-4-piperidine (TEMP) were obtained from Sigma-Aldrich (St. Louis, MO). 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Thiourea and sodium azide (NaN₃) were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Ascorbic acid was purchased from Beijing Aoboxing Biotech Co., Ltd (Beijing, China). Uranine

was purchased from Acros. Nitro blue tetrazolium (NBT) was purchased from Nacalai Tesque Inc. (Tokyo, Japan). Sodium-MMT (PGW, PGN and PGV grades; Nanocor) was used without further purification. A 0.1 M nitrite stock solution was prepared by dissolving 0.69 g NaNO₂

(Tianjin Chemical Reagent Company) in 100 mL of deionized water (Milli Q, Millipore, Barnstead, CA, USA). A 0.01 M nitrite working solution was freshly prepared by diluting the nitrite stock solution with deionized water. A mixed working solution of 0.05 M H₂O₂ and 0.02 M HCl was daily prepared by volumetric dilution of 30% (v/v) H₂O₂ (Beijing Chemical Reagent Company, China) and 36% (v/v) HCl (Beijing Chemical Reagent Company, China) with deionized water, respectively. The pH was adjusted with NaOH.

Apparatus

X-ray diffraction (XRD) measurements were performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu/K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ angle of the diffractometer was stepped from 3° to 70° at a scan rate of 10°/min. Transmission electron microscopy (TEM) images were recorded using a Tecnai G²20 TEM from USA FEI Company. The CL detection was conducted on a biophysics chemiluminescence (BPCL) analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). The CL spectrum was measured with high-energy cutoff filters from 400 to 640 nm between the flow CL cell and the photomultiplier tube (PMT). Electron spin resonance (ESR) spectra were measured on an ESR spectrometer (JEOL, JES-FA200 spectrometer, Tokyo). Fluorescence spectra were performed using a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). UV-vis spectra were measured on a USB 4000 miniature fiber optic spectrometer in absorbance mode with a DH-2000 deuterium and tungsten halogen light source (Ocean Optics, Dunedin, FL).

Preparation of MMT Nanosheets

1.0 g of MMT particles were dispersed in 100 mL of deionized water. After vigorous stirring for 24 h, the dispersion was centrifuged at 10000 rpm for 5 min to remove the unexfoliated particles. The resulting clear supernatant was collected for subsequent use. The concentration of exfoliated MMT nanosheets was determined by measuring the residual solid content. The exfoliated nanosheets were kept in aqueous solution and stable after several months.

CL Measurements

Static injection CL kinetic curves were obtained by batch experiments performed in the quartz cuvette. Peroxynitrous acid solution was freshly prepared from the reaction of 0.05 M H₂O₂ in 0.02 M HCl solution with 0.01 M NaNO₂. 100 μL of the as-prepared peroxynitrous acid solution was injected into 200 μL of aqueous suspension of MMT nanosheets by a microliter syringe from the upper injection port. The CL signals were monitored by a PMT adjacent to the CL quartz cell. The data were integrated at intervals of 0.1 s, and a work voltage of -1000 V was used for the CL detection.

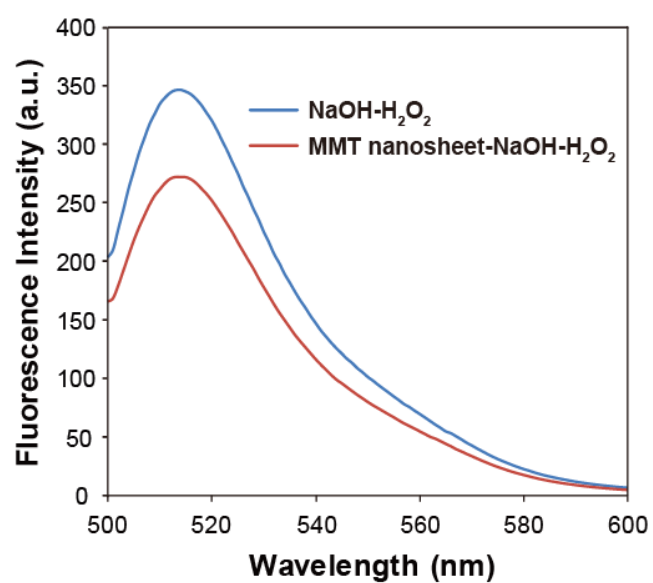


Fig. S1 Fluorescence spectra of uranine in NaOH-H₂O₂ mixture solution in the presence/absence of MMT nanosheets.

