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$KBrO_3$ and graphene as double and enhanced collaborative catalysts for the photocatalytic degradation of amoxicillin by UVA/TiO_2 nanotube processes

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ABSTRACT

In this study, we found a novel property of graphene and $KBrO_3$ as double and enhanced collaborative catalysts to degrade amoxicillin (AMX) on the photocatalytic behavior of TiO_2 nanotubes under UVA light irradiation. The synthesis of graphene-TiO_2 nanotubes (GN-TNT) is a necessary first step. AMX can be photo-degraded with GN-TNT, but its degradation rate reaches nearly 100% with the addition of $KBrO_3$, which has two roles in photo-degradation. Its first and more important function is the prevention of electron-hole recombination by acting as electron acceptor. Its second function is its direct participation as oxidant in the degradation of AMX. The effects of GN loading, $KBrO_3$ initial concentration, and AMX concentration on photocatalytic activity are explored in this study. Results of the kinetic study also show that degradation can be expressed by a first-order reaction kinetic model. The degradation mechanism of photocatalytic activity and the role of $KBrO_3$ are also discussed.

1. Introduction

In recent years, the influence of medical organic drug pollutants on water environments has become increasingly serious [1,2]. Pharmaceutical and personal care products (PPCPs) are widespread in municipal wastewater, surface water, groundwater, and even in drinking water. Among medical pollutants, antibiotic organics have gained increasing attention because of their strong toxicity, which easily escapes sewage treatment facilities and enters natural environments [3]. Antibiotics that are accumulated in the body can easily cause damage to the central nervous system and cause joint, kidney, and other severe diseases. Amoxicillin (AMX), which is classified under β-lactam antibiotics, is the most widely used among various kinds of antibiotics [4]. AMX frequently performs important functions in human medicine and treatment of animal diseases. However, this antibiotic can be metabolically discharged because of its indigestibility. At present, the mass concentration of AMX in secondary water drainage and surface water is at μg L^{-1} level [5,6]. AMX exhibits abundant special characteristics, such as stable chemical properties, serious biological toxicity, and low biodegradation rate. Thus, removing it by traditional biological treatment processes is difficult.

In addition, traditional physical treatment methods, such as activated carbon adsorption, air flotation, and reverse osmosis, can only capture PPCPs but not completely degrade AMX [4,6]. Furthermore, other advanced oxidation processes, such as ozone oxidation, light–Fenton oxidation, and semiconductor catalytic oxidation, require a large amount of energy or chemicals to achieve high performance. Among the numerous photocatalysts, TiO_2 is recognized as one of the most common and effective because of its unique conduction band position and surface structure [7]. Given their advantages of large specific surface and strong ion exchange capacity, titanium nanotubes (TNTs) synthesized from TiO_2 have received considerable attention recently. As photocatalysts, TNTs can use ultraviolet light with wavelengths of less than 360 nm, which account for only 4% of solar energy [8,11]. Graphene (GN)–doped TNT can transfer the maximum excitation wavelength of TNTs to the near-ultraviolet or visible region to improve the photocatalytic activity of TNTs.

In general, photo-degradation is triggered by the electrons and holes in semiconductor materials. However, these electrons and holes exist in a state of balance [11]; in other words, they recombine to achieve balance. Thus, preventing the recombination of electrons and holes is an important step to improve the rate of photo-degradation. This study found that $KBrO_3$ is a good electron acceptor [9,10] with a redox potential of 1150 mV. From the perspective of thermodynamics, it has a very strong ability to accept electronic [12,15]. The efficiency of photocatalytic reaction largely

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Table 1.
Characteristics of AMX.

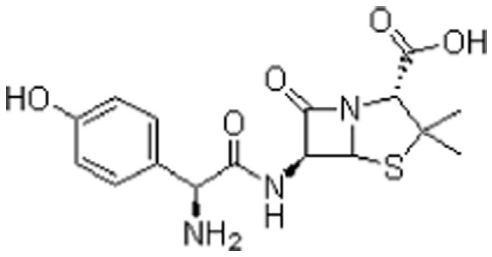
Name	Molar mass (g/mol)	λ_{max} (nm)	Molecular formular	Structure
Amoxicillin	419	230	$C_{16}H_{19}N_3O_5S_3H_2O$	

Fig. 1. The TEM of TNT (a) and GN-TNT (b), the EDX of GN-TNT(c).

depends on the effective separation of electrons and holes, and $KBrO_3$ has a great ability to accept photo-electrons and therefore can significantly influence the rate of photocatalysis.

2. Experimental

2.1. Materials and reagents

Commercial TiO_2 (P25, 80% anatase and 20% rutile) and GN were purchased from ACROS. AMX was supplied by ACROS. The properties of AMX are illustrated in Table 1. $KBrO_3$ was purchased from Nihon Shiyaku. All the chemicals were of analytical grade and were used as received. Experiments were conducted at room temperature.

2.2. Photocatalytic performance assessment

TNTs were obtained via the transformation of commercial TiO_2 using the hydrothermal method [18,19]. The GN content of the GN-TNTs—3%, 5%, 10%, and 15%—was mixed with water and