

Research progress of uranyl photocatalyst-promoted organic transformation

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Abstract: Nowadays, using uranium to enhance the quality of life is no longer a problem as controllable nuclear fission and other technologies have been invented. However, most forms of uranium in nature exist as U^{238} instead of U^{235} . Unlike U^{235} , U^{238} cannot generate chain nuclear fission, which means that it loses the most common use of uranium. But with the development of investigation in the realm of uranyl, a common compound of uranium, scientists have found uranyl could be used as an efficient photocatalyst, which could make use of U^{238} . This study explores the photocatalyst potential of uranyl complexes and summarizes their role in promoting various organic reactions. This review sheds light on the mechanisms and applications of uranyl-catalysed organic transformations, providing insights into the ongoing development of sustainable and efficient catalysis.

Keywords: Uranyl-photocatalysis, photoredox catalysis, hydrogen atom transfer, C-H activation, oxygenation

1. Introduction

Credited to the German chemist Martin Klaproth with the first documented identification of uranium in 1789, uranium has achieved a special status in the fields of nuclear energy, scientific research, and environmental studies due to its ability to confer favorable properties on fundamental constituents within their respective domains. In its natural state within the Earth's crust, uranium comprises predominantly two isotopes: uranium-238 (U^{238} , constituting 99.275%), and uranium-235 (U^{235} , making up approximately 0.72%)^[1].

Beyond its historical discovery, U^{235} serves a dual role within nuclear power plants and nuclear weapons, exploiting its exclusive properties in distinct ways. In the first place, the fission of uranium atoms replaced the typical combustion of coal or gas. This sets off a process in which the U^{235} atoms split, generating heat. The heat is then captured to produce steam, which in turn powers a turbine connected to a generator, enabling the creation of electricity. The resulting thermal energy is directed to produce steam that drives a turbine linked to a generator, ultimately resulting in efficient electricity generation. Similarly, nuclear weapon follows a parallel curriculum, using the fission energy high-level radioactive of U^{235} .

U^{235} is the fissile isotope used in nuclear reactions. Uranium enrichment is the process of increasing the concentration of U^{235} in uranium. This is typically done for nuclear reactor fuel or the production of nuclear weapons. After the uranium enrichment process, the remaining uranium that has a lower concentration of U^{235} compared to natural uranium is called depleted uranium (U^{238}). Depleted uranium is primarily composed of U^{238} , with a much lower proportion of U^{235} (International Atomic Energy Agency). While depleted uranium has been controversial due to its potential health and environmental risks, it has been applied in various fields, including various industrial and military applications^[2]. Depleted uranium had an application as a fluorescent additive in dental porcelain crowns (although this is no longer in use). Due to its price, accessibility and pyrophoricity, depleted uranium as conventional weapons has been used as ballast in the rudders and flaps of commercial aircraft and forklifts, and even in the keels of sailing yachts. In addition, depleted uranium has found applications as a radiation shielding material in the medical imaging domain, including CT scanners. This is on account of its dense composition and effective capacity to absorb radiation. Its application involves the fabrication of shielding components to ensure the safety of patients and healthcare professionals by minimizing unnecessary radiation exposure^[3]. Within the realm of inorganic uranyl compounds, a distinctive presence is manifested by uranyl compounds. This category showcases polyhedra layers that encapsulate uranyl pentagonal bipyramid trimers, linked solely through shared vertices with other polyhedra^[4].

Uranyl compounds have garnered significant attention due to their potential uses in the realm of functional materials, specifically in areas related to luminescence, photoelectric conversion, and photocatalysis. Uranyl compounds find use as staining agents in the preparation of samples for detailed structural morphology examination, cytochemical analysis, and immunocytochemistry^[5]. Moreover, employing a biofilm-supported ion exchange mechanism, a hydrogen uranyl phosphate-based material is also utilized to effectively extract cobalt, strontium, and cesium from aqueous solution^[6].

Uranyl compounds, featuring the uranyl ion (UO_2^{2+}), display distinctive physical and chemical properties. In terms of their physical properties, these compounds encompass a spectrum of colors ranging from yellow to green, attributed to the optical absorption of uranyl ions. At moderate to high densities, they are of value in applications requiring dense materials, while some exhibit luminescence upon radiation excitation, proving advantageous for sensing. The diverse crystal structure of compounds further influences their properties, and their solubility in water varies from soluble to relatively insoluble forms. On the chemical front, uranyl compounds form coordination complexes driven by their ability to accept electron pairs from Lewis bases as Lewis acids. Their +6 oxidation state affects their chemical behavior, enabling participation in redox reactions that transfer electrons between species. While stability is universal under certain conditions, compounds can react in the presence of appropriate reagents. These properties collectively highlight the multifaceted potential of uranyl compounds across a variety of applications^[1].

