ACHIEVING SUSTAINABLE WATER PURIFICATION: TAILORED GRAPHITIC CARBON NITRIDE FOR THE REMOVAL OF ORGANIC PERSISTENT CONTAMINANTS

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Background

Challenges

- Great challenges from *environmental pollution;*
- Many *organic pollutants are recalcitrant in*conventional wastewater and water treatment process;
- Pollutants include pharmaceuticals and personal care products, pesticides, and endocrine disrupting compounds.

Figure 1. Persistent organic pollutants in water
Modified from *http://www.nytimes.com/2007/04/03/science/earth/03water.html?ref=health&_r=0*

Photocatalysis

- ***Photocatalysis:***
  - An promising *green technology* to utilize renewable *solar energy for water purification*;
  - Numerous photocatalysts explored in the past decades are suffered from limited visible light adsorption, low reactivity, instability, and high cost.

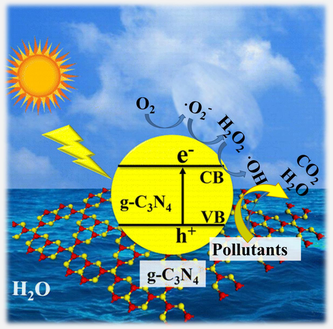


Figure 2. Photocatalytic degradation of pollutants
Modified from *Cao and Yu, J. Phys. Chem. Lett., 2015, 5, 2101-2107*

g-C_3N_4

- ***Graphitic carbon nitride (g-C_3N_4)*** :
  - A novel polymeric photocatalyst;
  - Visible light responsive (460-650 nm);
  - Physically and chemically stable;
  - Low cost for production;
  - Limited research on persistent organic pollutants removal.

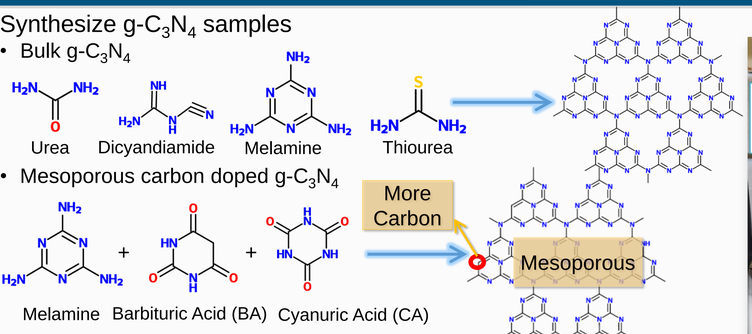
Objectives

- We aim to explore the potential applications of
  - *A new visible-light-responsive photocatalyst based on g-C_3N_4*
  - *A novel photocatalytic membrane reactors*

  for water decontamination to achieve sustainable water treatment and water reuse.

Methods

- Synthesize g-C_3N_4 samples
  - Bulk g-C_3N_4



  - Mesoporous carbon doped g-C_3N_4

- Photocatalytic degradation tests (Figure 3)
  - Phenol was selected as a probe contaminant;
  - The optimal supramolecular g-C_3N_4 was applied for the degradation of persistent organic micropollutants (i.e., atrazine, carbamazepine, and sulfamethoxazole);
  - Their longevity in matrixes representative of water treatment was evaluated;
  - The reactivity was evaluated under both simulated solar irradiation (visible light) and LED irradiation;
  - Contaminant was analyzed by high performance liquid chromatography (HPLC).

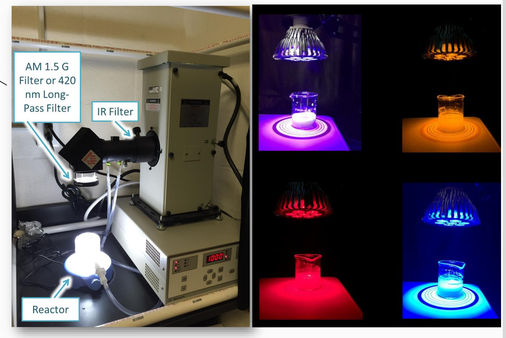


Figure 3. Photocatalytic experiment setup
Left: Simulated solar irradiation (visible light)
Right: LED irradiation

Results

- Bulk g-C_3N_4 from different precursors
  - Urea-based g-C_3N_4 shows the highest photocatalytic activity in phenol degradation pseudo-first-order rate constant of *0.026 min^{-1}*, and its rate constant is *6-8.7 folds* higher than those of g-C_3N_4 synthesized from the other precursors.
  - This is likely due to a larger surface area and *self-carbon-doping* (i.e., increased C/N) resulted increased visible light adsorption.