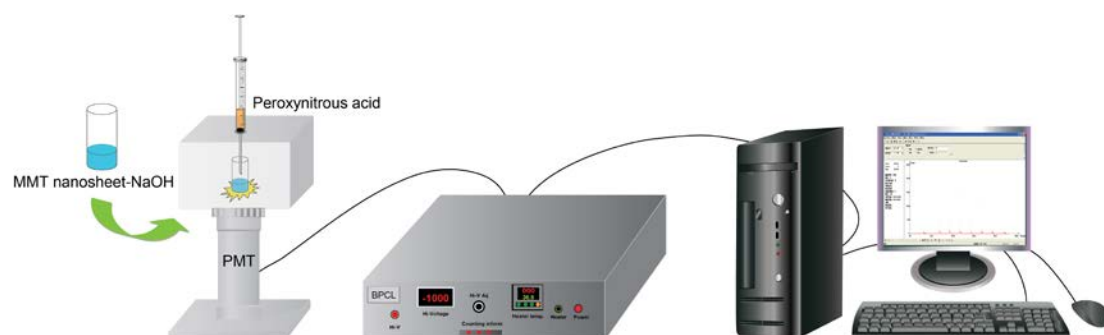


Fig. S2 Schematic diagram of a static CL setup.

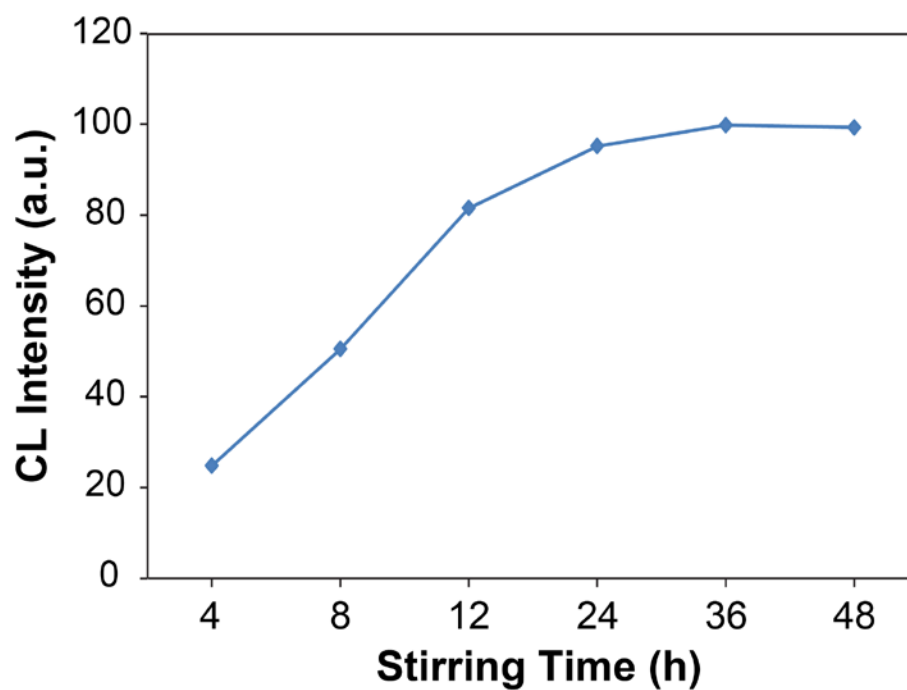


Fig. S3 Effect of stirring time on the MMT nanosheet-peroxynitrite CL system.