2. C-H Activation

Nowadays, the study of photocatalysts has set off a wave, and according to the work of Yu's group^[7] and Capaldo's group^[8], one of the newest and the most effective uses of uranyl is taking advantage to catalyze organic reaction. There are several ways to speed up the reaction by transferring electrons which could help the formation of bonds for photocatalysts while most of them depend on a common procedure called single-electron transfer (SET). SET would be estimated as the simplest operation that moves an electron straightly, but this indeed brings some inadequacies, the available substrates are often limited in a very small range which means such a method has no universality. However, there are some decent alternatives to SET, indirect photocatalyzed hydrogen atom transfer (i-HAT) and direct photocatalyzed hydrogen atom transfer (d-HAT) are two of them. Different from SET, i-HAT, and d-HAT both have a thermal hydrogen atom as a medium of electron transport, which can highly increase the number of usable substrates and the possibility of bond formation, especially the C-C bond, the basic bond of organic chemistry. Nevertheless, they also face some problems preventing the substance from being a beneficial photocatalyst. Although i-HAT is going an intermolecular way which could get in touch with the faraway C-H bond in this molecule, this also means i-HAT is much more complex in internal mechanism than the others, hence is hard to control. The case is not the same when it comes to d-HAT. D-HAT is an easier process due to the added reagent where photocatalyst can break the C-H bonds directly, whereas the d-HAT catalysts are often extremely rare and even need more severe conditions, UV light, particular temperature, and so on, with poor yield.

Gratifyingly, the two teams have found that uranyl nitrate hexahydrate $[\text{UO}_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a compound of uranyl, would be an ideal d-HAT photocatalyst, and the uranyl ion is the photosensitizer. Comparing with other d-HAT substances, uranyl nitrate hexahydrate can be easily produced from its raw material U^{238} at a very low price due to the dominant position of uranium in the environment. More importantly, this would also be the compensation for the inefficient use of U^{238} . Unlike most of the d-HAT catalysts, uranyl nitrate hexahydrate only needs visible light to motivate, which will save a lot of energy than using UV light. In this situation, it makes the best of both worlds. As a photocatalyst, the uranyl ion $[\text{UO}_2^+/\text{UO}_2^{2+}]$ in uranyl nitrate hexahydrate can give out a redox potential of +2.36 V vs. SCE and +2.6 V vs. SHE which is much higher than other photocatalysts. This also makes uranyl nitrate hexahydrate an appropriate catalyst as it can easily create a medial cleavage on the C-H bond by absorbing the hydrogen atom from it.

The establishment of several experiments by the two research groups found the best conditions for uranyl nitrate hexahydrate while catalyzing. Yu's group developed a series of control experiments of the p-QMs alkylation reaction, which involves a radical to react. They demonstrated when the uranyl nitrate hexahydrate is 5 mol% and acetonitrile is the solvent, the reaction will have the highest rate under its autofit environment, using blue light and under argon conditions. Moving to Capaldo's work, they did the same thing to show the preferable situation of uranyl nitrate hexahydrate by setting up Michael's addition reactions with a completely randomized design. However, because the reaction types are different, the most suitable condition for catalyzing the Michael addition reaction is not the same as

catalyzing the p-QMs alkylation reaction as well. They found it would be best to use 8 mol% uranyl nitrate hexahydrate with acetone solution under air condition, irradiated by a 456 nm Kessil lamp. Whatever the reaction is, the two groups both verified uranyl nitrate hexahydrate can be used in most photocatalytic reactions, but there are some exceptions indeed. One example is the p-QMs with insufficient sterically hindered would not react even with longer reaction time. Yu's group also found out that the radical with stronger regioselectivity will have better yield, which is mainly because this sort of substance is active to react through uranyl nitrate hexahydrate, and this means uranyl nitrate hexahydrate will provide a bright future in pharmaceutical usage and organic functional materials.

