



# Mesoporous silica-based carbon dot/TiO<sub>2</sub> photocatalyst for efficient organic pollutant degradation



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## ABSTRACT

Carbon dots (CD) and Ti species were assembled in the mesoporous silica matrix by a one-pot co-condensation strategy. The CD and Ti in the silica matrix were demonstrated to interact in two ways: on the one hand, part of the carbon in CD was doped into the Ti species; on the other hand, CD worked as photosensitizers for Ti species. The synergy effect between CD and Ti in the silica matrix along with the unique physical properties of the composite including ordered pore channels, large surface area and wide-range light absorption from UV to near IR made this composite be an excellent photocatalyst, as demonstrated by the photocatalytic degradation of azo dye acid orange 7. In addition to the degradation of organic pollutant, this newly developed mesoporous composite is expected to have promising applications in various areas related to environment and energy such as photoreduction of CO<sub>2</sub> and photocatalytic H<sub>2</sub> production.

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## 1. Introduction

Mesoporous silica materials based on Si–O framework have attracted widespread interests in applications of catalysts [1–3], biolabels [4,5], adsorbents [6–8], and sensor devices [4,9,10] due to their unique structural features like exceptionally high surface area, uniform and well-defined pore topology, since the first synthesis of MCM-41 in 1992 [11]. However, it is also known that mesoporous silica materials composing of only Si and O atoms do not possess any oxidation capacity and any ability for absorption of UV or visible light [12], which greatly limit their applications in the field of catalysis, in particular for photocatalysis. In order to expand their applications for photocatalysis, many efforts have been carried out. For instance, nanoparticles of semiconductors have been dispersed into the mesopores to form mesoporous composites with efficient photocatalytic activity [13–19]. This kind of composites has been

commonly reported for TiO<sub>2</sub> [2,16,17,19], Bi<sub>2</sub>WO<sub>6</sub> [13], WO<sub>x</sub> [14,15,18] and so on. On one hand, the mesopores help to prevent the agglomeration of semiconductor nanoparticles, thus acquiring relatively better catalytic activity. On the other hand, however, the nanoparticles in the pore channels inevitably sacrifice the pore volume and even lead to the pore blockage, which hinder further improvement of the photocatalytic activity. Nevertheless, this shortcoming can be well resolved by introducing the species with photocatalytic activity into the mesoporous framework rather than into the mesopores. As it has attracted a great deal of attention recently, transition metal species (e.g., titanium, cerium [20], chromium [21], vanadium [22], and molybdenum [23]) were incorporated as photoactive sites into the frameworks of mesoporous materials. By dispersing the photoactive sites in the silica matrix, the mesopores were well maintained and considerable catalytic activity was obtained for specific catalytic and photocatalytic reactions. However, this advantage was actually achieved at the expense of light-absorption range of photocatalyst. For example, the high dispersion of Ti species in silica framework increased splitting degree of energy level, leading to wider

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forbidden band than that of common  $\text{TiO}_2$ , therefore resulting in the blue-shift of absorption spectrum [24].

Recently, carbon dots (CD) have attracted great attention due to its non-toxicity, good chemical stability and excellent optical properties. It has been applied to couple with various semiconductors to extend their light absorption to visible or even NIR range for better photocatalytic performance. For example, Li et al. reported the design of  $\text{TiO}_2/\text{CD}$  photocatalysts that harnessed the full solar spectrum [25]. Liu and coworkers developed hematite/CD nanocomposites with a quasi-cube morphology and a single crystal structure around 600 nm in size. They investigated the effective photocatalytic activity towards the degradation of benzene and methanol under the visible-light irradiation [26]. More recently, Guo et al. explored a novel CD/carbon nitride hybrid photocatalyst that responded to infrared light irradiation [27]. However, up to now, there are still few reports about the combination of CD and photocatalytically active species in the mesoporous silica matrix to simultaneously utilize the advantages of CD and mesoporous materials.

Herein, we assembled CD and Ti species in the mesoporous silica matrix by a one-pot co-condensation of tetraethyl orthosilicate (TEOS), silylated carbon dot (Si-CD) and tetrabutyltitanate (TBOT). Mesoporous silica SBA-15 was chosen in consideration of its uniform and ordered pore structure and large surface area. The resultant CD and Ti co-incorporated mesoporous composite possessed excellent light absorption from UV to NIR. Experimental results demonstrated that this mesoporous composite had relatively high photocatalytic activity towards degradation of organic pollutant acid orange 7. Moreover, the composite containing both CD and Ti had greatly enhanced catalytic capability, compared to those materials containing only either CD or Ti. The mechanism for the improved photocatalytic activity was finally proposed based on the XPS analysis, the electrochemical and photophysical measurements.

