Sustainable Solar-Driven H_2O_2 Production from H_2O and O_2

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Background

Challenges

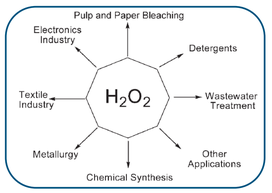


Figure 1. Principal uses of hydrogen peroxide
Angew. Chem. Int. Ed. 2006, 45, 6962 – 6984

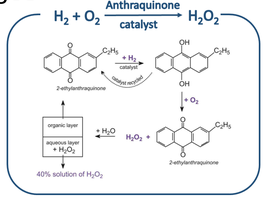


Figure 2. Industrial production of H_2O_2 via the anthraquinone process

- **5.5 Million** metric tons H_2O_2 had been consumed globally per year (reported on 2015).
- H_2O_2 is widely used in almost all industrial areas, particularly in the chemical industry and **environmental protection**.
- However, the current industrial production of H_2O_2 is **not sustainable**, because it requires **significant energy input** and generates **waste**.

A Solution and Limitations

- **Photocatalysis** is a promising **green technology** for H_2O_2 generation, because it
  - generates H_2O_2 ***in situ*** under sunlight;
  - eliminates hurdles in the transport, handling, and storage for on-site applications;
  - promotes sustainability by **reducing the energy and chemical demand**.

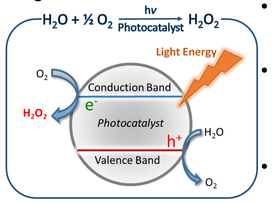


Figure 3. The scheme of photocatalytic H_2O_2 generation

- **Graphitic carbon nitride (g-C_3N_4)** has recently emerged as a novel photocatalyst for multiple applications;

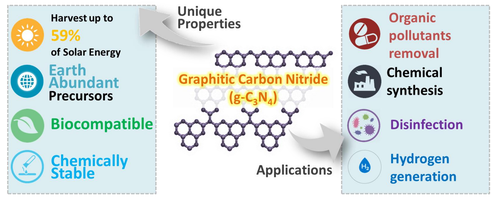


Figure 4. The unique properties of g-C_3N_4 and its applications.

- However, the application of g-C_3N_4 for H_2O_2 generation is at its **nascent stage**;
- Its practical application is challenged by the inefficient photocatalytic performance and reactor design.

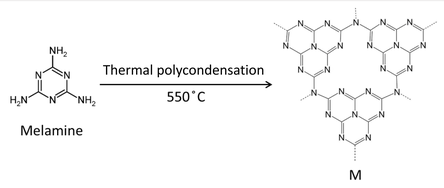
Objectives

- We aim to explore the potential applications of g-C_3N_4 for sustainable H_2O_2 generation via
  - **Developing g-C_3N_4 based photocatalyst with improved photocatalytic performance;**
  - **Understanding mechanisms of H_2O_2 generation on g-C_3N_4;**
  - **Designing a solar photocatalytic reactor.**

Methods

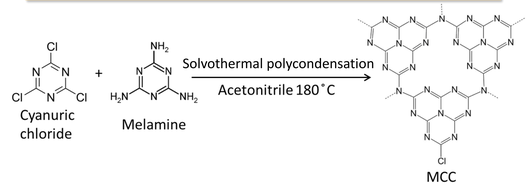
- Synthesis of chlorine doped g-C_3N_4 (MCC) using a solvothermal method.

Conventional method: Bulk g-C_3N_4
Thermal polycondensation



VS.

Innovative method: Cl doped g-C_3N_4
Solvothermal polycondensation



- Photocatalytic generation of H_2O_2 on g-C_3N_4.
  - The experiments were conducted under simulated visible light (xenon lamp, λ> 400nm), LED irradiation (7 W), outdoor sunlight;
  - The catalyst loading was 1 g/L;
  - pH was adjusted by using a phosphate buffer.
  - H_2O_2 was measured colorimetrically by the DPD method.

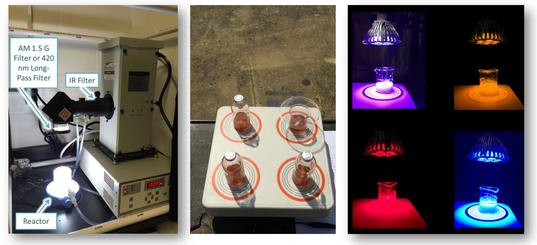


Figure 5. From left to right: Photocatalytic experimental setup with simulated solar irradiation (both visible light and AM 1.5 G sunlight), outdoor sunlight, and LED irradiation.

Results

- MCC had a **fiber structure** and a **smaller particle size** (Figure 6) resulted from solvothermal polycondensation (**high product yield** from the precursors: ~ 53%).
- MCC generated H_2O_2 of notable concentrations (up to ca. **650 μM in 6 h**, with a rate of **1.19 ± 0.06 μM/min**) (Figure 7), while the bulk g-C_3N_4, M, only generated about 3 μM in 6 h under visible light irradiation (λ > 400 nm).