Both two groups developed Stern-Volmer fluorescence quenching experiments to seek out the mechanism of uranyl nitrate hexahydrate and their results are similar. The uranyl $[\text{UO}_2^{2+}]$ in uranyl nitrate hexahydrate is stimulated to its excited state $[\text{UO}_2^{2+*}]$ by the irradiation of visible light at first. This process involves ligand-to-metal charge transfer (LMCT), bringing an active U(V) oxygen radical species that has a high oxidation potential. When another radical approach, the U(V) oxygen radical will grab a thermal hydrogen atom to form U(V)O(OH)^{2+} , meanwhile allowing the other radical to have an unpaired electron to react with other substances more easily. Since the existence of resonance after the reaction, the single electron will precisely transfer to a suitable place (depending on the reactants) where can allow the reduction reaction of U(V)O(OH)^{2+} happens. Ultimately, the product gets the thermal hydrogen atom which is originally given to the photosensitizer while U(V)O(OH)^{2+} is reduced to UO_2^{2+} at the same time. These processes form a more effective cycle of electron transformation, therefore making uranyl nitrate hexahydrate an efficient photocatalyst.

The reactions that uranyl nitrate hexahydrate can make an effort is not only restricted to alkylation reaction but Michael addition reaction which we have already mentioned before. This includes some other C-H activation reactions, which also give numerous down-to-earth applications.

However, the concept of uranyl nitrate hexahydrate as a photocatalyst was not first mentioned by Yu's group nor Capaldo's group. Actually, as early as 2016, West's group^[9] has already done a battery of experiments to improve the unactivated C-H bonds fluorination which uses bench-stable fluorine atom as a source. They successfully used uranyl nitrate hexahydrate to accelerate the reaction rate, instead the traditional method which uses an inconvenient UV-active photocatalyst.

Since Second World War, C-H bonds fluorination has been used in myriad realms. We can see them everywhere in our daily life, from material to medicine, even the crops we eat every day utilize this reaction. As most of the required near-UV photo-HAT catalysts, multitudinous energy is used during the complex manufacture before. Meanwhile, The World Health Organization in *Radiation: Ultraviolet (UV) radiation* states that UV light has radiation that may be harmful to humans. Hence, the cost of C-H bonds fluorination was quite too high. As a result of that, many scientists were trying to find a new method for catalyzing, saving cost and simplifying the craft. Uranyl nitrate hexahydrate was developed by West's group in this case. At first, they found the high redox potential of uranyl cation which is similar to the aforementioned two groups. Then they used a uranyl source as a photocatalyst under blue light to test whether has improved. There was indeed some increment of yield than the case with near-UV photo-HAT catalysts. After that, they changed the photocatalyst to uranyl acetate tetrahydrate $[\text{UO}_2](\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and uranyl nitrate hexahydrate $[\text{UO}_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Same with Yu's and Capaldo's work, West's work found uranyl nitrate hexahydrate perform better during the experiments. In the same way, they tested the availability of different substrates. Nonetheless, they only discovered a few substrates can be fluorinated under blue light by using uranyl nitrate hexahydrate as a photocatalyst. However, their attempts are not without results. They surely improve the technique of unactivated C-H bond fluorination with higher efficiency and product yield. It just means, there is much more the uranyl nitrate hexahydrate can be developed and improved.

The further development of uranyl nitrate hexahydrate came again in 2021, Mao's group^[10] was researching the possibility of improving the C-H alkynylation and olefination of amides by using a catalyst. As a result of the improvement in C-H arylation and alkylation of amides which successfully uses nickel and photocatalysts to expedite the reactions, the potential of catalysts on the cross-coupling reaction of amides has been considered by scientists. Before uranyl nitrate hexahydrate is used in alkynylation, the reaction always proceeds through complicated preparation procedures. Such alkynylated reactions usually needs to go through an α -addition/ β -elimination sequence. Prefunctionalised alkynylating reagents are added in the α step, common are alkynyl sulfones and ethynylbenziodoxolones. Although using precast halogenoalkynes can simplify this process, there are side reactions like hydroalkylation generally happen. However, this does not mean we can only obtain alkynylated amides in this way. Mao's group deemed that a highly oxidative photocatalyst would be an alternative solution to alkynylation. They quickly locked their eyes on a cheap and prone-to-find material,

uranium. They found that uranyl has a superior oxidizability in contrast to other photocatalysts, and uranyl nitrate hexahydrate is exactly what they want. Several experiments were established to confirm the feasibility of using uranyl nitrate hexahydrate. Afterward, they contrasted the uranyl-catalyzed alkynylation under different situations to find the optimal reaction conditions, under 452 nm LED, 25 °C, with 8 mol% uranyl nitrate hexahydrate. After that, the test of substrates universality was set up. They also found uranyl nitrate hexahydrate can be employed in olefination, alkenylation and allylation. At all events, the practicality of the work is one of the most essential parts. Their study showed that uranyl in organic synthesis was enlarged by this newly used photocatalyst.