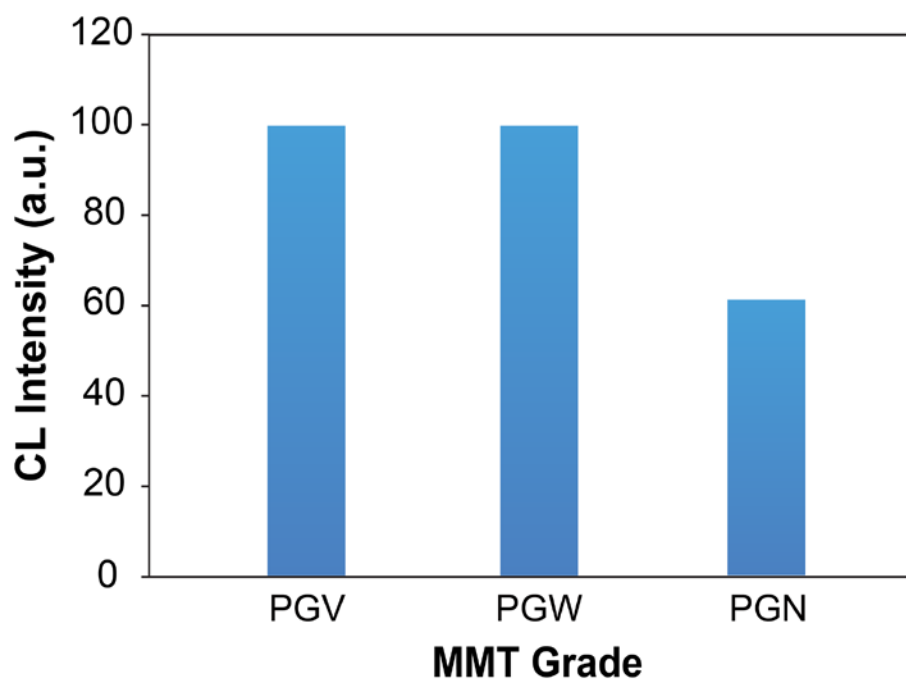


Fig. S4 Effect of MMT grades on the MMT nanosheet-peroxynitrite CL system (PGV grade, aspect ratio = 150-200; PGW grade, aspect ratio = 200-400; PGN grade, aspect ratio = 300-500).

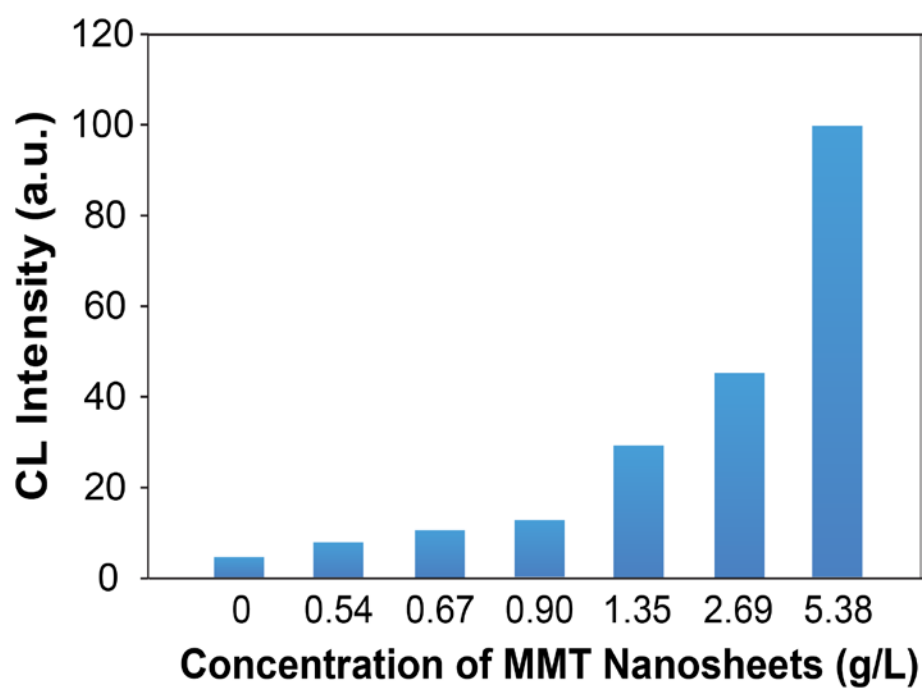


Fig. S5 CL intensity of MMT nanosheet-peroxynitrite CL system with different MMT nanosheet contents (PGW grade).

