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Synthesis of Cu-Cy nanoparticles for treating PFAS in water

by

Ligang Wang

Presented to the Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

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MAY 2024

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ABSTRACT

This work aims to address the cumulative harm caused by perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water to human health and the ecological environment around the world. Reducing or removing PFAS pollution is an urgent need. Cu-Cy nanoparticles are photosensitizers, which were developed for photodynamic therapy of cancer in the first place. In this work, we use Cu-Cy for the catalytic degradation of PFAS. Synthesis of Cu-Cy nanoparticles in deionized water at 90 degrees Celsius is a low-cost and efficient method. We demonstrated the detailed process of synthesizing Cu-Cy nanoparticles. Under ultraviolet illumination, the synthesized Cu-Cy nanoparticles turned yellow as an initial successful indicator. The Cu-Cy nanoparticles were further characterized by ultraviolet absorption spectrum and X-ray power diffractogram (XRD) to confirm their successful synthesis. Through seven sets of control experiments, the photocatalytic degradation of PFAS by Cu-Cy nanoparticles was confirmed. Cu-Cy alone could achieve better degradation performance of PFAS than H₂O₂ alone. Combination of Cu-Cy and H₂O₂ could further improve the decomposition of PFAS. In future, more comprehensive investigations of optimal Cu-Cy treatment strategies of PFAS water pollution are warranted.

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1. INTRODUCTION

Water is essential for humans and all life on Earth. However, with the development of modern industry, the problem of water pollution is becoming more and more severe. One type of pollutant is called perfluoroalkyl and polyfluoroalkyl substances (PFAS), which is causing more and more serious harm. Perfluoroalkyl substances are also known as perfluorinated compounds, where all the remaining hydrogen atoms connected to carbon atoms are replaced by fluorine atoms, except for the hydrogen atoms of any functional group. When at least one of the hydrogen atoms connected to the carbon atoms of an aliphatic substance is replaced by a fluorine atom, the compound is called a partially fluorinated compound, also called a polyfluoroalkyl substance. To date, approximately 5,000 to 10,000 PFAS have been discovered. PFAS is difficult to decompose in most natural conditions, such as soil, seawater, and fresh water. Therefore, PFAS is also called "forever chemicals." [1]

Perfluoroalkyl and polyfluoroalkyl compounds are widely used in human production and life, including but not limited to smoke suppressants, surfactant carpets, insecticides, adhesives, paints, foams, lubricants, paper, product packaging, and other high-performance chemicals. [2] PFAS has unique properties because of its large number of fluorinated areas, such as repelling oily substances and water. Its chemical structure remains stable even at high temperatures. It is acid-resistant, alkali-resistant, antioxidant oxidation, and reducing agent reduction, so it is a commonly used surfactant in industry. Humans began producing fluorinated organic chemicals in the 1950s, including perfluoro octane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) [3], which are also known as traditional PFAS. Persistent organic pollutants (POPs) are new PFAS that have become widely used. A 2020 investigation by Sinclair et al. identified and reported hundreds of previously unreported PFAS and PFAS-related compounds that may degrade into legacy PFAS in the natural environment. Emerging PFAS have shorter carbon chains and have hydroxyl groups. They are more likely to spread to a wider range with water flow in rivers, lakes, and oceans, posing a more profound threat to natural organisms and human health. Emerging PFAS are found in seawater, river water, aquatic products, aqueous film-forming foam (AFFF), sediments, and several other ecological media. [4]

In addition to the direct harm to humans and organisms in the environment, PFAS will enter the food chain, which will cause long-term toxic effects on human health. In 2015, the direct and indirect exposure of mankind to PFAS reached 8,740 tons. PFAS is difficult to excrete out of the body after being ingested by organisms, which causes it to accumulate in organisms along the food chain, leading to bioaccumulation and

biomagnification. The main ways PFAS enters the body are ingestion, inhalation, and skin contact.[5]

PFAS can cause serious health problems such as reproductive system diseases, kidney failure, immunotoxicity, and reduced birth weight of newborns. New research also shows that PFAS can interfere with the human endocrine system and cause different types of cancer. Since the Stockholm Convention on Persistent Organic Pollutants has banned the use of long-chain PFAS, short-chain PFAS are manufactured in large quantities by industry to replace the use of long-chain PFAS. Short-chain PFAS are highly mobile on the soil surface and in the earth's water cycle and have been found to persist in nearly all types of ecosystems and organisms. Since its properties are also different from long-chain PFAS, it is important to develop a safer, more efficient, and thorough way to remove them. Legacy PFAS can also become emerging contaminants after degradation processes, which requires development of more efficient and flexible removal methods [6]. Figure 1 shows a summary of structure, regulation, research, and impact on ecosystem and health of PFAS [7]. Note that the recent EPA regulation sets 4.0 parts per trillion for PFOR and PFOS.

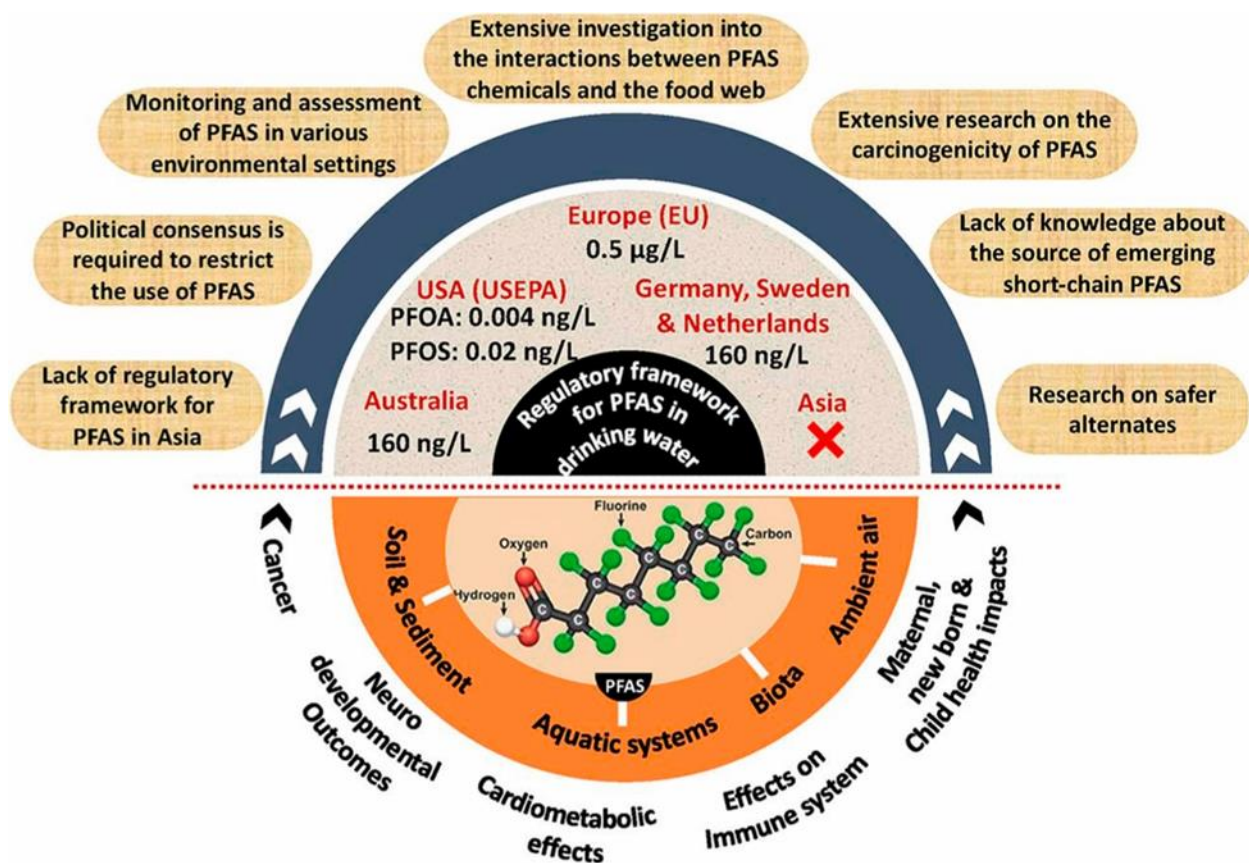
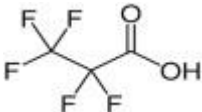
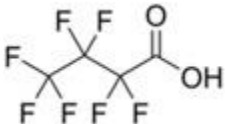
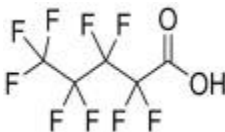
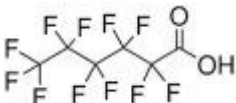
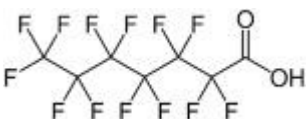