2022, Jiang's group has developed stepwise benzylic oxygenation^[10]. Stepwise benzylic oxygenation is a series of oxygenation, usually includes three types called primary, secondary and tertiary methyl, respectively. These reactions could be occurred by replacing the methyl groups on benzyl with hydrogen atoms under particular ambient conditions, often involving catalysts. The primary reaction which displaces three methyl groups can form carboxylic acids. And the secondary reaction with two hydrogen alternatives will have a product of ketones. Alcohols are considered as the end-product of the tertiary reaction which substitutes only one hydrogen atom. These products are all high-valued as raw materials of fossil, agrochemicals, pharmaceuticals and organic materials. As a result of the complexity of the regular production of carboxylic acids, ketones and alcohols which needs to synthesize from the beginning, using these more simplified ways will save lots of resources. Moreover, the simplification of the method would also bring benefits in clinical pharmaceuticals, natural products and photoelectronic materials synthesis. Xenalipin and tafamidis are two instances that can adjust the amount of cholesterol and triglyceride in plasma and cure TTR amyloid polyneuropathy separately. These reactions often need highly active oxidants to rise the oxidation states, usually some metallic oxide as a catalyst including KMnO_4 , CrO_3 and others. However, each previous catalyst could only catalyze one or two reactions but not all of them. This was a great difficulty for scientists. On account of the foregone semblable study of stepwise sulfidic oxygenation by Jiang's group, they had already found the strong oxidizing property and tunable photoactivity of uranyl cation [UO_2^{2+}].

Their research started with the experiments of electron-poor alkylbenzenes to find out the first-rank conditions of uranyl catalyzing for each of the aforesaid reactions. They realized that the reactions should happen under visible light which has standard pressure and room temperature, and the oxygen is indispensable in the reactions. Every given reaction type among the stepwise reactions, they have its own requirements. Methanol is essential to activate the selective C–H bond in the production of alcohol. The oxidation of benzyl to ketones could be facilitated with the addition of the solvent of acetone. Carboxylic acid could not be acquired without the additive HCl. The diversity of substrates with various functional groups including electron-withdrawing group, electron-donating group and neutral group was then tested. The experiments showed that most of the substrates and functional groups have at least medium even excellent yield. And the further investigation of strained rings and epoxy triumphantly demonstrated the compatibility between the substrates. Meanwhile, the product structure was also proved by X-ray single-crystal diffraction. It is noteworthy that they designed a flow apparatus, a loop-locked system consisting pump, containing a polytetrafluoroethylene (PTFE) tube and a round-bottom flask, which is applicable for the fabrication in industry. The oxygenated solution with uranyl acetate $\text{UO}_2(\text{OAc})_2$ is pumped into the tube, which is irradiated by blue light. The 20 mmol-scale reactions were set up and there were three reaction rates in the tube, which are 0.111, 0.135 and 0.133 mmol per hour. The result revealed that the efficiency is fifteenfold, twentyfold and thirtyfold severally compared to the tube operation.

They also investigated C–C bond activation in oxygenation under a controllable pathway. The research showed that acetone prefers to have a single C–C bond cleavage while double C–C bond cleavages are arisen with excess equal of sulfuric acid. Further experiments were built to discuss the principle of stepwise oxygenation. Firstly, the characteristics of the radicals in these reactions were manifested by radical quenching experiments which involve 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO) and butylated hydroxytoluene (BHT). They also set fluorescence quenching experiments to approve the interactions that occurred between the active catalyst and substrates. What's more, the reaction rate of different substitutions on alkyl benzenes indicated HAT is a necessary section of the reactions, and the kinetic isotope effect experiments of deuterated toluene made clear that HAT did not affect the speed of the reactions. Furthermore, the Stern-Volmer experiments attested methanol/HCl (aq) and active uranyl species can cause an effective quenching effect. Finally, they sought out important evidence that such reactions can occur. By reason of the comparatively low catalytic properties of uranyl in methanol which inhibited the scissions of C–C bonds, the tertiary alcohol in benzylic oxygenation could not react more, which allows it to maintain in the solvent. Conversely, the oxidizability of uranyl would be increased in an acidic medium hence accelerating the reactions. In other words, they found the catalytic activity of a catalyst is controlled by additives and solvents, adding acids could increase the