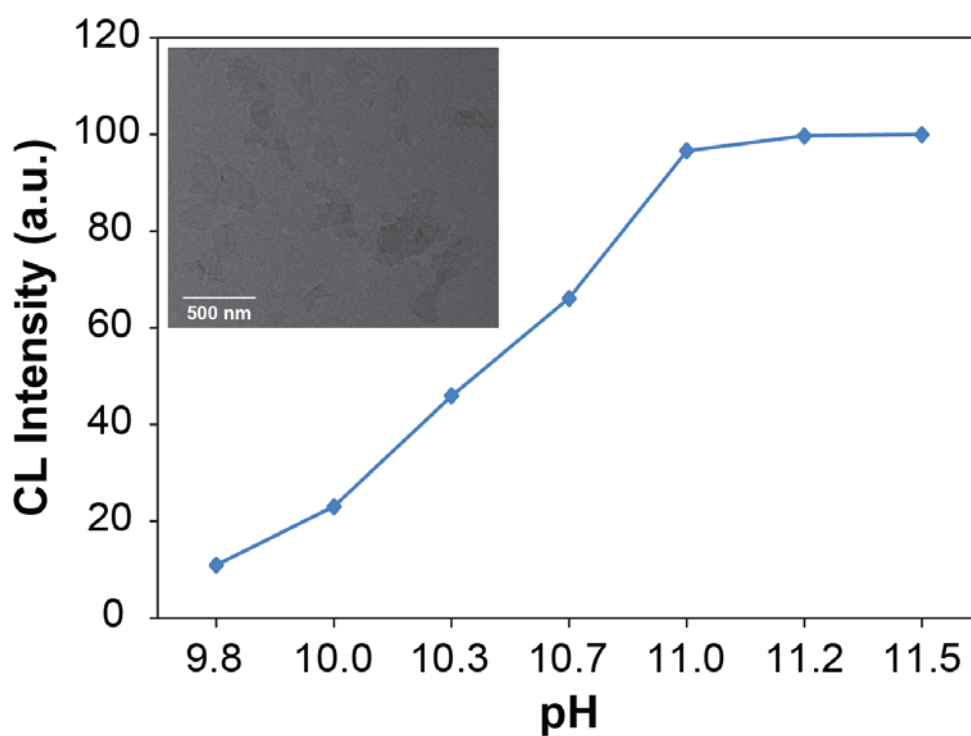


Fig. S6 Effect of the reaction pH on the peroxyntirite CL intensity. (inset: TEM image of MMT nanosheets at pH 11.0).

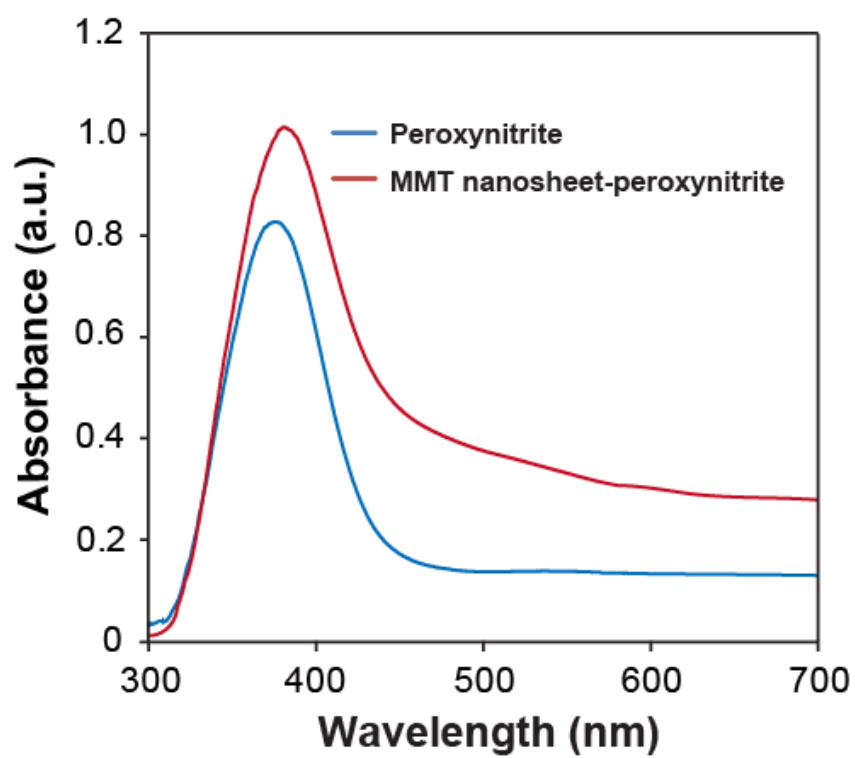


Fig. S7 Absorption spectra of NBT in peroxynitrite system before and after the addition of MMT nanosheets into the peroxynitrite system.