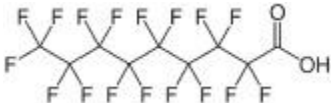

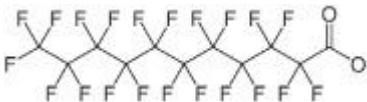

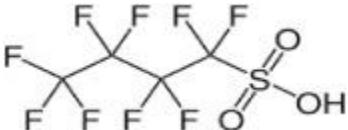
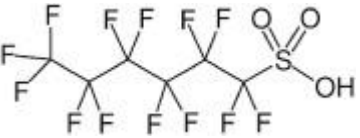



Figure. 1. Structure, regulation, research, and impact on ecosystem and health of PFAS [7].

Studying the physical and chemical properties of PFAS is critical to predicting the migration patterns and distribution of PFAS in different earth environments. The common structure of PFAS is a carbon backbone with at least one functional group on which the carbon atoms are saturated with fluorine atoms. The large number of fluorine atoms in PFAS molecules makes PFAS hydrophobic, and their functional groups make PFAS polar. Table 1 shows physical properties of the most common PFAS. As shown in Table 1, most PFAS are solid at room temperature. Short-chain PFAS such as fluorotelomer sulfonate (FTS), perfluoroalkyl carboxylic acid (PFCA), acid variants of perfluoroalkyl sulfonic acid (PFSA), and fluorotelomers with 4 to 6 carbon tails. Physical alcohol (FTOH) is liquid at room temperature. The movement of PFAS in the environment is related to its density. After testing the penetration capabilities of 29 PFAS, it was found that the separation of PFAS occurred in the soil. The concentrations of perfluoro octane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluoro hexane sulfonate (PFHxS) decreased with increasing depth.[8] The longer the carbon chain length, the higher the melting and boiling points of PFAS. The higher the concentration of ions in water, the less solubility of PFAS. The growth of the carbon backbone increases the vapor pressure of PFAS. The high vapor pressure makes PFAS easily transported over long distances in the environment. PFAS is surface active and can easily form micelles. PFAS in groundwater is more likely to accumulate than in surface water due to reactions of PFAS with soil particles or an increase in the density of soil voids.[9]

Table 1. Physical properties of the most common PFAS[8].

PFAS type	Structure	Molecular weight (g/mol)	Solubility in water	Boiling point (°C)	Density
Pentafluoro propionic acid (PFPrA)		164.03	Very high	96–97	1.561 g/mL at 25 °C
Perfluoro butanoic acid (PFBA)		214.04	Very high	120	1.645 g/mL at 25 °C
Perfluoro pentanoic acid (PFPeA)		264.05	Partly soluble	140	1.713 g/mL at 25 °C
Perfluoro hexanoic acid (PFHxA)		314.05	Soluble	157	1.757 g/cm3
Perfluoro heptanoic acid (PFHpA)		364.06	Insoluble in water	175	1.792 g/mL at 25 °C
Perfluorooctanoic acid (PFOA)		414.07	Water soluble	189	1.8 g/cm³
Perfluoro nonanoic acid (PFNA)		464.08	Water soluble	218	1.8 g/cm³
Perfluoro decanoic acid (PFDA)		514.08	Water soluble	218	No standard data available
Perfluoro undecanoic acid (PFUnDA)		564.09	Insoluble in water	160	1.75 g/cm³
Perfluoro dodecane acid (PFDoDa)		614.01	Insoluble in water	245	1.76 g/cm³
Perfluoro butane sulfonic acid (PFBS)		300.01	Water soluble	211	1.811 g/mL at 25 °C

PFAS type	Structure	Molecular weight (g/mol)	Solubility in water	Boiling point (°C)	Density
Perfluoro hexane sulfonic acid (PFHxS)		400.11	Water soluble	238	1.84 g/cm ³
Perfluoro octane sulfonic acid (PFOS)		500.13	Water soluble	133	1.8 g/cm ³

PFASs are widely circulated in the biosphere due to their unique physical and chemical properties. Researchers have detected PFAS almost everywhere, including in agricultural soil, surface and groundwater, air, seafood, and in the blood of wildlife. Humans are easily exposed to PFAS in daily life. Table 2 lists the use of PFAS in different industries:

Table 2. Use of PFAS in different industries [8].

Industrial PFAS	Applications	References
Textile and leather	Used in Shoes, car seat covers, carpets, umbrellas, Parasols, bags, tents, outer membranes and sails as oil, dirt and water repellent.	[14]
Cosmetic products	Body lotions, sunscreen, cosmetic products contain Polyfluoroalkyl phosphate as emulsifier, oil and water repellent and viscosity regulators.	[15]
Electronic components and equipment	As fluoropolymers does not conduct electricity, they are used in PVDF films and circuit board. Also used in scanners, mobile phones, printers and digital cameras.	[16]
Paper and Food Packaging	Used as water and grease repellent in paper and food packaging, popcorn bags, masking papers, cartons, plates and containers.	[17]
Household products	Used in paints, cooking vessels, inks, car care products, window polish, waxes and floor polish	[18]
Fire fighting foams	Class B Foam	[19]

The content of PFAS in water bodies is very high. Different types of PFAS enter water bodies from different sources, including surface water or groundwater, thereby affecting the health of humans and animals and causing damage to the ecosystem. In industry, PFAS will enter the aquatic system during the production process of aqueous film-forming and fluoropolymer manufacturing plants, electronic and electrical equipment manufacturing, electroplating, refineries, oil, natural gas, textile industry, wood industry and other industries, polluting water resources. Other sources of PFAS in water bodies are cosmetics, paints, biocides, fabrics and building materials. Municipal dumps, biosolids, landfills, and wastewater treatment plants also cause significant diffusion of PFAS

contamination of soil and water. Low concentrations of PFAS in household waste can accumulate in biosolids after diffusion. However, sewage and wastewater treatment plants also cannot remove PFAS. Domestic waste contains antifouling and hydrophobic coatings on various packages with high concentrations of PFAS used daily by residents. After domestic waste is landfilled, PFAS in it seeps into groundwater. Fabrics, paints and building materials contain long-chain PFAS, and other industrial waste and household waste contain higher proportions of short-chain PFAS, which are more difficult to remove.[20]