activity while it is decreased in alcohols. Based on those proofs, they summarized the possible mechanism of how uranyl catalysts played a crucial role in the reactions. Anyhow, it is still the analogical process to the preceding one that we have already mentioned, so we will not talk about it again here.

3. Oxygenation

In 2019, Jiang's group elucidates the potential of uranyl cations (UO_2^{2+}) as a catalyst for the selective oxygenation of sulfides. Sulfides, sulfoxides, and sulfones play pivotal roles in wide field. Unfortunately, existing methodologies for their oxidation suffer from limitations in selectivity. To overcome these constraints, the authors suggest employing uranyl cations (UO_2^{2+}) as photocatalysts to enable selective oxygenation. The chemical inertness of uranyl cations (UO_2^{2+}) towards oxygen is attributed to the 2p orbital of oxygen and the 5f and 6d primary valence shells of uranium. The authors propose a hypothesis wherein a ligand-to-metal charge transfer (LMCT) process from the 2p orbital of oxygen to the 5f orbitals of uranium generates a U(V) center with an oxygen radical species. To validate their hypothesis, a series of experiments were conducted to optimize conditions for the selective oxygenation of sulfides. Experiments and calculations have confirmed the strong oxidizing power of UO_2^{2+} ($E_o = 2.6 \text{ V}$) in its excited state. This property enables its utilization for the oxidation of molecules with high oxidation potentials. Notably, acetonitrile was identified as beneficial for producing sulfones, while the incorporation of *o*-xylene as an additive improved reaction yield. Moreover, the implementation of a parallel photoreactor effectively enhanced reaction efficiency, resulting in reduced reaction times and increased yields. Subsequently, the refined conditions were successfully extended to diverse substrates, thereby underscoring the generality of the uranyl-catalyzed oxygenation process. This technique exhibited tolerance towards different functional groups, encompassing halogen substituents, hydroxy groups, nitrogen-containing backbones, alkenes, and alkynes, facilitating the synthesis of both sulfones and sulfoxides.

Through rigorous investigations, singlet oxygen, superoxide radicals, and hydroxyl radicals were ruled out as the predominant oxygen species responsible for the oxidation process. Notably, although hydrogen peroxide was detected, its indispensability to the reaction was negated. The proposed mechanistic pathway involves LMCT from oxygen to uranium, generating an active uranyl species (UO_2^{2+*}). Subsequently, the sulfide donates an electron to UO_2^{2+*} , giving rise to a sulfide radical cation. The reaction between ground-state oxygen and the sulfide radical cation yields a persulfoxide radical, which then undergoes a sequence of electron transfer and radical intermediates, ultimately leading to the formation of sulfoxides and sulfones.

A selective and highly compatible late-stage oxygenation reaction of sulfides utilizing uranyl acetate and ground-state oxygen was successfully established. The pivotal role of ground-state oxygen in the reaction's compatibility was highlighted. This unique approach, founded on ground-state oxygen and adjustable photocatalysts, presents promising prospects for future research endeavors in both industrial and academic settings^[11].

In 2021, the continuous advancement of uranyl-photocatalyzed oxygenation hydrolysis was achieved about hydrolysis of diaryl ethers in ambient conditions using uranyl photocatalysis to facilitate targeted degradation of 4-O-5 lignin. Lignin, a substantial renewable source of aromatic compounds, has garnered attention due to its potential to alleviate the environmental impact caused by fossil resource consumption^[12]. Jiang's group focused on the activation and cleavage of specific C-O links within lignin, especially the challenging 4-O-5 link. Drawing from their prior investigations into uranyl compounds, the ligand-to-metal charge transfer (LMCT) mechanism and impressive oxidative process [$E_{ox} = +2.60 \text{ V vs SCE}$] presents significant possibilities for activating DPE [$E_{ox} = +1.88 \text{ V vs SCE}$]^[15]. In this context, they successfully developed a process for photocatalytic hydrolysis of diaryl ether into two phenols by uranium catalysis under standard temperature and pressure conditions, using visible light as a stimulus.