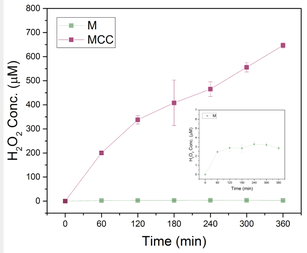


Figure 7. H_2O_2 generation on g-C_3N_4 samples (M and MCC) under simulated visible sunlight irradiation (λ > 400 nm, xenon lamp).

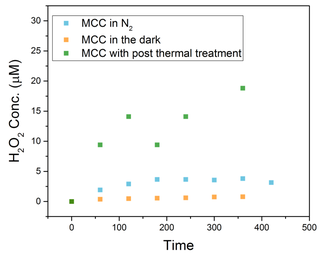


Figure 8. H_2O_2 generation on MCC and MCC with post thermal treatment under light irradiation and dark condition with/without oxygen.

- **pH matters:** the rate constant of H_2O_2 generation was increased by 1.9 fold with the decrease of pH from 7 to 3, likely due to the proton-coupled electron transfer (**PCET**) mechanism and proton dependence of H_2O_2 production (Figure 9).
- MCC can generate H_2O_2 under different light resources, such as LED, direct sunlight, etc. The rate constant can reach up to **2.32 ± 0.10 μM/min** under AM 1.5 G solar irradiation.
- MCC was stable after 6 h reaction, with the only loss of chloride, indicated by the XPS analysis (Figure 11).

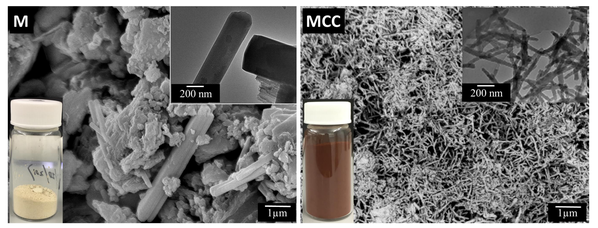


Figure 6. SEM and TEM (insets) images of g-C_3N_4 samples.
TEM of MCC was revised from Angew. Chem. Int. Ed. 2012, 51, 11814 –11818

- **Light energy** and **oxygen** are required for the photocatalytic generation of H_2O_2 on MCC (Figure 8).
- The generation of H_2O_2 was largely inhibited on MCC with the post thermal treatment (500 °C in N_2) (Figure 8), which may due to the loss of chlorine on MCC after the thermal treatment (Figure 11).

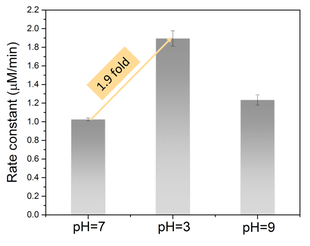


Figure 9. Rate constants of H_2O_2 generation on MCC in the buffer solution with different pH.

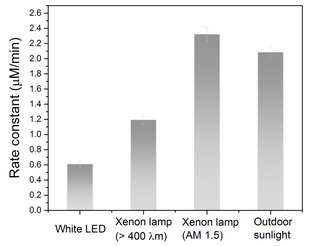


Figure 10. Rate constants of H_2O_2 generation on MCC under different light irradiation.

Results

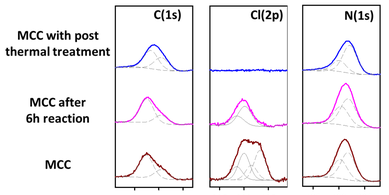


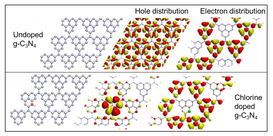
Figure 11. The X-ray photoelectron spectroscopy (XPS) spectra of C 1s, Cl 2p, N 1s for different MCC samples.

Conclusions

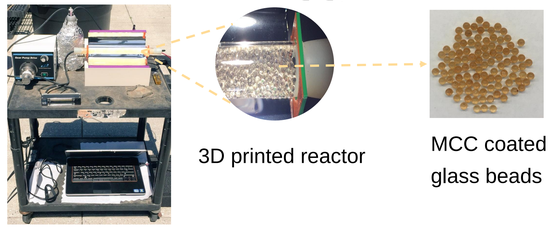
- MCC, a Cl-doped g-C_3N_4 shows **promise** for sustainable H_2O_2 generation because of its low cost, high photocatalytic efficiency, and stability.
- **Chlorine** in MCC may play a crucial role in H_2O_2 generation.
- MCC is **robust** under the irradiation of different light sources.
- This work will pave a new avenue for **on-site** H_2O_2 generation and its applications of disinfection, medical care, hygiene, and water purification for remote areas, developing countries, and regions after natural disasters.

Future works

- Molecular simulations to understand the role of chlorine



- Potable solar reactor for on-site H_2O_2 production



Applications

- On-site H_2O_2 generation for water treatment, disinfection, hygiene, and medical care for remote areas, developing countries, and regions after natural disasters.

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Publication

Environmental Science & Technology

Zheng, Q., Durkin, D. P., Elenewski, J. E., Sun, Y., Banek, N. A., Hua, L., Chen, H., Wagner, M. J., Zhang, W., **Shuai, D**. Visible-Light-Responsive Graphitic Carbon Nitride: Rational Design and Photocatalytic Applications for Water Treatment. *Environ. Sci. Technol.* 2016, 50 (23), 12938–12948.

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