## 2. Experimental

### 2.1. Synthesis of silylated carbon-dots (Si-CDs)

Si-CDs were obtained with a novel one-step synthetic route following the method described previously [28]. The reaction proceeded through pyrolysis of anhydrous citric acid. N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane (AEAPMS) (10 mL) was put into a 50 mL three-necked flask, and raised the temperature to 240 °C with stirring under the nitrogen atmosphere. Then anhydrous citric acid (0.5 g) was added into the flask quickly. After 1 min, the heating was stopped and the reaction mixture was cooled to the room temperature. The oily liquid product was obtained after being washed with hexane twice, sealed with hexane and stored in the refrigerator.

### 2.2. Synthesis of the mesoporous silica (MS) composites incorporated with CD and Ti

The MS composites were prepared using Pluronic P123 as the template by a method similar to that described before [30]. Typically, Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M_{\text{av}} = 5800$ , Aldrich) (0.5 g) was dissolved into 2.0 M HCl solution (120 mL) to get a homogeneous solution by vigorous stirring at 38 °C. Then, TEOS (9 mL) and appropriate volume of Si-CDs were added and the mixture was stirred continually for 24 h at 38 °C. The volume ratio of TEOS and Si-CDs was controlled as 20, 15, 10 and 5. Subsequently, the mixture was transferred into an autoclave and hydrothermal at 100 °C for 24 h. Then the samples were filtered, washed with deionized water for three times, dried at 60 °C under vacuum condition. To protect

the CDs in the framework, we used a facile extraction method to remove the P123 template. The as-prepared samples (50 mg) were added into a solution of sodium acetate (60 mg) in ethanol (5 mL). The mixture was stirred under reflux for 1 h at 92 °C, then centrifuged and washed with water for at least three times, dried and calcinated at 450 °C for 4 h under nitrogen atmosphere. The heating rate was 1 °C  $\text{min}^{-1}$ . The obtained samples with TEOS/Si-CDs ratios of 20, 15, 10, and 5 were named as CD-MS-20, CD-MS-15, CD-MS-10, CD-MS-5, respectively.

The above samples contained only CDs in the framework. The samples simultaneously incorporated with CD and Ti were prepared by a similar method. The volume ratio of TEOS and Si-CDs was set at 15 and different volumes of TBOT were added after the addition of TEOS and Si-CDs. The obtained samples were named as CTi-MS-15-X, where X represented the volume ratio of TEOS and TBOT which was 100,150 or 200.

As a comparison, we also synthesized CD incorporated silica nanoparticles without mesopores by a Stöber method [31] described as follows. Deionized water (7 mL), ethanol (25 mL) and ammonia (5 mL) were mixed in a flask by magnetic stirring while TEOS (3 mL) and ethanol (35 mL) were mixed in another flask. After 30 min, the two solutions were merged, and Si-CDs (150  $\mu\text{L}$ ) were soon added. The solution was then stirred for 3 h at room temperature. Then the sample was centrifuged and washed with deionized water for several times, dried and calcinated at 450 °C for 4 h under nitrogen atmosphere. And the rate was 1 °C  $\text{min}^{-1}$ . The finally obtained sample was named as  $\text{SiO}_2$ -CDs-20.

### 2.3. Evaluation of photocatalytic activities

The photocatalytic activities were evaluated by the decomposition of the aqueous solution of Acid Orange 7 (AO7, 10  $\text{mg L}^{-1}$ ). A 300-W high-pressure Xe lamp for which the emission wavelength is about 200–800 nm was used as a light source of the home-made photo reactor, cooled with flowing water in a quartz cylindrical jacket around the lamp. For a typical photocatalytic experiment, a total of 50 mg of catalyst powders was added 50 mL of the above simulating pollutants solution in the quartz tube. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. The above suspensions were kept under constant air equilibrate conditions before and during the irradiation. At given time intervals, about 4 mL aliquots were sampled, immediately centrifuged and filtered through syringe filters (cellulose acetate membranes) with the size of 0.22  $\mu\text{m}$  to remove the photocatalysts. The filtrates were analyzed by recording variations in the absorption in UV–vis spectra with using a Shimadzu UV-2450 ultraviolet visible spectrometer.

### 2.4. Catalyst characterization

The morphology of as-made CD-MS and CTi-MS-15 series samples was characterized by transmission electron microscopy (TEM, JEM2000EX) and scanning electron microscopy (SEM, JEOL JSM-6360LV microscope at an accelerating voltage of 15 kV). Small angle XRD patterns which were conducted to identify the samples' microstructure characteristics, were collected in the range of 0.5–5° ( $2\theta$ ) and recorded on a Rigaku D/MAX-2550 diffract meter using  $\text{Cu K}\alpha$  radiation of wavelength 1.5406 Å, typically running at a voltage of 40 kV and current of 100 mA. UV–visible absorbance spectra were achieved for the dry-pressed disk samples using a Scan UV–visible spectrophotometer (SHIMADZU, uv-2450), and using  $\text{BaSO}_4$  as a reflectance sample. BET surface area measurements were carried out by  $\text{N}_2$  adsorption at 77 K using an ASAP2020 instrument. By utilizing the Barrett–Joyner–Halenda (BJH) model,

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