The researchers' innovation lies in the utilization of uranyl photoredox catalysis for efficient C-O bond activation. The approach involves the generation of UO_2^{2+*} via the ligand-to-metal charge transfer (LMCT) process, followed by a single electron transfer (SET) process between UO_2^{2+*} and DPE. This interaction yields UO_2^+ and a radical cation, which undergoes oxygen atom transfer (OAT) mediated by uranyl peroxide species. The resulting phenyl oxygen couples to the protective and further SET process, ultimately leading to the formation of phenols and the regeneration of catalysts.

The study's achievements are substantial, with successful degradation of symmetrical and unsymmetrical diaryl ethers, even with challenging substitutions. Importantly, the methodology is scalable, as demonstrated by the implementation of a streaming device that significantly enhances the

efficiency of the transformation. This aspect is particularly relevant for applications such as lignin degradation, where phenol recovery is crucial. This work opens new avenues for advancing lignin valorization and aligns with the goals of sustainable chemistry and resource utilization^[12].

Beyond biomass, uranyl photocatalysts have revealed a remarkable prowess in the elegant conversion of anilines to phenols. In 2022, the study on photoredox catalysis to address a challenging issue in chemical catalysis within the realm of organic chemistry was subsequently achieved^[13]. Carbon-nitrogen (C-N) bond activation has long presented a formidable obstacle due to the high bond dissociation energy and coordinating abilities of nitrogen-containing compounds, particularly anilines. Traditional strategies for C-N bond transformation have often required prefunctionalization steps and complicated synthetic processes. However, recent advances in photoredox catalysis have provided new avenues for such transformations.

The investigation begins with an exploration of uranyl photoredox catalysis and its potential for C-N bond activation. Uranyl catalysts, characterized by ligand-to-metal charge transfer (LMCT) processes and remarkable oxidative abilities, were identified as promising candidates for this task. Previous work by researchers in uranyl photoredox catalysis laid the foundation for exploring C-N bond activation in anilines. This research's central objective is to harness the synergistic potential of single electron transfer (SET) and oxygen atom transfer (OAT) processes mediated by uranyl species to achieve C-N bond activation in a variety of anilines, leading to the synthesis of phenols^[13].

The authors embark on their experimental subject by investigating the conversion of various anilines to phenols using uranyl photoredox catalysis. The study's design involves irradiating protogenetic anilines, N-substituted anilines, and aniline-containing natural products/pharmaceuticals with blue light in the presence of uranyl catalysts. Through a comprehensive range of experiments, the authors established that the combination of uranyl catalysts and blue light triggers a single-electron transfer (SET) process between protonated anilines and uranyl catalysts. This is followed by an oxygen atom transfer (OAT) process involving the radical cation of protonated anilines and uranyl peroxide originating from water splitting^[13].

Critical mechanistic insights are gained through radical quenching experiments, Stern-Volmer analysis, and labeling experiments with H₂¹⁸O and ¹⁸O₂. These findings confirm the involvement of radical intermediates, the interaction between uranyl species and protonated anilines, and the origin of the oxygen atom in the final phenol product. The authors also present a proposed reaction pathway, highlighting the key steps in the catalytic process^[13].

Moreover, this work demonstrates the broader applicability of this strategy through extensive substrate-scope investigations. A wide range of anilines, including those with electron-rich, neutral, and electron-deficient substituents, were successfully transformed into corresponding phenols using this method. The compatibility of various functional groups, as well as the application to natural products and pharmaceuticals, underscores the versatility of uranyl photoredox catalysis for C-N bond activation.

Furthermore, This work establish the efficiency of the reaction by implementing flow reactions, demonstrating a significant improvement in reaction rates compared to traditional tube reactions. This aspect holds significant promise for potential industrial synthetic applications.

In brief, the integration of uranyl photoredox catalysis, SET, and OAT processes provides a novel approach to achieving this transformation, leading to the synthesis of phenols from a diverse range of anilines. The study not only offers mechanistic insights into the catalytic process but also demonstrates its practicality and applicability through substrate scope investigations and flow reactions. As ongoing research delves further into uranyl-catalyzed reactions, the study presents a promising avenue for advancing synthetic methodologies in the realm of C-N bond activation.