PFAS in rainwater mainly comes from agricultural wastewater, domestic and industrial wastewater and landfill leachate. The concentration of PFAS in rainwater is lower than that in landfill leachate and industrial wastewater, but both long-chain and short-chain PFAS were detected in rainwater samples. Short-chain PFAS are more abundant and widespread in surface water. Long-chain PFAS are more likely to be deposited, while short-chain PFAS are more mobile in the environment. In agricultural production, the use of chemical fertilizers, wastewater irrigation, atmospheric decomposition, sewage, sludge and pesticides can cause PFAS pollution to soil and water bodies. PFAS comes from various industries, agriculture, manufacturing, use and disposal of daily necessities, and then enters soil and water bodies. Adsorption, distribution, and complexation reactions prevent PFAS from being decomposed, thus causing persisting toxicity.[21]

PFAS circulates in both groundwater and surface water. PFAS in groundwater can lead to contamination of drinking water and irrigation water into crops. PFAS moves more widely and persists longer in groundwater. Surface water can also cause drinking contamination or accumulate in the human body through the food chain. [22]

Humanity's annual large-scale use of PFAS results in the presence of PFAS in the earth's environment. PFAS is difficult to degrade in the natural environment and its biological half-life is very short. People in all industrialized countries have PFAS being detected in their blood. Figure 2 depicts the routes and transport of PFAS and their arrival in human food.[10] The hazards of PFAS have been widely studied, but due to the reasons of a shortage of funding, the lack of unified research standards in the academic community, and background contamination of laboratory materials, the toxicity of PFAS is still not very clear.

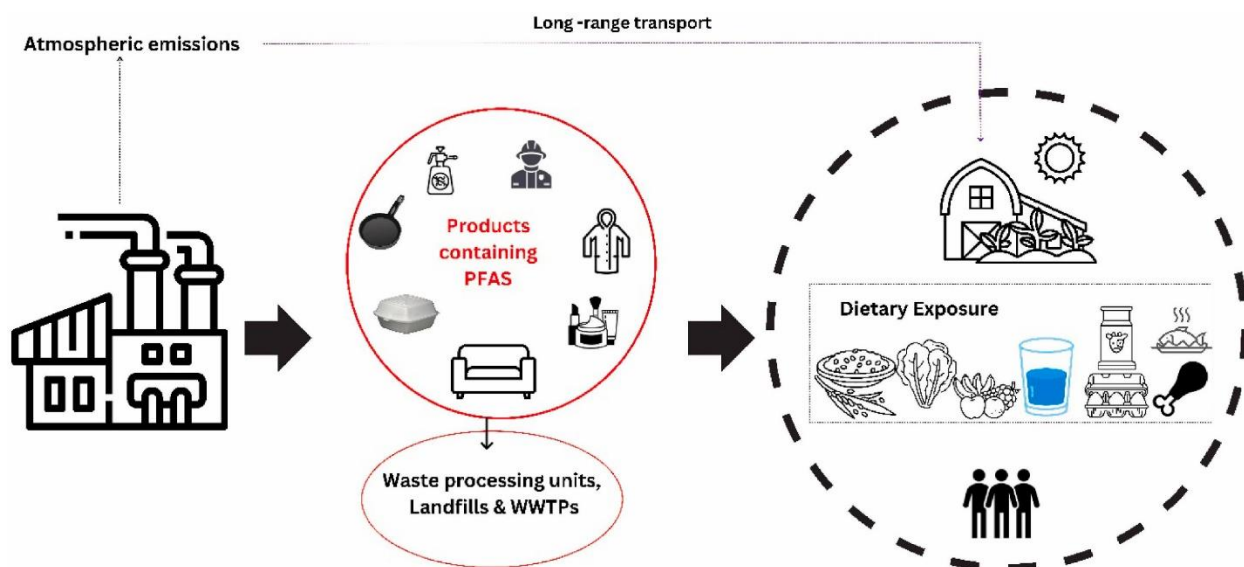


Figure. 2. Emission, transport, route, and human exposure of the PFAS (Reprinted with permission [8]).

The toxicity of PFAS includes ecotoxicity, animal toxicity and human toxicity.

PFAS are produced, used, and discarded by humans, and then spread to all corners of the biosphere along with the global water circulation system. It has been found that PFAS in the soil can be absorbed by plants. Short-chain PFAS is more likely to penetrate into the soil. Short-chain PFAS in agricultural soil can also get into the leaves through the transpiration of plants and water molecules. Persistent pollutants containing PFAS in irrigation water will eventually remain in the low humus soil layer. This means that, the ecotoxicity of PFAS exists in soil and water sources of the ecosystem.[11]

The impact of PFAS on wildlife has also been confirmed by research. The researchers cultured marine organisms in a solution containing difluoro [2,2,4,5-tetrafluoro-5-(trifluoromethoxy) 1,3-dioxolane-4-yl], a PFOA and PFAS alternative. It was found that oxyacetic acid (C6O4) in seawater would change the microbiota in the digestive system of marine animals, thereby affecting their health. PFAS will affect the gene transcription expression of clams and cause genetic variation in clams. Also, PFAS affects pregnancy and liver function in mice. These studies show that PFAS are highly toxic to wildlife in different ecosystems.[12]

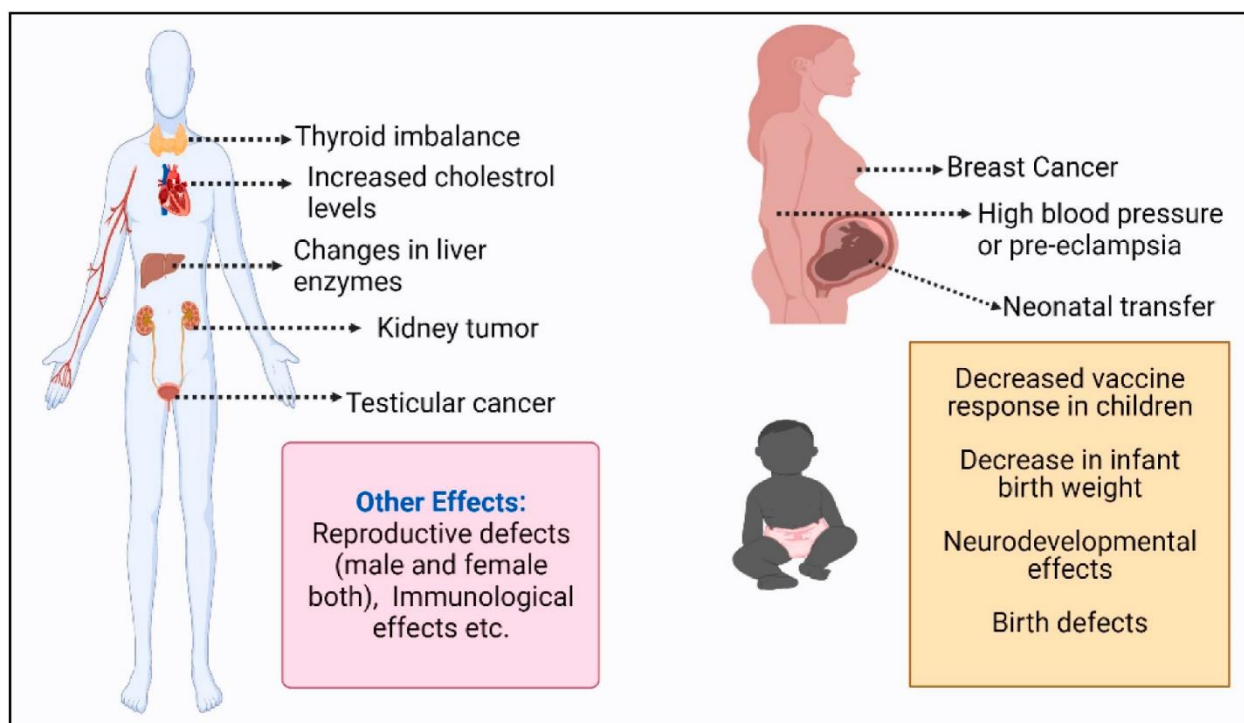


Figure. 3. Toxicities, health problems and comorbidities associated with the PFAS exposure (Reprinted with permission) [8].

