

Titanium Dioxide-Functionalized Carbon Nanomaterials for Catalytic Degradation of Antibiotics in Water

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Abstract. Antibiotic residues in the environment are a type of pollution that is becoming more common. These residues can be harmful to ecosystems and human health. Although titanium dioxide photocatalysis shows promise for treating such contaminants, its practical application is limited by inherent drawbacks, including the rapid recombination of photogenerated electron-hole pairs and a spectral response confined to ultraviolet light. This review looks at how to make TiO₂-carbon nanomaterial composites to create efficient and stable catalytic systems for breaking down antibiotics in water. It looks at how to design and make multicomponent composites using green methods, how to assess the performance and stability of coupled catalytic systems, how to investigate interfacial mechanisms and degradation pathways in detail, and the challenges and opportunities in complex aquatic environments. This paper uses existing research to: outline the current research landscape; identify key scientific questions; and provide theoretical guidance and a framework for developing low-cost, high-performance TiO₂-based water purification materials suitable for large-scale application.

Keywords: Titanium dioxide, carbon nanomaterials, antibiotic degradation, heterojunction, advanced oxidation processes

1. Introduction

Using too many antibiotics and not getting rid of them properly has led to them being found in water all over the world. These pollutants can cause antibiotic resistance genes, which is a long-term threat to aquatic ecosystems and public health [1,2]. But the stable molecular structure of antibiotics makes them resistant to conventional biological treatments, so we need efficient, advanced water purification technologies. TiO₂ photocatalysis is one of the most promising solutions among various advanced oxidation processes. This is because it can use solar energy, achieve complete mineralisation and is environmentally friendly [1]. But the wide bandgap of intrinsic TiO₂ restricts its light absorption to the ultraviolet region, while the high recombination rate of photogenerated charge carriers results in low quantum efficiency, severely limiting its practical application [3]. But carbon nanomaterials have been shown to be great at working together with other materials, because they can conduct electricity really well, have a large surface area and can be changed to have

different surface chemistry. This can help to split charges, make the response to light better and get rid of contaminants [4,5].

Titanium dioxide is also useful in other areas. For example, when used as a special coating on insulators in power systems, it makes them more resistant to pollution and improves their ability to clean themselves [6]. When modified by ion implantation, TiO_2 can be used for highly sensitive hydrogen peroxide sensing [7]. It also serves as an interface platform for biomineralization processes [8]. These advances show how useful TiO_2 surface and interface engineering can be for designing structures for water treatment.

Research on TiO_2 photocatalytic degradation of antibiotics has evolved from single-material modification towards multi-component composites and a deeper understanding of how it works. In material design, the focus has moved on from simple TiO_2 /carbon binary composites to precise control of the interface and how different components work together. For example, nitrogen-doped reduced graphene oxide loaded with Pt/ TiO_2 nanoparticles can break down tetracycline by 81% in a mild environment [4]. Similarly, Fe_2O_3 /Pt/ TiO_2 nanowire arrays can improve norfloxacin breakdown by 1.69 times compared to pure TiO_2 through a photocatalytic-Fenton cascade reaction [6]. In practice, building special structures (like Z-type and S-type) has been shown to be very important for improving how well light can be used to create electricity [2,3]. In addition, combining photocatalysis with other processes, such as persulphate activation and pseudo-Fenton reactions, produces a number of reactive species that can break down antibiotics. Using calculations from density functional theory along with experiments has provided more information about how atoms interact with each other, how pollutants attach to the surface, and how pollutants break down at the atomic level [3].

This review looks at how TiO_2 -modified carbon nanomaterials have been used to speed up the breakdown of antibiotics. It looks at how things are made, how they work as well as how they react. The methods for preparing TiO_2 -carbon composites are explained in a step-by-step way. The ways these two parts work together are explained, with a focus on systems that use catalysts made of metals that are not precious or rare. Experiments and calculations are used together to understand how charge moves at the surface where the two parts meet. We also talk about how active species are made and how pollutants are broken down. We will check how stable, reusable and adaptable these materials are in real water environments. We look at how toxic degradation by-products can change. Finally, we outline the current research's limitations. We suggest some ideas for the future. These include using green synthesis methods, investigating reaction mechanisms more, and making progress with engineering applications. The aim of this work is to support the translation of related technologies from laboratory research to engineering practice.

2. Design and green synthesis of multicomponent composites

Multicomponent composites, constructed by integrating carbon-based materials (e.g., nitrogen-doped reduced graphene oxide, multi-walled carbon nanotubes) with narrow-bandgap semiconductors (e.g., TiO_2 , ZnFe_2O_4) into ternary systems, can significantly enhance the visible-light absorption, charge separation efficiency, and pollutant adsorption capacity of photocatalysts. Green synthesis methods, such as hydrothermal and solvothermal approaches, have proven effective and environmentally friendly for regulating material composition, structure, and interfacial properties.