In 2023, Jiang's group conducted a comprehensive study of the degradation of plastic waste into valuable chemicals and monomers using visible light^[14]. The motivation behind this study stemmed from the alarming rise in plastic production, projected to reach 1.12 billion tons by 2050^[15]. The improper disposal of plastic has led to environmental pollution and accumulation issues. Between 1950 and 2017, the production of plastics reached a staggering 9.2 billion tons, which in turn necessitated their disposal through landfill and incineration^[16]. This disrupts natural equilibria and results in CO₂ emissions, highlighting the urgent need for chemical recycling and plastic degradation to mitigate carbon impacts.

The composition of plastics significantly affects their resistance to degradation. Plastics consist of alternating crystalline and amorphous structures, as well as complex molecular chains. These features hinder efficient molecular diffusion and intermolecular interactions. Reaction sites tend to be irregular

and lie within the disordered conformations of molecular chains. Notably, recent studies by Stache's group^[17] and Xiao's group^[18] demonstrated the recycling of polystyrene into valuable chemicals via hydrogen atom transfer under visible light. Given this context, investigating the photodegradation of plastic waste using uranium could yield valuable insights.

The experiments involved mixing plastics with specific chemicals and exposing them to blue light. The resulting products were then obtained through purification methods. This work also outlines a large-scale depolymerization process for waste PET bottles using a continuous-flow photoreactor.

Subsequently, the text elaborates on the depolymerization of different plastic types using uranyl cations as photocatalyst. PS plastic with a C-H bond at the benzylic site is transformed into benzoic acid and isolated oligomers. SAN and ABS plastics were successfully depolymerized in acetone with trichloroacetic acid, yielding benzoic acid. PES was degraded into the monomer bis(4-hydroxyphenyl) sulfone, albeit with some by-products. PC underwent degradation to yield bisphenol A, bisphenol carbonate, and oligomers. PET and PBT resulted in terephthalic acid (TPA) with high yields through degradation. It is worth noting that a continuous flow photoreactor achieves efficient PET degradation with reduced catalyst dose and solvent volume. The TPA obtained from PET contained negligible uranium residues^[14].

The degradation of plastic was closely monitored using tracking methods that provided insights into the process. Initially, the amorphous regions of the plastic underwent disintegration, followed by subsequent swelling and dissolution. Detailed morphological changes in the plastic samples were revealed through scanning electron microscopy (SEM). Additionally, the water contact angle exhibited a decrease, indicating an increase in hydrophilicity. X-ray diffraction analysis further displayed the shrinking and disappearance of crystal peaks. The molecular weight of the plastic decreased, as evidenced by gel permeation chromatography results. Furthermore, the characterization of the degradation process involved measurements of viscosity variation and glass transition temperature.

This study presents a versatile, mild, and scalable method for the photocatalytic degradation of plastics using uranyl ions. The method is compatible with both air and water conditions. The successful depolymerization of various plastic types into commercial chemicals exemplifies the potential of uranyl photocatalysis. This approach also demonstrates the ability to transform mixed plastics into valuable end products. The pivotal role of synergistic integrated mechanisms, encompassing single electron transfer (SET), hydrogen atom transfer (HAT), and oxygen atom transfer (OAT), is established in facilitating this transfer process. This demonstrated success of large-scale depolymerization underscores the promise of this protocol in mitigating environmental pollution and resource depletion arising from plastic waste.

4. Conclusion

In summary, we have discussed about the basic information and applications of different types of uranium, including U^{235} , U^{238} and particularly a compound of uranium, uranyl. According to previous research about uranyl, we have analyzed the fundamental theory of uranyl photocatalysis and various types of reactions that use uranyl as an improved catalyst. Except all of the reaction types mentioned above (alkylation, Michael addition, fluorination, alkynylation, olefination, alkenylation, allylation and oxygenation), other known reactions that can be catalyzed by uranyl nitrate hexahydrate so far are cyanation and hydroalkylation. Moreover, we have summed up the research procedure of the foregone studies on uranyl photocatalysis. The researchers often catch a current problem that can be enhanced by using uranyl as a photocatalyst at the beginning. Based on the problem, the research work will test the optimal conditions and universality of substrates through experiments. In the end, all the work gave the mechanism of uranyl photocatalysis. Because of the reliance on catalysts nowadays and the good development prospect of uranyl, we conformably believe that uranyl would have better prospects for more applications in the near future.

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