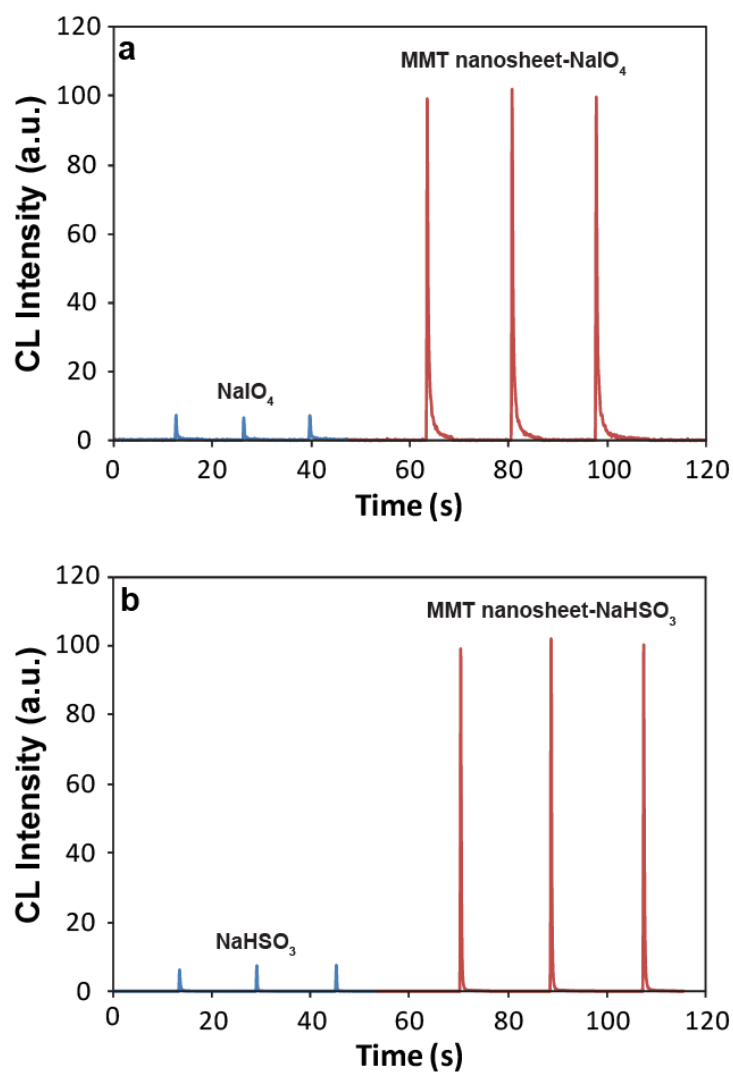


Fig. S8 CL kinetic curves of (a) NaIO₄-H₂O₂ CL system (H₂O₂ solution was injected into basic NaIO₄ solution and MMT nanosheet-NaIO₄ mixture solution, respectively. H₂O₂, 0.01 M; NaIO₄ 0.01 M; injection volume, 100 μ L); (b) NaHSO₃-H₂O₂ CL system (H₂O₂ solution was injected into basic NaHSO₃ solution and MMT nanosheet-NaHSO₃ mixture solution, respectively. H₂O₂, 0.1 M; NaIO₄ 0.1 M; injection volume, 100 μ L).

Table S1. The detailed components of commercial MMT.

Elements	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe
Content (%)	48.35	4.76	2.36	12.32	28.95	0.01	0.13	0.18	0.21	0.11	0.02	2.25

Table S2. Effects of radical scavengers on MMT nanosheet-peroxynitrite CL system.

Radical scavengers	CL intensity (%)	Relative deviation (%)
Ascorbic Acid (0.1 mM)	0.35	± 2.84
Thiourea (1 mM)	5.42	± 2.28
DABCO (0.01 mM)	42.83	± 1.42
Sodium Azide (1 mM)	60.64	± 0.48
NBT (0.1 mM)	98.72	± 0.61