Exposure to PFAS has adverse effects on human health. There is still little awareness of the dangers of PFAS, even though American companies continue to produce new PFAS every year.

Scientists' research on the toxic effects of PFAS mainly comes from PFOA and PFOS. Although countries around the world have stopped producing PFOA and PFOS, levels in human blood are still detectable. Emerging PFAS are also present in significant amounts in human blood. Based on existing research, PFAS may cause the following pathologies after being consumed by humans:

- Impact on baby's development
- Reduction of a woman's chance of pregnancy
- Reduced baby's birth weight
- Interference with the body's natural hormones
- Increased cholesterol levels
- Adverse effects on the immune system
- increased risk of cancer
- changes in liver enzymes
- Hormone disorders and increased risk of thyroid disease

- High blood pressure or preeclampsia during pregnancy
- Reduced vaccine response in children
- Increased risk of kidney or testicular cancer [13]

Due to the widespread existence and biological toxicity of PFAS, regulatory agencies are increasingly paying attention to PFAS contamination. It is urgent to deal with the pollution caused by PFAS. PFAS is converted into PFAA in the environment and within organisms. There are several ways to remove PFAS, but each has some drawbacks:

- Granular activated carbon (GAC) is the most commonly used method to remove PFAS pollution from water. GAC is effective for long-chain PFAS but has a low removal efficiency for short-chain PFAAs;
- Anion exchange resins are effective at removing a wider range of long and short chain PFAA, but still cannot handle the shortest chain PFAA;
- Chemical oxidation is suitable for removing some PFAAs, but it can form shorter chain PFAAs and may also cause rebound;
- Electrochemical oxidation destroys the structure of PFAS, but produces unwanted by-products;
- Heat treatment of PFAS is completely unrealistic to treat PFAS contamination as the required temperatures are too high.[23]

Based on the need to remove PFAS and the development of modern nanoscience, the use of nanoparticles to remove PFAS water pollution has become a feasible method. The large surface area and quantum properties of nanoparticles will play a huge role in adsorbing PFAS from wastewater and drinking water. Different nanoparticles have unique advantages and disadvantages in applications. Nanoparticles adsorb PFAS through their hydrophobic and electrostatic interactions. The high electronegativity and ionization of PFAS creates a negatively charged shell around PFAS, which makes it easier for PFAS to be captured by metal nanoparticles. Ion exchange and hydrogen bonding also help nano adsorbents remove PFAS. Table 3 summarizes the major findings of nano adsorbents for PFAS removal in recent years.[24]

Table 3. Recent reports on nanoparticle based PFAS removal strategies[8].

Type of nanoparticles	Major findings of the study	Reference
Fluorinated carbon nanotubes/silk fibroin (F-CNTs/SF) nanofibers	Successful in detecting even trace amounts (0.006–0.090 $\mu\text{g L}^{-1}$) of PFAS in water. Composite formation improves the mechanical strength of SF nanofiber.	[25]
Nano-MgAl ₂ O ₄ modified carbon nanotubes (CNTs)	Successful in removing 100 % Perfluorooctanoic acid (PFOA) from water in 3.5 hours of treatment	[26]
Silver nanocomposite - activated carbon	Maximum adsorption of 454.1 mg/g and 321.2 mg/g were recorded for perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA)	[27]
Magnetic γ -Fe ₂ O ₃ nanoparticles grafted with N-(2-aminoethyl) aminopropyltrimethoxysilane (AE-APTMS)	Maximum adsorption capacity of 78 % for perfluorooctane sulfonate (PFOS) and 65 % for perfluorooctanoate (PFOA)	[28]
Fe ₃ O ₄ nanoparticle composite loaded on granular activated carbon (GAC)	Reported to have 28.8 % higher adsorption capacity than the parent GAC at final pH 4.0 in removing perfluorooctanoate (PFOA)	[29]
Multiwalled carbon nanotubes (MWCNTs) doped with metallic nanoparticles	Observed to have high efficiency in removing PFOA. PFOA removal was observed to be regulated by intra-particle diffusion	

In this work, we propose to use copper cysteamine (Cu-Cy) nanoparticles to effectively break down PFAS. The molecular formula of copper cysteamine (Cu-Cy) is $\text{Cu}_3\text{Cl}(\text{SR})_2$ ($\text{R} = \text{CH}_2\text{CH}_2\text{NH}_2$). Cysteamine is an organosulfur compound with the formula $\text{HSCH}_2\text{CH}_2\text{NH}_2$. The sulfur group and amine group of cysteamine in the Cu-Cy we use are both bonded with copper ions, and the valence state of copper ions is positive monovalent. Copper cysteamine nanoparticles are photosensitizers that were initially developed to treat cancer and have been proven effective in photodynamic therapy for cancer and photocatalysis. Using Cu-Cy nanoparticles to decompose PFAS under photocatalysis can take full advantage of the nanoparticles' postal and chemical reactions.[30]

2. Nanoparticles for PFAS removal

For refractory organic pollutants in sewage, such as PFAS, there are existing methods, such as adsorption, precipitation, filtration, biological treatment, advanced oxidation process (AOP), etc.

Among them, AOP is an emerging method that can effectively remove PFAS from water. The principle of AOP is to degrade and remove organic pollutants by generating highly oxidizing free radicals (mainly OH). It converts organic matter into harmless substances such as H₂O and CO₂. AOP needs to be able to operate at ambient temperature and may be combined with other decontamination methods in practical applications.

The Fenton-based oxidation system is the most convenient and commonly used AOP, where H₂O₂ catalyzes the generation of OH oxidation radicals. Among the Fenton oxidation method, the Fe-Fenton system (H₂O₂ and Fe catalyst) is the oxidation decontamination technology most recognized by scientists and the most skillfully operated. The Fe-Fenton system is widely used to remove PFAS in practical applications, but it has two serious limitations: (1) The narrow pH window (2.5~3.5) increases the cost of equipment and the economic burden of maintaining PH; (2) Removing PFAS contamination creates new contaminants. Our solution is to use copper instead of iron, since copper-based oxidation systems are just as efficient and have a wide pH window when treating wastewater. The reaction speed of copper ions and hydrogen peroxide is 150 times that of the reaction speed of iron ions and hydrogen peroxide.