Moharrami and Keshipour prepared TiO_2 /Pt nanoparticles via pyrolysis-chemical reduction and stuck them on nitrogen-doped reduced graphene oxide (NRGO) to construct a ternary TiO_2 /Pt@NRGO composite [4]. The cool thing about this innovation is that it uses the high surface

area and excellent conductivity of NRGO while also boosting the capture of visible light through the localised surface plasmon resonance effect of the Pt nanoparticles. Experiments showed an 81% tetracycline breakdown rate under mild conditions. This case shows that combining carbon materials and noble metals can effectively increase the light-response range and encourage charge separation. The main benefits are that it has mild reaction conditions, uses less energy, and stays very stable after being used lots of times, which shows it has a lot of practical potential. But using Pt, which is expensive, can increase material costs and make large-scale industrial use more complicated. The high-temperature pyrolysis step doesn't seem to align with green synthesis principles either. So, it's still a big challenge to come up with low-cost, low-energy synthesis methods that don't affect performance.

Varghese and his team used a hydrothermal method to make a ternary composite material made up of $\text{ZnFe}_2\text{O}_4/\text{MWCNTs}/\text{TiO}_2$ [5]. The cool thing about this study is that it combines narrow-bandgap ZnFe_2O_4 (with a bandgap of about 1.4 eV) with TiO_2 , using multi-walled carbon nanotubes (MWCNTs) as the electron transport pathway. This structure helps to move charge around. When exposed to light, this material was able to break down 99.2% of penicillin. After eight cycles, it was still going strong at 91% [5]. Studies show that carbon-doped multi-component composites can boost light absorption and charge separation efficiency. These materials usually have high catalytic activity and stability. The narrow bandgap of ZnFe_2O_4 means it responds to a wider range of light. MWCNTs speed up carrier migration, which improves quantum efficiency. The way these components interact with each other makes them more stable and resistant to photocorrosion. But this synthesis method needs precise control over the ratios of the components and the way they bond at the interface. Inhomogeneous composites can sometimes make it hard for carriers to transport, which can lead to reduced performance. The hydrothermal process is sensitive to crystal growth and morphology, so tiny changes in process parameters could affect how well you can reproduce the experiment.

3. Performance and stability assessment of coupled catalytic systems

Systems that use catalysts, like photocatalytic Fenton and persulphate-activated processes, have been shown to speed up the breakdown of antibiotics by combining the effects of oxidants (like H_2O_2 , persulphates) and photogenerated charges. To move things forward, we need to do a proper investigation into how well these systems work and how stable they are when the water quality changes.

Nguyen and his team designed and made $\text{Fe}_2\text{O}_3/\text{Pt}/\text{TiO}_2$ nanowire array composites to help with the photofenton degradation of norfloxacin [9]. The most exciting part is the way they combine the Fe_2O_3 -induced Fenton-like reactions and the Pt/TiO_2 photocatalysis, which makes a huge difference to the amount of $\cdot\text{OH}$ radicals produced. When we exposed norfloxacin to 10 mM H_2O_2 for 2 hours, it degraded by 87.92%, which is a 1.69-fold increase compared to pure TiO_2 . This shows that photocatalytic-Fenton coupling is a great way to quickly get rid of antibiotics. The good things about this include faster reaction rates because of the way the electrons and iron react together, which stops the recombination of carriers and makes sure there's continuous ROS generation. The system also has high mineralisation capabilities, converting norfloxacin into CO_2 and H_2O , which reduces toxic intermediate accumulation and secondary pollution risks. The only limitations are that you need to be precise with the H_2O_2 dosing, because too much of it leads to $\cdot\text{OH}$ self-depletion, and it performs optimally at an acidic pH of around 3, which makes it hard to use in neutral or near-neutral waters and makes it more complicated to use.

In the detection and monitoring of exogenous oxidants (substances that can cause oxidation), such as hydrogen peroxide (H_2O_2), recent research has developed high-performance electrochemical sensors based on platinum-ion-implanted carbon-doped TiO_2 nanotube arrays. These sensors are very sensitive to H_2O_2 and can also be used to detect other substances [7]. Using these technologies provides strong analytical tools for optimising oxidant dosing and enabling real-time monitoring within coupled systems.

Khairy and his team created special tiny particles called g- C_3N_4 -modified sulfated TiO_2 quantum dots (CN@ST) and tested how well they could break down the drug ciprofloxacin using persulfate. The innovation involves making TiO_2 surfaces more acidic and increasing the amount of oxygen vacancies by adding sulfation, combined with g- C_3N_4 to form a Z-scheme heterojunction to improve charge separation. With 2 mM persulfate, 20 ppm ciprofloxacin achieved 91.5% degradation within 140 minutes. This case shows that combining persulfate activation with photocatalysis makes it much more effective at breaking down pollutants, and the process can be run using just sunlight. The visible-light response has been shown to improve how solar energy is used, meaning we don't need to rely as much on UV sources. The presence of more than one type of ROS (e.g. $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$) means that they can attack different pollutants. The method has two limitations. First, adding persulfate can cause secondary pollution. Second, adding the catalyst can deactivate in complex waters. This is because natural organic matter competes with the catalyst for space. This is because the organic matter can cover active sites and get rid of radicals.

