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# Anchoring titanium dioxide on carbon spheres for high-performance visible light photocatalysis

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## ABSTRACT

The interfacing carbon materials can improve the visible light absorption of titanium dioxide ($TiO_2$). Here $TiO_2$ was anchored on carbon spheres (CSs) obtained by the hydrothermal polymerization of sucrose to bathochromically expand its light-response region. Nano-$TiO_2$ is condensed on the CS surface upon hydrothermal treatment to generate a core–shell structure ($TiO_2$@CS). Because of interface formation between the two materials, $TiO_2$@CS achieved an enhanced visible light absorption compared to pure $TiO_2$. In addition, it degraded organic pollutants, such as methyl orange, bisphenol A, and Oseltamivir, more efficiently than pure $TiO_2$ and the well-known graphene–P25 $TiO_2$ nanocomposite under visible light irradiation. This promoted visible light photoactivity was evidenced by the enhanced photocurrent responses and structure-dependent changes of electron spin resonance spectra that disclosed the critical role of an interfacial structure containing a doping level formed by tuning electrons from CS to $TiO_2$. Therefore, the facile hydrothermal formation of $TiO_2$@CS reveals new avenues for cost-effective ultraviolet-free photocatalysts exhibiting high efficiency.

## 1. Introduction

Since the discovery of its ability to promote the photolysis of water in 1972 [1], titanium dioxide ($TiO_2$) has attracted tremendous research interest in the fields of chemistry, materials, energy, and environmental science. The excitation of $TiO_2$ by a photon with sufficient energy generates electrons and holes in the conduction band (CB) and valence band (VB), respectively. These charge carriers react with $H_2O$, $O_2$, and other organic species to form hydroxyl radicals ($^\bullet OH$) and superoxide radicals ($^\bullet O_2{}^-$), facilitating many photoinduced reactions such as water splitting and organic pollutant decompositions [2–9]. However, $TiO_2$ exhibits a wide band gap (3.2 eV for anatase), which limits photoexcitation wavelengths needed to activate these reactions to ultraviolet (UV) light ($\lambda < \sim 400$ nm). Because UV light represents 3%–5% of the solar radiative energy, the majority of the solar energy is superfluous and thus is wasted when $TiO_2$-catalyzed photoreaction is carried out under solar energy excitation. Prompting significant efforts to endow $TiO_2$ with visible light photoactivity by widening its light absorption range toward visible light wavelengths has been a challenging requirement [10–12]. Wide-spectrum photocatalysts active from UV to visible light wavelengths are also expected to find use in various UV-free applications. For instance, the photocatalysts can be used in indoor environment remediation, where common incandescent lamps or energy-saving light-emitting diodes are employed to avoid damage of human skin and eyes by harmful UV, and in clothing materials inside which Mie scattering from cloth fibers tend to cut UV light.

Doping using nonmetals (C, N, or S) in $TiO_2$, metal or plasmonic nanoparticle deposition on $TiO_2$, dye-sensitizer employment, and semiconductor coupling have been attempted to achieve visible light-activated photocatalysis using $TiO_2$ [3,7,8]. In particular, combining $TiO_2$ with carbon materials has been proven to be an effective way to improve its visible light absorption ability [13–27]. For example, Zhang et al. synthesized graphene–P25 $TiO_2$ composite in a one-step hydrothermal reaction [28]. Petronella et al.

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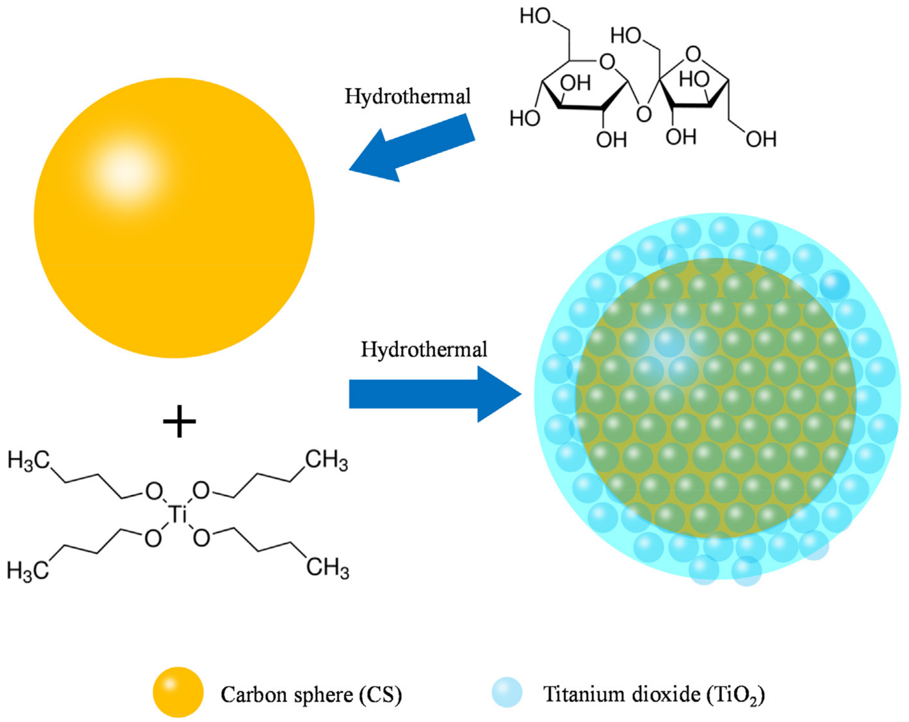