Copper-based heterogeneous catalysts have also been developed to address organic pollutants. Although they are highly efficient at degrading organic matter, these copper-based heterogeneous catalysts suffer the complicated synthesis process. We proposed a more direct and efficient method to synthesize copper-based heterogeneous catalysts, e.g. Cu-Cy. The advantages of Cu-Cy are: 1) it does not require complicated synthesis methods; 2) it does not pollute the environment; and 3) it does not require high-cost equipment, thus leading to low-cost production. Cu-Cy has been shown to be effective in killing cancer and bacterial cells in photodynamic therapy. Now, using Cu-Cy nanoparticles to deal with PFAS is another innovative application. The catalytic degradation efficiency of Cu-Cy is positively related to the amount of microwave radiation in the environment. Cu-Cy under different excitation sources can generate reactive oxygen species (ROS), which will efficiently degrade stable organic pollutants in water. Copper cysteamine (Cu-Cy) nanoparticles have been found to produce various types of reactive oxygen species (ROS) upon stimulation by ultraviolet light, microwaves, X-rays, and ultrasound when used

in the treatment of cancer and infectious diseases. Therefore, when studying Cu-Cy nanoparticles (NP) to treat PFAS water pollution, we will study the ability of ultraviolet, microwave, X-ray, and ultrasonic waves, and their different combinations to degrade PFAS.

3. Synthesis and characterization methods of Cu-Cy nanoparticles

3.1. Aqueous synthesis of Cu-Cy nanoparticles

3.1.1 Materials

The following chemicals are used for Cu-Cy synthesis: Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), cysteamine hydrochloride, sodium hydroxide (NaOH), polyethylene glycol 4000 (PEG-4000).

3.1.2 Synthesis of Cu-Cy Nanoparticles in Aqueous Solution

Copper cysteamine iodide will glow yellow luminescence under ultraviolet light. The method presented here is to synthesize Cu-Cy nanoparticles using a hydrolysis method, i.e. in water.

First, three substances are needed to prepare cysteamine copper iodide: a copper source, a cysteamine halogen, and a substance to control mild dispersion. In this case, blue copper chloride dihydrate will be used. In the experiment, the molar ratio between copper chloride and cysteamine needs to be measured as 1 to 2. In this experiment, 683 mg of polyethylene glycol (PEG, the chain molecular weight value is 3400) was added. Finally, a source of iodide is required, namely potassium iodide.

Put 20 ml of deionized water in a small beaker, add a magnetic rotor to stir, and place a pH tester to detect the pH concentration during the experiment. We then dissolved 170mg copper fluoride in 20 milliliters of water DI water. The reason is that solutions with higher copper ion concentration contribute to the monodispersing of nanoparticles. We wait for it to finish dissolving until the solution takes on a nice turquoise color. Then we add 226 mg of cysteamine hydrochloride to the beaker so that the molar ratio of copper chloride and cysteamine is 1 to 2. After adding cysteamine hydrochloride, the solution becomes more acidic and the pH decreases. Now the system is kind of sticky with a pH value around 1.91. We add 682 mg PEG. Finally, sodium hydroxide is added to adjust the PH to 7. This is achieved by adding sodium hydroxide quickly at the beginning, and slowly drip it in after the pH reaches 5. Color can also be used as an indicator of pH, because as the pH of a solution approaches neutralization, it will turn golden. Afterward, the magnetic rotor will stir the solution for 3 minutes (Fig. 4).

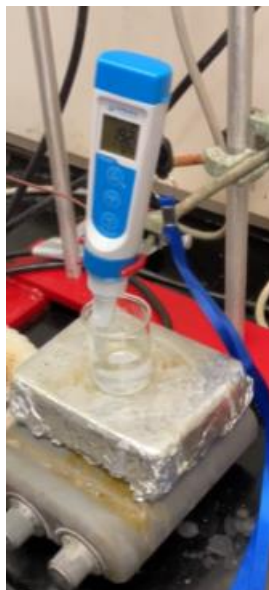


Figure 4. A solution stirring device with a PH tester placed above the solution.

After PH neutralization, the solution will be placed in a three-neck flask, which is placed in the thermal insulation shell. The middle outlet of the flask is connected to the condenser tube. The three-neck bottle wrapped in the insulating shell will be placed on the heating table. We place a round-bottomed metal magnetic stirring rod into the three-neck flask and pour the neutralized solution into the flask from the left outlet. The three-neck flask is sealed with nitrogen with a cleaned thermometer pointer inserted into the solution from the right outlet (Fig. 5). We turn on the stirrer switch and make the stirring rod rotate at 600RPM. We then turn on the heating switch to raise the temperature of the solution to about 90 degrees Celsius and maintain it. At the same time, we increase nitrogen by slowly opening the main valve and observe the oil on the bubbler until we see flow, indicating that the nitrogen has successfully sealed the reaction bottle. We also open the condenser coil to ensure that all water condenses back into the reactor.

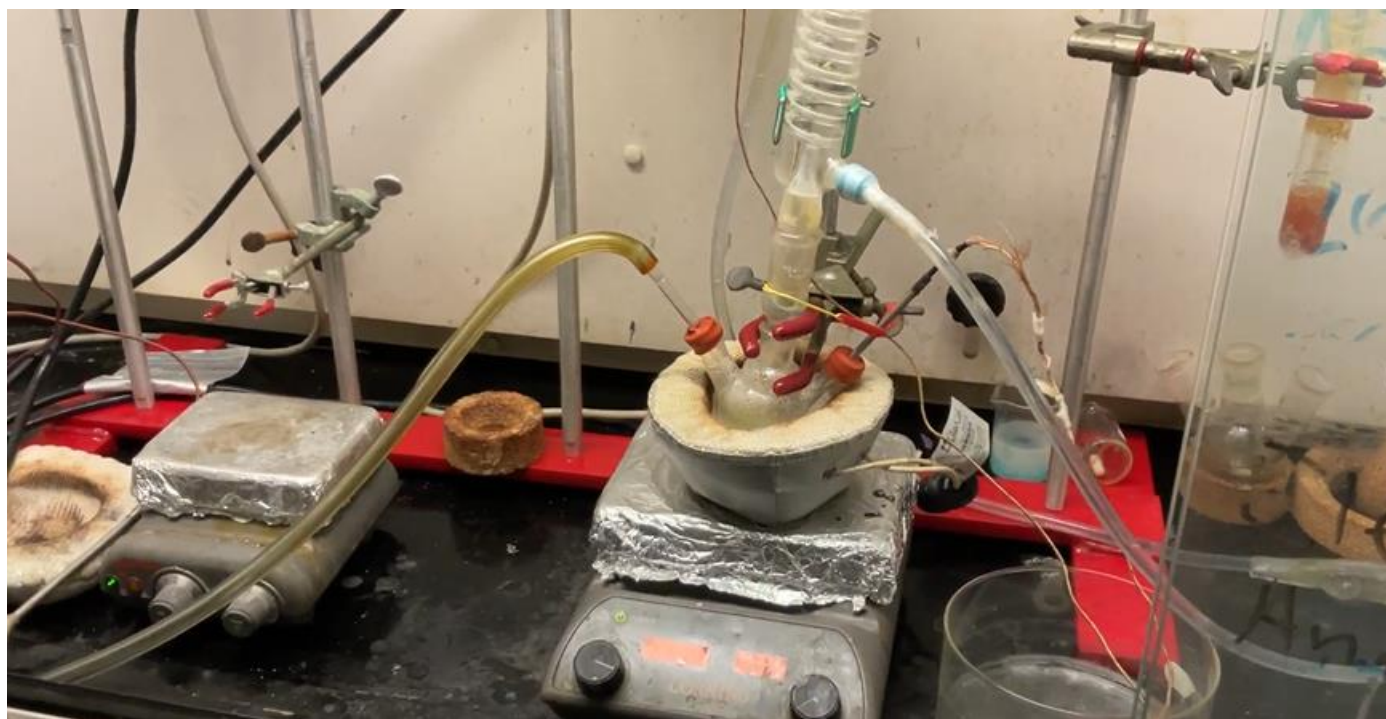


Figure 5. A three-neck flask was used to produce Cu-Cy nanoparticles. Nitrogen is input from the left outlet and output from the condenser tube (middle outlet). The rubber cap is used to hold the thermometer on the right outlet to measure the solution temperature.