4. In-depth investigation of interfacial mechanisms and degradation pathways

To improve the design of catalysts and encourage their use, it is important to understand how photocatalysis works. By combining radical trapping experiments, electron spin resonance (ESR), liquid chromatography-mass spectrometry (LC-MS) and density functional theory (DFT) calculations, we can understand how reactions happen at the molecular level.

Khairy and his team found that h^+ and $\cdot\text{OH}$ were the main active species in the CN@ST system. They used DFT calculations to analyse how ciprofloxacin and indigo carmine adsorb on the catalyst surface [3]. This work uses electronic levels to clearly explain how contaminants stick to the (001) crystal plane and where reactions happen. It also explains how Z-scheme heterojunctions help to separate charge. This shows that combining DFT with experiments provides a deep understanding of what happens at the interface, offering a clear understanding of how things work and the ability to make predictions. However, computer models based on ideal surfaces may not be the same as real complex interfaces. This is because factors such as surface defects, adsorbed impurities, and dissolution effects are not fully included, which can lead to differences between theoretical and experimental results.

Wu Xi used DFT calculations and LC-MS to work out what happens to tetracycline when it degrades in $\text{Fe}^0/\beta\text{-TiO}_2$ and Fe^0/MoS_2 systems, and used T.E.S.T. (toxicity assessment software) to analyse the ecotoxicity of the intermediates [2]. The new idea is to combine the study of how things break down with the study of how toxic substances change over time. This helps us to check how safe they are for the environment. The results showed that photocatalysis was responsible for over 60% of the antibiotic mineralisation, and the final products were much less toxic. This case shows that combining studies of how things work with tests of how dangerous they are gives better safety proof for using catalysts. It also gives a better way of doing the studies and makes the results more reliable. However, intermediate identification relies on reference standards and database coverage. Some transformation products, especially isomers from non-canonical pathways or short-lived radicals, may not be fully identified, which introduces uncertainty.

When studying how things stick together at the surface of a material (like a metal), tools like quartz crystal microbalance (QCM) can be used to watch what is happening in real time. This method of tracking the movement of material across the surface of a material could be used to better understand how pollutants are absorbed, how intermediate compounds are formed, and how they are released.

5. Research gaps and future development

Titanium dioxide photocatalytic technology has the potential to break down bacteria, but it is still difficult to use in practice. Firstly, this approach often uses precious metal co-catalysts (such as platinum), which are costly and not very sustainable [4,9]. As a result, we need to develop non-precious metal systems. This involves creating S-type or Z-type junctions and adding carbon materials, magnetic oxides, or nitride semiconductors to improve charge separation [2,3,5]. Secondly, we need to understand how photocatalysis and persulphate activation or Fenton-like reactions work together. This is because the ways that the different components interact, how the carbon materials work, and how the active species are made are not yet clear [3,9,10]. Also, in engineering applications, there are limitations. These include the catalyst not being stable in the long term, it not being able to resist interference, difficulty in recovering it, and the potential for it to pollute real water bodies. All of these things mean that its development is limited [2,10]. Most research at the moment is on how quickly antibiotics are removed, but there is a lack of proper analysis of the substances that are formed during the process, how dangerous they are, and the complete process of how minerals are made. This means that it is difficult to ensure that the process is safe for the environment [2].

To make this happen, we need to do more research. In material design, we should develop efficient and stable composite materials made from non-precious metals. Using carbon materials to enhance electron conduction and adsorption is important when constructing heterojunctions with strong intrinsic electric fields [2,3,5]. When it comes to studying how things work, it's important to understand how charges and active species move at the atomic level. This can be achieved by looking at the characteristics of the surface where things are happening, as well as by doing theoretical calculations [2,3]. To evaluate how well they work, catalysts need to show that they can adapt and be stable across a wide range of pH levels and different ionic conditions. It is very important to check how the system changes and how toxic it is to the environment. In the end, by working with the water treatment processes we already have and checking that they work on a small scale, we can find ways to use solar energy to make antibiotics cleaner and more pure.

In addition, the effective use of TiO₂ in electrical insulation, sensing, and biointerfaces shows the value of its surface modification, structural regulation, and performance evaluation methods in different fields. In the future, we should work together across different subjects to come up with more ideas for using TiO₂ in water treatment.

6. Conclusion

This review shows that building connections between TiO₂ and special carbon materials, along with advanced cleaning processes like persulfate activation, can greatly improve how well antibiotics break down. The core mechanism involves carbon materials working together to help charge separation at the interface and generate reactive oxygen species, which can then lead to coordinated radical and non-radical oxidation. However, there are still some problems, including photogenerated charge recombination that hasn't been solved yet, interference from complex water matrices, and the

formation of toxic intermediate compounds. The most important part of this work is to create a research plan that includes structural design, how well things work, and explaining how things work. This will change the focus from how quickly things break down to whether they are safe for the environment. In the future, we should focus on precise engineering of interfaces and bandgaps (for example, S-scheme heterojunctions) to efficiently separate charges, and use in situ characterisation and theoretical calculations to reveal how multi-process coupling and pollutant transformation work together. This will provide a scientific foundation for efficient, stable, and environmentally friendly practical water treatment technologies.

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