**Scheme 1.** Schematic illustration on synthesis approach of $TiO_2$@CS.

directly grew $TiO_2$ on carbon nanotubes (CNTs) [29]. Long et al. incorporated $C_{60}$ into $TiO_2$ by hydrothermal reaction [30]. These composite materials degraded organic pollutants more significantly than pure titania under visible light irradiation. However, the utilization of nano-carbons such as graphene, CNT, and $C_{60}$ usually causes high cost and sometimes toxic issues.

In 2004, Sun et al. derived a colloidal carbon sphere (CS) exhibiting a highly hydrophilic surface by hydrothermal carbonization (HTC) of glucose. This carbon sphere served as a substrate for the immobilization or encapsulation of noble metal particles, such as Au, Ag, and Pt. It also acted as a template for the formation of hollow spherical shell structures [31]. Low cost and biocompatibility make CS a cost-effective and environmental friendly precursor applicable for various energy storing and environmental purposes [32–38]. A few recent studies have led to $TiO_2$-loaded CS, albeit under harsh preparation conditions such as low pH or high temperature pyrolysis. In addition, these composites presented greater photocatalytic activity than pure $TiO_2$ under UV irradiation [39,40]. Zhao et al. constructed a spherical structure by one-pot hydrothermal treatment (HTT) of furfural and titanium precursor. In this structure, $TiO_2$ and carbon moieties are contacted like brick and mortar, which endowed the materials with a visible light activity by the so-called dyad-type charge transfer mechanism [23]. Zhuang et al. modified this synthesis using surfactants to produce a similar but hollow $TiO_2$–C spherical shell with an open mouth, which showed a higher photocatalytic activity than its solid counterpart [24].

Here an ultrathin $TiO_2$ shell of nanosize thickness was anchored over the CS core surface by a facile hydrothermal treatment, giving rise to an efficient visible light-driven photocatalyst toward the degradation of organic pollutants. The core–shell structure $TiO_2$@CS produced by this simple but effective and inexpensive approach achieved considerably higher photoactivity than pure $TiO_2$ and the graphene–P25 nanocomposite. Detailed photocurrent and electron spin resonance (ESR) analyses elucidated the structure-based sophisticated charge transfer mechanism explaining this enhanced photoactivity. These findings proved that the unusual $TiO_2$–CS interfacial structure played a critical role in the visible light photocatalysis.

## 2. Materials and methods

### 2.1. CS synthesis

Carbon spheres were synthesized by a hydrothermal method. Typically, sucrose (1.368 g, Wako, JIS Special Grade) was dissolved in aqueous solution (20 mL) by ultrasonic treatment for 2 min. The solution was transferred to a 25 mL Teflon container, which was sealed in a stainless steel autoclave and subjected to hydrothermal treatment at 448 K for 4 h. After cooling down to room temperature, the powdered product in the treated solution was collected by centrifugation and washed sufficiently with distilled water. The wet powdered product was transferred using 11.65 mL distilled water to a glass vial to form a CS dispersion (solution A) with a concentration of 5 mg $L^{-1}$. The powdered product of CS was also obtained after drying at 323 K overnight.

### 2.2. *Fabrication of CS-$TiO_2$ core-shell structure ($TiO_2$@CS)*

Titanium (IV) Tetrabutoxide monomer ($Ti(OBu)_4$) (Wako Special Grade) was selected as the $TiO_2$ precursor. First, a determined volume of $Ti(OBu)_4$ was added to 15 mL ethanol (EtOH, Wako, JIS Special Grade) under stirring to form a light yellow solution B and the solution was kept stirring for 2 min. Next, a certain amount of solution A was added into solution B under stirring and the mixture was kept stirring for another 2 min. The mixture was then poured into a 25 mL Teflon container which was sealed in a stainless steel autoclave and subjected to hydrothermal treatment at 433 K for 3 h. (refer to Supporting Information, Section 2 for the relationship of synthesizing temperature and photocatalytic activity). After cooling down to room temperature, the powdered product was collected by centrifugation, sufficiently washed with both distilled water and EtOH, and finally dried at 323 K overnight. The obtained $TiO_2$@CS samples are denoted as CST*n* where *n* stands for the vol-