During the heating process, to ensure safety, the lights should be turned off and protective glasses should be worn. An ultraviolet lamp is used to shine into the bottle to check the luminescence (Fig. 6). After seeing the yellow glow, we turn off the heating switch and quickly lower the temperature to room temperature. It is important not to measure the luminescence too often, as UV light may affect the reaction. In this experiment, after the solution temperature reached 90 degrees, the luminescence phenomenon can usually be seen after maintaining the temperature for 5 minutes.

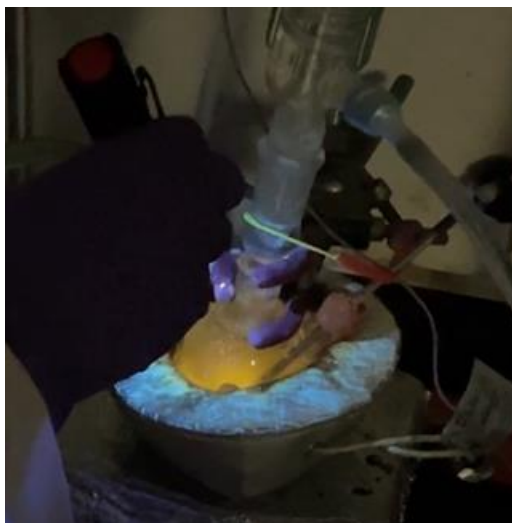


Figure 6. After heating the solution at 90 degrees Celsius for five minutes, an ultraviolet light is used to illuminate the three-neck flask in a dark environment to determine the synthesis of Cu-Cy nanoparticles.

After turning off the heat, we turn off water and nitrogen. We need to stop the reaction by rapidly lowering the temperature (so called quenching). Now that the formation of nanoparticles has stopped, we check its luminescence which should be very yellow. This is the ideal situation for successful nanoparticle production. The only drawback of this synthesis protocol is no way to replace the chlorine source. If we do element mapping on the nanoparticles, we will see some chlorine.

We wait until the temperature reaches around 30 degrees Celsius before removing the nitrogen environment as the Cu-Cy iodide will lose its luster in oxygen. After it cools down, it is washed three times with deionized water to remove any remaining precursors, then centrifuged at 3000 RPM for 10 minutes per cycle for three to four cycles. After drying in vacuum (avoid oxygen), the Cu-Cy nanoparticles can be obtained.

3.2 Characterization of Cu-Cy Nanoparticles

The synthesized Cu-Cy nanoparticles are characterized using UV-visible (UV-Vis) absorption and fluorescence spectra and X-ray powder diffraction (XRD).

For UV-Vis absorption and fluorescence spectroscopy, the synthesized Cu-Cy nanoparticles are suspended in deionized water and photographed using a Shimadzu RF-5301PC fluorescence spectrophotometer. The emission spectra of the samples dispersed

in deionized water are recorded by exciting the samples with a visible light with 365 nm wavelength, whereas the excitation spectra are obtained using emission wavelengths of 607 nm and 633 nm.

For XRD, the Cu-Cy nanoparticles are made into a solution, then dropped onto a glass substrate. The XRD sample can be obtained after drying at room temperature. The sample is subjected to X-ray powder diffraction in the 2θ angle range from 5 to 70, with a voltage of 40 kV, a current of 40 mA, and a scanning speed of 0.02 degrees/second. The XRD experiment is carried out by a Rigaku Ultima IV diffractometer.

3.3 Test of PFAS degradation performance of Cu-Cy nanoparticles

We prepare solutions with the following concentrations in DI water: 20 μ M PFAS, 3 mM H₂O₂, 333 μ g/ml Cu-Cy, Britton-Robinson buffer, 1 μ M Eosin Y, 20 μ M PEI. We add a certain amount of each concentration of solution into 7 small tubes according to Table 4. The total volume for each of the 7 newly obtained solutions after addition is 3000 μ L, which is easy to calculate and obtain the desired concentration.

Sample #	20 μ M PEI (μ L)	1mM Eosin-Y (μ L)	B-R Buffer (μ L)	3mM H ₂ O ₂ (μ L)	333 μ g/ml CuCy (μ L)	DI water (μ L)	20 μ M PFAS (μ L)
1	1000	300	200	-	-	1050	450
2	1000	300	200	500	-	1000	-
3	1000	300	200	-	500	1000	-
4	1000	300	200	500	-	550	450
5	1000	300	200	-	500	550	450
6	1000	300	200	500	500	500	-
7	1000	300	200	500	500	50	450

Table 4. The amount of each raw material used to prepare seven solutions.

After preparing the solution to be observed, we use a Shimadzu spectrophotometer (UV-2450 UV-Vis) to record the absorption spectrum. This design of the experiment enables us to clearly obtain multiple sets of control results. We can obtain the degradation of PFAS under different conditions, such as with and without Cu-Cy catalysis, or with and without hydrogen peroxide.

4. Results and discussion

4.1 Synthesis of Cu-Cy nanoparticles

The synthesis of Cu-Cy nanoparticle is not difficult and can be easily scaled up in the future to treat water pollution. Cu-Cy nanoparticles were successfully synthesized by wet method. Because the synthesized Cu-Cy nanoparticle sample shows a bright yellow color under ultraviolet light, as shown in Fig 7. By calculating and weighing, the molar ratio of copper ions and cysteamine is 1:2. As described in the above experimental process, the synthesis of Cu-Cy nanoparticles only requires stirring, detecting, adjusting the pH, and maintaining the solution at 90 degrees under the protection of a nitrogen environment for 5 to 10 minutes. Under the illumination of a UV lamp (wavelength of about 365 nm), if the solution appears yellow, it can be initially determined that the synthesis process is successful as shown in Fig. 6. The pH range is adjusted from 1.9 at the beginning to about 7 at the end. Since the equipment requirements and the cost are low, and the synthesis time is very short, the possibility of large-scale production in the future is very high. The large-scale production of Cu-Cy nanoparticles and its application in the treatment of PFAS pollution in water can be easily achieved.



Figure 7. UV light (365 nm) to quickly test the synthesized Cu-Cy. (Yellow indicates the success of the synthesis).

4.2 Characterization of Cu-Cy nanoparticles

To verify that the obtained sample is Cu-Cy, two characterization techniques are used. Fig. 8 upper is the result of UV-Vis fluorescence spectrum of the sample. As shown in the upper figure, the sample is dispersed in DI water with the maximum absorbance wavelength of the solution is 365nm365nm., which is in a good agreement with previously published results Fig. 8 bottom.[31]. It can be confirmed that the sample synthesized by the water method is Cu-Cy.

