

Immobilized rGO/TiO₂ photocatalyst for water purification

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Abstract

The preparation of immobilized graphene-based photocatalyst layers is highly desired for environmental applications. In this study, the preparation of an immobilized reduced graphene oxide (rGO)/TiO₂ composite by electrophoretic deposition (EPD) was optimized. It enabled quantitative deposition without sintering and without the use of any dispersive additive. The presence of rGO had beneficial effects on the photocatalytic degradation of 4-chlorophenol in an aqueous solution. A marked increase in the photocatalytic degradation rate was observed, even at very low concentrations of rGO. Compared with the TiO₂ and GO/TiO₂ reference layers, use of the rGO/TiO₂ composite (0.5 wt% of rGO) increased the first-order reaction rate constant by about 70%. This enhanced performance was due to the increased formation of hydroxyl radicals that attacked the 4-chlorophenol molecules. The direct charge transfer mechanism had only limited effect on the degradation. Thus, EPD-prepared rGO/TiO₂ layers appear to be suitable for environmental application.

Keywords: electrophoretic deposition, photocatalysis, TiO₂, reduced graphene oxide, water purification.

1. Introduction

Graphene-based nanomaterials possess unique properties that can be applied to environmental remediation [1–5]. The interest in these nanomaterials originates from graphene's unique physicochemical properties, notably its exceptionally high surface area, electron and thermal mobility, and mechanical strength. One of the most popular approaches for preparing graphene-based nanomaterials involves the use of graphene oxide (GO) because of its lower production costs. GO is an oxidized form of graphene, showing a high density of oxygen functional groups (carboxyl, hydroxyl, carbonyl, and epoxy) in the carbon lattice. However, the oxidation of graphite to GO introduces defects into the carbon structure that results in significantly altered physicochemical properties.

By the reduction of GO, a large fraction of its oxygen content can be removed, which leads to a substantial change in its physico-chemical properties. The formed reduced graphene oxide (rGO) possesses enhanced electronic (higher mobility of electrons), optical and

surface properties (decreased wettability) [4]. However, the complete reduction of GO is challenging. Composite graphene-based photocatalysts have been mostly tested in the form of suspensions, [1] which is favorable from the point of view of the mass transport of reactants and degradation products. However, for environmental remediation and clean-up applications, immobilized photocatalysts are often. To the best of our knowledge, no study has reported the preparation of an immobilized rGO-based photocatalyst for the removal of environmental pollutants.

In this study, we optimized the suspension and process parameters of the electrophoretic deposition (EPD) process to prepare an rGO-based photocatalyst immobilized on stainless-steel substrates for the photocatalytic degradation of 4-chlorophenol. Our criteria were rGO/TiO₂ layer homogeneity, good mechanical stability in aqueous media, strong adhesion to the substrate, and, in particular, high photocatalytic activity.

2. Results and Discussion

As a test reaction, we used the photocatalytic degradation of 4-chlorophenol because this compound is a common water pollutant that exhibits good chemical stability, undergoes negligible photolysis, and possesses relatively low adsorption on the photocatalyst surface.

First, the effect of the stability of the deposited layers on their photocatalytic performance was determined. Experiments showed that the layers deposited on the stainless steel surface exhibited very good adhesion, with no leaking of titania or carbonaceous particles during the photocatalytic tests. No particles were detected in the solution after the experiments.

Having determined the adhesion properties of the composite, we investigated the photocatalytic performance of the GO/TiO₂ and TiO₂ layers. As they exhibited similar activities, the doping with GO did not produce any substantial improvement in photocatalytic activity. This performance is due to the physico-chemical properties of GO, which is an insulant with abundant oxygenated surface groups. This drawback was removed by the reduction of GO, which transformed the insulant GO into more or less highly conductive rGO.

The improved photocatalytic performance is shown in Figure 1, in which the decrease in 4-chlorophenol concentration using rGO/TiO₂ was statistically

significantly much faster. The first-order reaction rate constant for rGO/TiO₂ was 0.0053 min⁻¹, which was 70% higher than that for GO/TiO₂ or TiO₂. When reused, the layers showed no deterioration in photocatalytic performance, which is very important from the application point of view.

Generally, a photocatalytic process involves two different mechanisms: a direct transfer of charge carriers and an attack by radicals, especially by hydroxyl ones. Depending on the reaction conditions, these mechanisms may act separately or jointly.

3. Conclusion

We have shown that our optimized EPD technique enables the fast and simple preparation of an immobilized

rGO/TiO₂ composite photocatalyst and that the addition of rGO, even at low concentrations (0.5%), can substantially increase the rate of pollutant degradation compared with GO/TiO₂ and pristine TiO₂. The reduction of GO with hydrogen at higher temperatures led to marked changes in morphological and chemical properties. In terms of morphology, rGO exhibited a much smaller surface area accompanied by the formation of micropores, which is very different from graphene itself. Concerning the chemical properties, such as thermal stability and the content of surface oxygenated groups, they approached those of graphene. The presence of rGO in the composite photocatalyst led to the increased formation of hydroxyl radicals, which explains the enhancement in photocatalytic performance itself.

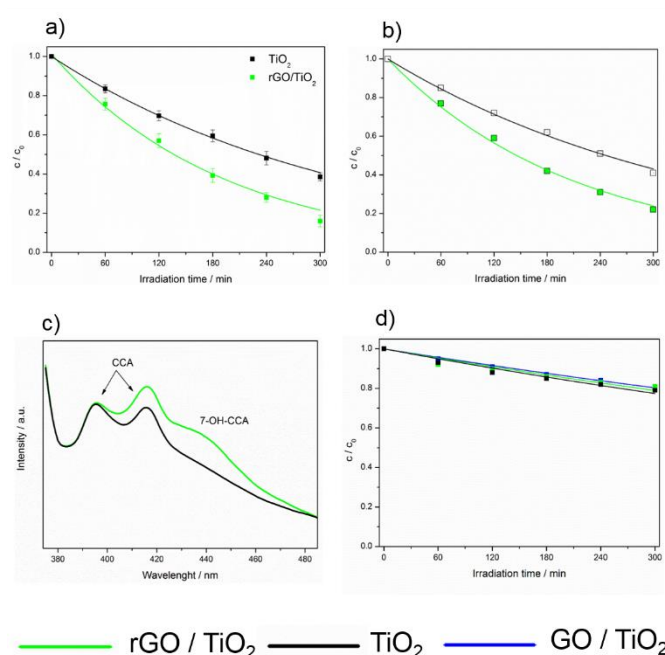


Figure 1. a) Course of the photocatalytic degradation of 4-chlorophenol on TiO₂ and rGO/TiO₂ photocatalysts, b) Reusability of TiO₂ and rGO/TiO₂ photocatalysts, c) Fluorescence spectra of 7-OH-coumarin-3-carboxylic acid after irradiation of TiO₂ and rGO/TiO₂ with 365 nm light for 30 seconds, d) Effect of OH radical scavenger (2-propanol) on the course of the 4-chlorophenol photocatalytic degradation on TiO₂, GO/TiO₂ and rGO/TiO₂.

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