- Carbon doped g-C_3N_4
  - The color of carbon doped g-C_3N_4 becomes darker with increased carbon content (Figure 4);

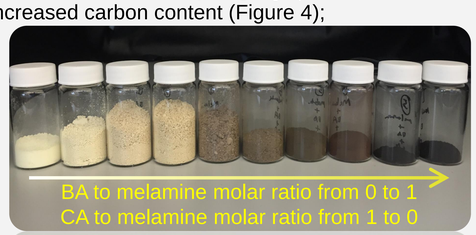
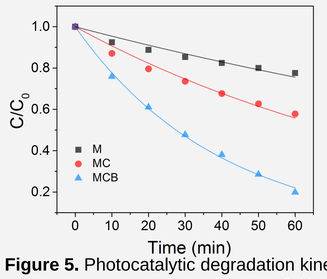


Figure 4. The color change of carbon-doped g-C_3N_4 (BA as the precursor for carbon doping)

  - The photocatalytic reactivity is increased by *6.7 folds* at an optimum carbon doping level (melamine/cyanuric acid/barbituric acid = 2/1.93/0.07 by weight), first order rate constant of *0.027 min^{-1}* vs. *0.0040 min^{-1}* (Figure 5)



U: Bulk g-C_3N_4 from urea

M: Bulk g-C_3N_4 melamine

MC: g-C_3N_4 from melamine + CA;

MCB. Optimal g-C_3N_4 from melamine + BA + CA

Figure 5. Photocatalytic degradation kinetics of phenol on carbon doped g-C_3N_4

Results

- MC and MCB have mesoporous structures (Figure 5 Left) resulted from the self-templating of supramolecular structure and the subsequent removal of less-thermally stable CA during the heat treatment for g-C_3N_4 synthesis.

- The reduction of PL intensity and red-shifted peak both indicate that the addition of CA and BA may lower the charge recombination compared to M only derived from melamine.(Figure 5 Right)

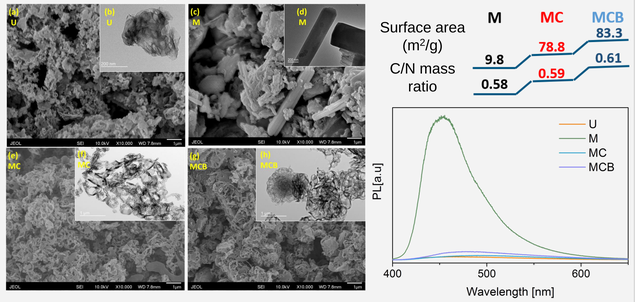


Figure 6. Left: SEM (a,c,e,g) and TEM(b,d,f,h) images; Right: Photoluminescence (PL) spectra

- The optimal supramolecular g-C_3N_4, MCB still performs the best on the degradation of other persistent organic micropollutants under visible light irradiation. (Figure 7)

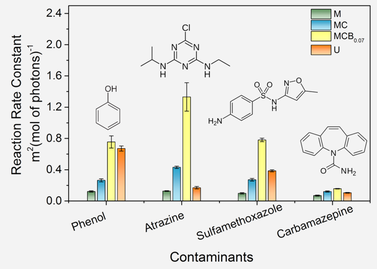


Figure 7. Photocatalytic degradation kinetics of phenol and persistent organic micropollutants by g-C_3N_4 samples (SMX: Sulfamethoxazole; CBZ: Carbamazepine)

Results

- Little to no inhibition on atrazine degradation kinetics was observed in simulated complex water (Figure 8 left)as well as water samples collected from different stages in water and wastewater treatment process (Figure 8 right).

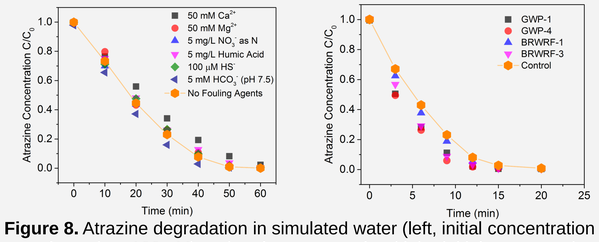


Figure 8. Atrazine degradation in simulated water (left, initial concentration of atrazine: 100 uM) and real water samples (right, initial concentration of atrazine: 20 uM)

- A comparable photocatalytic activity was achieved under multichromatic white LED and Xenon lamp irradiation (>400nm) (*0.55 vs. 1.76 m^2(mole of photons)$^{-1}$*);
- The reactivity under LED irradiation at a shorter wavelength is higher than that under Xenon lamp irradiation.

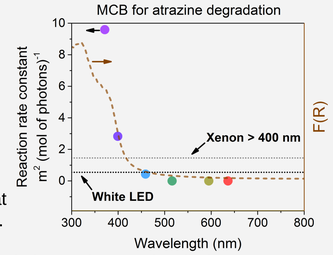


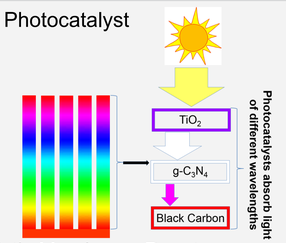
Figure 9. Atrazine degradation under LED irradiation

Conclusion

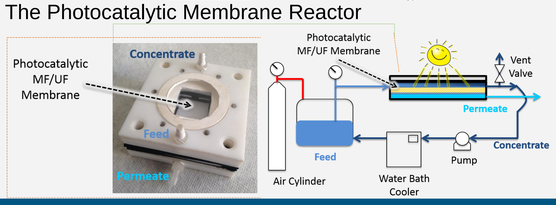
- MCB, the optimal g-C_3N_4 synthesized via supramolecular method has the highest reactivity for organic persistent micropollutants degradation under visible light (>400 nm), which was contributed to the increased surface area and improvement of charge separation when compare with M.
- g-C_3N_4 holds promise for contaminant degradation in water treatment or advanced wastewater treatment practices.
- The energy-efficient LEDs are a promising alternative light source for the photocatalytic degradation of persistent contaminants when sunlight is not available.

Future Work

- The “Rainbow” Photocatalyst



- The Photocatalytic Membrane Reactor



Acknowledgement

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