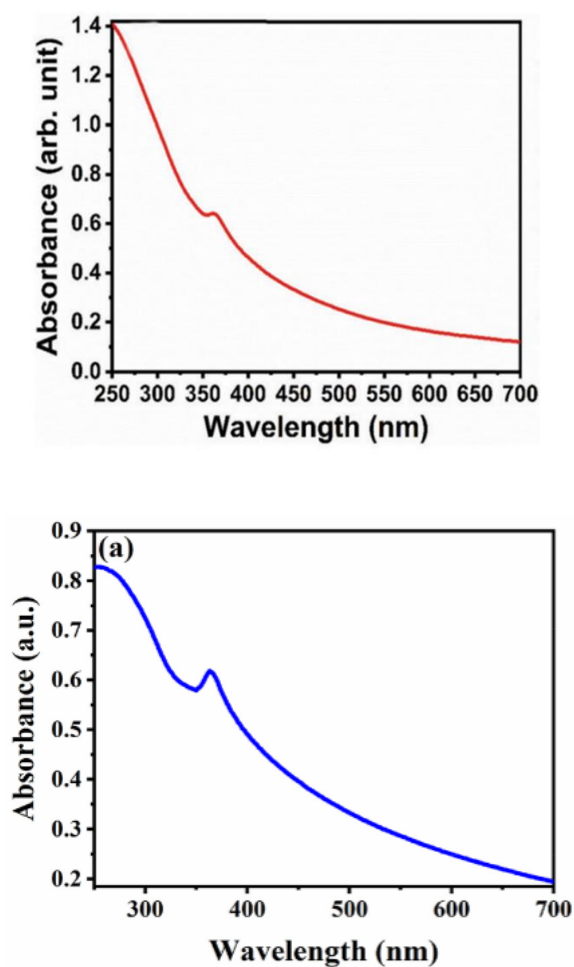


Figure 8. Upper: UV-Vis absorption spectrum of the Cu-Cy nanoparticles dispersed in DI water in this work; Bottom: UV-Vis absorption spectrum of the Cu-Cy nanoparticles in published paper from [31].

Fig. 9 upper is the result of XRD diffractogram of the sample. Again, it is consistent with the results in literature [31] (Fig. 9 bottom) and there are no redundant peaks. This result shows that the Cu-Cy nanoparticles synthesized in the experiment are very pure.

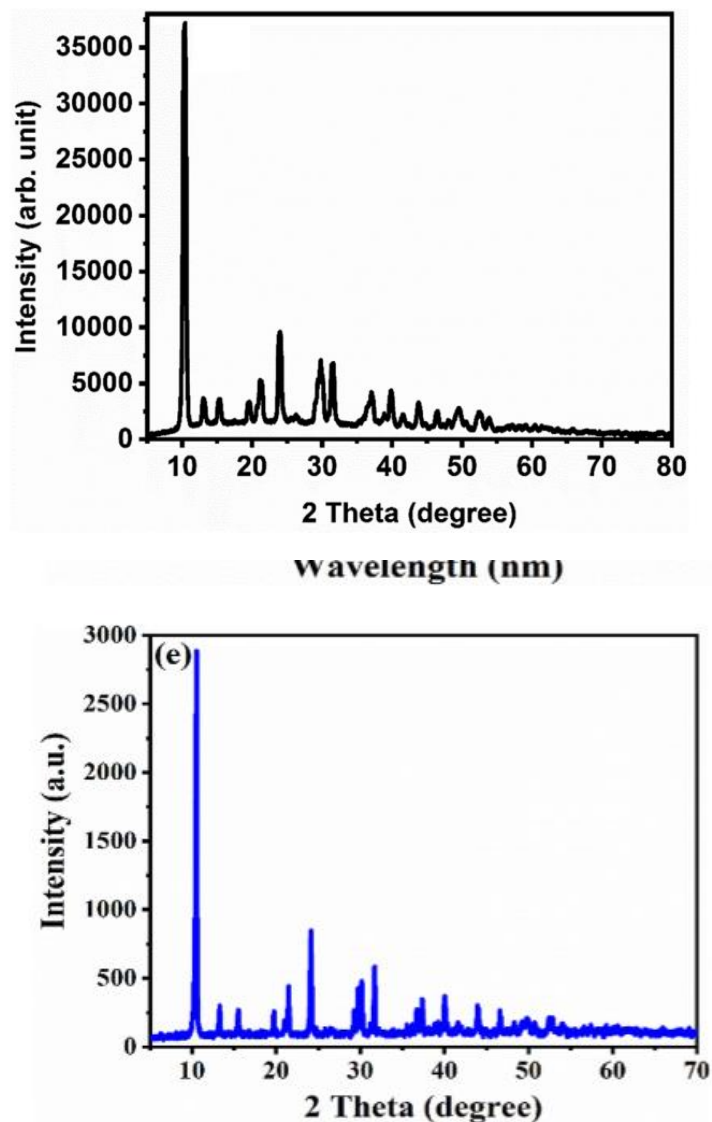


Figure 9. Upper: XRD pattern of the synthesized Cu-Cy nanoparticles in this work; Bottom: XRD pattern of the synthesized Cu-Cy nanoparticles from [31].

4.3 Cu-Cy degradation ability results of PFAS

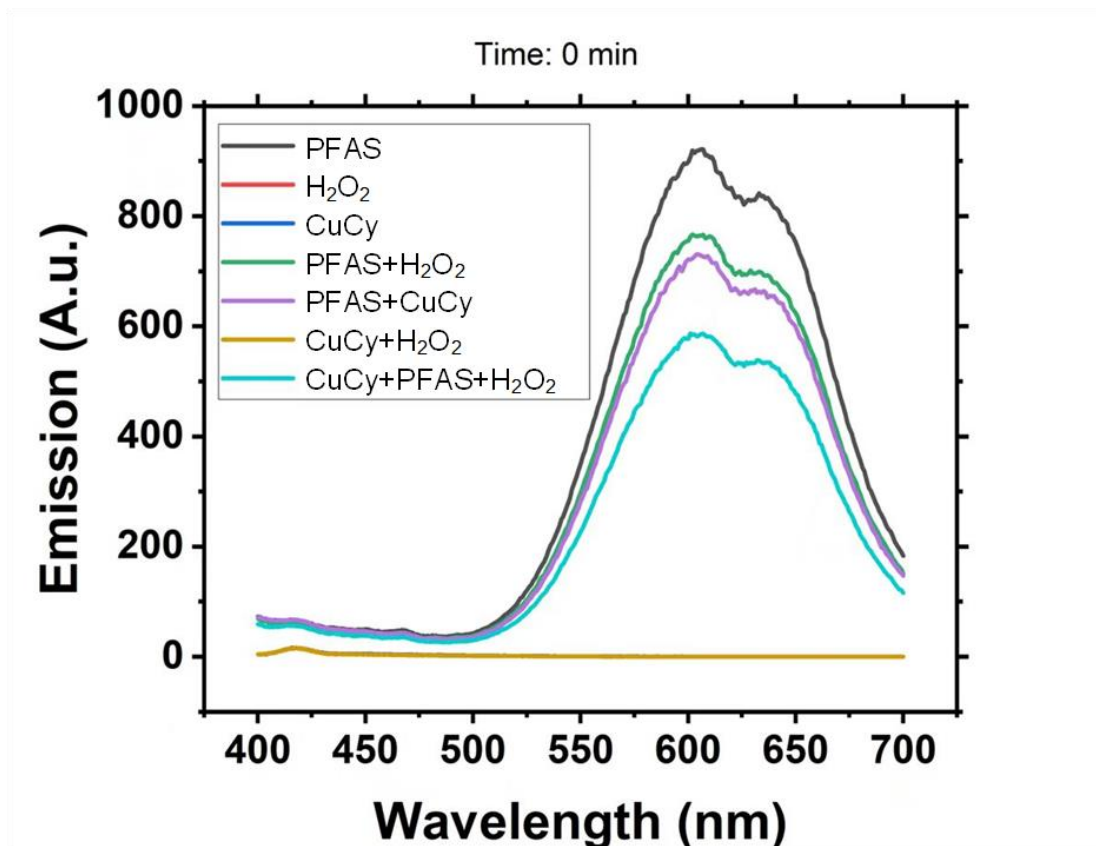


Figure 10. UV absorption spectra of Solutions with 7 samples right after mixture (0 minute).

In Fig. 10, Eosin-Y and PEI are already present in the all solutions.. In the solution where only PFAS is added, the emission is the highest. The order of increasing emission with PFAS from the bottom line is: PFAS+H₂O₂, PFAS+Cu-Cy, PFAS+Cu-Cy+H₂O₂. The bottom line indicates that the emission is 0: only Cu-Cy, only H₂O₂, and Cu-Cy+H₂O₂.

The principle of detecting the PFAS concentration in the solution is that Eosin-Y and PEI without PFAS will not emit light, but when PFAS is added, they will emit light. Therefore, the higher the emission, the higher the concentration of PFAS. The three lines with Emission approximately 0 occur for only Cu-Cy, only H₂O₂, and only Cu-Cy+H₂O₂ in the solution. It can be verified that Cu-Cy and H₂O₂ exist alone and together will not affect emission. It can be guaranteed that emission in the experiment is only related to the PFAS concentration. As can be seen in the upper part of the figure, the emission from large to small

is PFAS, PFAS+H₂O₂, PFAS+Cu-Cy, PFAS+Cu-Cy+H₂O₂. This shows that H₂O₂ will decompose PFAS. At this concentration, the ability of Cu-Cy alone to promote the decomposition of PFAS is stronger than that of H₂O₂ alone. The lowest PFAS+Cu-Cy+H₂O₂ indicates that Cu-Cy and H₂O₂ have mutually increasing effects on PFAS degradation. This is consistent with our expectations.

Fig. 11 shows emission intensity of seven samples after 1 hour, the shape of each line is consistent with Fig. 10, and the total emission has decreased. Emission from high to low is PFAS, PFAS+H₂O₂, PFAS+Cu-Cy, PFAS+Cu-Cy+H₂O₂. The emission of solutions with only Cu-Cy, only H₂O₂, and Cu-Cy+H₂O₂ is still 0. Comparing Fig. 10 and 11, the following conclusions can be drawn:

1. The emission of the solution is not affected by the presence of Cu-Cy and H₂O₂ alone or together from 0 minutes to 1 hour. The emission is only related to the concentration of PFAS.
2. H₂O₂ will decompose PFAS in a small amount. Cu-Cy has a stronger catalytic decomposition of PFAS than H₂O₂. The decomposition of PFAS is strongest when they coexist.
3. According to Figure 10 and Figure 11, the emission of the solution containing only PFAS after 1 hour has dropped by a certain amount compared with that just mixed (0 minute). Since PFAS is a very stable substance, this experimental phenomenon is different from the theory. The reason may be that the emission is not the direct measure of the PFAS concentration. The reaction between PFAS and Eosin-Y/PEI may reduce the emission intensity. Although this compromises the absolute measurement of PFAS concentration, the relative order of PFAS removal effectiveness from H₂O₂, Cu-Cy, and their combination should not change. In future experiments, EPA suggested direct measurement of PFAS concentration could be considered.

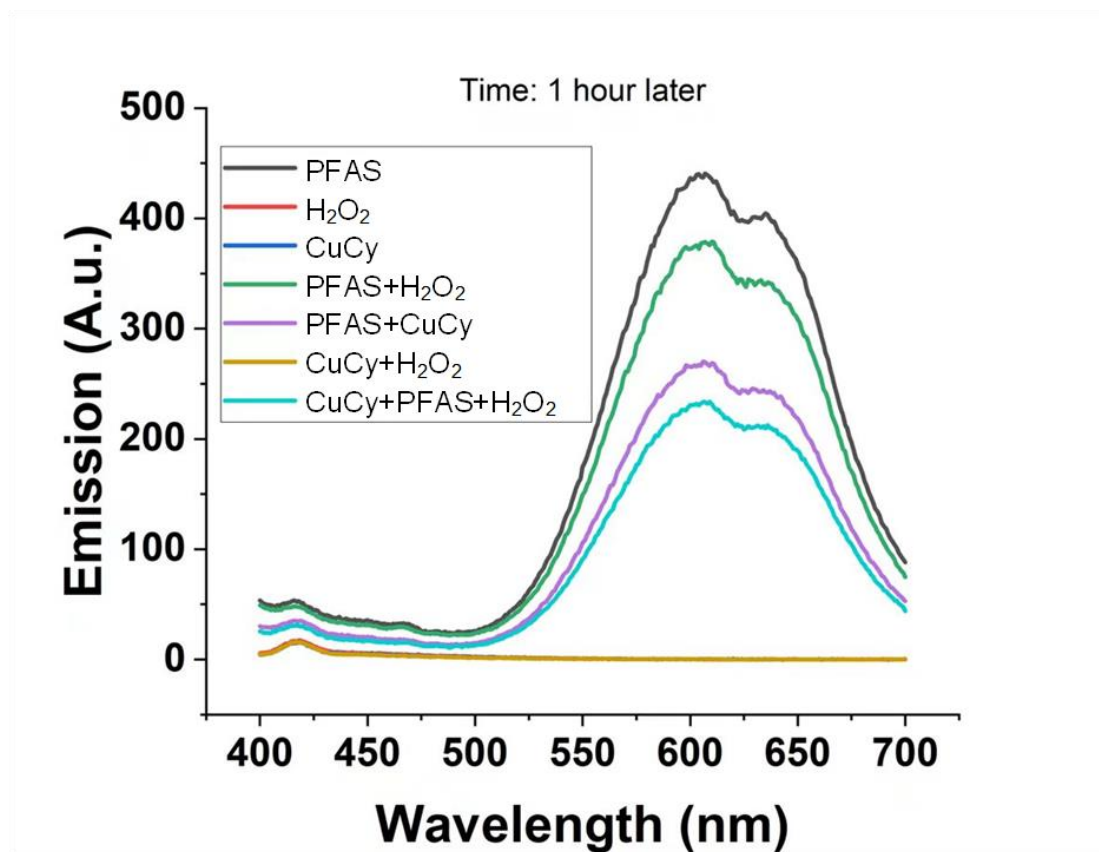


Figure 11. UV absorption spectra of Solutions of 7 samples after 60 mins.

5. Conclusion and future work

In this work, we successfully synthesized the Cu-Cy nanoparticles using a simple and cost-effective aqueous method. These nanoparticles were measured using UV-Vis and XRD to verify their characteristics, which matched previously published results. The initial water treatment experiments were conducted to show that Cu-Cy could decompose PFAS faster than the conventional H₂O₂ using an indirect measure of UV absorption spectra.

To refine the experimental procedure, it's imperative to employ more precise methodologies for assessing PFAS concentrations, thereby gauging the effectiveness of Cu-Cy in catalytic degradation. Cu-Cy induces ROS to dismantle PFAS and can be further potentiated by microwave, ultrasound, and ultraviolet irradiation, alongside H₂O₂ augmentation, amplifying its catalytic prowess. Subsequent investigations should delve into the synergistic effects of these stimuli on Cu-Cy's PFAS decomposition capacity, either in isolation or in tandem. Such endeavors are pivotal for optimizing PFAS decomposition devices in water treatment facilities and ensuring both cost-effectiveness and efficiency in real-world scenarios. Given PFAS's ubiquitous presence in water sources, scalability in Cu-Cy nanoparticle production is paramount for practical deployment. Furthermore, efforts should focus on engineering Cu-Cy nanoparticles that exhibit recyclability, to permit multiple uses in catalytic PFAS degradation, thereby enhancing sustainability in water treatment strategies.

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