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# Seed-induced growing various $TiO_2$ nanostructures on $g-C_3N_4$ nanosheets with much enhanced photocatalytic activity under visible light

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# HIGHLIGHTS

- "Seeding" endows 2D g-C $_3N_4$  with anchoring sites to grow various TiO $_2$  nanostructures.

- 0D, 1D, 2D and 3D nanostructured TiO<sub>2</sub> on the surfaces of g-C<sub>3</sub>N<sub>4</sub> are readily tunable.
- The hybrids demonstrate remarkably enhanced photocatalysis upon visible light.

• Photoinduced holes are well involved in photocatalysis due to the charge separation.

# ARTICLE INFO

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# ABSTRACT

In this study, we provide a seed-induced solvothermal method to grow various  $TiO_2$  nanostructures on the surfaces of  $g-C_3N_4$ , such as 0D nanoparticles, 1D nanowires 2D nanosheets and 3D mesoporous nanocrystals. We show that the "seeding" endows  $g-C_3N_4$  with anchoring sites toward the heterogeneous nucleation growth of  $TiO_2$ , and the distribution of the loaded  $TiO_2$  can be controlled by tuning the amount of nucleation in the dispersion. Among synthesized nanostructures, seed-grown Meso- $TiO_2/g-C_3N_4$  hybrids exhibit the highest photocatalytic activity upon visible light irradiation using methyl orange and phenol as probe organics, which are about 2–4 times and 29–37 times as high as those of direct-grown Meso- $TiO_2/g-C_3N_4$  without seeding and bare  $g-C_3N_4$  for degradation of MO and phenol, respectively. The enhancement of photocatalysis can be ascribed to the adequate separation of photogenerated electrons at the heterojunction interfaces and dominant contribution of photoinduced holes mainly caused by the well-constructed nano- architectures.

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# 1. Introduction

2D (two-dimensional) nanosheet based hybrids have attracted intensive interest owing to the unique electronic and optical properties of their component individuals and the synergistic effect between the host and guest materials caused by the formation

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http://dx.doi.org/10.1016/j.jhazmat.2015.03.006 0304-3894/© 2015 Elsevier B.V. All rights reserved. of nanojunction [1–3], as well as their promising applications in energy storage and conversion such as lithium-ion batteries, solar cells, water splitting, environmental purification, photocatalytic synthesis and bioimaging [4–8]. Like many other photocatalysts, the efficiency of 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets is limited by its high recombination rate of photogenerated electron–hole pairs, which prompted a number of efforts to be directed toward the modification of g-C<sub>3</sub>N<sub>4</sub> [9–15]. Among various strategies, coupling g-C<sub>3</sub>N<sub>4</sub> with guest semiconductors to form a heterojunction is an effective way to improve the photoconversion efficiency [16,17]. The construction of nanojunction increases the driving force for efficient charge transfer across the hetero-interface, promoting the spatial separation of electron–hole pairs and leading to enhancement of overall photoconversion efficiency [18]. Thanks to intrinsic







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2D structure similar to graphene, g-C<sub>3</sub>N<sub>4</sub> nanosheet provides an ideal host substrate for supporting guest materials on the surfaces. There have been previous reports on the decoration of  $g-C_3N_4$ nanosheets with metal oxide nanoparticles [19-21], in which TiO<sub>2</sub> is probably one of the most ideal guest semiconductors owing to its well-known characteristics as well as suitable band-edge positions matching with g-C<sub>3</sub>N<sub>4</sub> [22]. Among reported literatures on TiO<sub>2</sub>, mesoporous nanostructure and faceted TiO<sub>2</sub> have been highlighted, demonstrating excellent photo-/conversion/chemical properties [23-27]. At the present stage,  $g-C_3N_4$  based hybrid photocatalysts were usually prepared by liquid deposition or cothermal treatment of precursor mixture, which resulted in 0D/2D nanojunction [28,29], nevertheless, controlling the microstructures of loaded metal oxides with desired dispersity and size distribution on 2D g- $C_3N_4$  nanosheets is still a challenge [30]. To the best of our knowledge, there is few study about the effect of different TiO<sub>2</sub> nanostructures on the photocatalytic activity of host g-C<sub>3</sub>N<sub>4</sub> nanosheets.

Herein, we demonstrate a seed-induced growth approach to construct various  $TiO_2/g-C_3N_4$  hybrid nano-architectures, in which the microstructure and morphology of  $TiO_2$  are readily tunable. The seeding affords microscopic nucleation sites for crystal growth, and overwhelms homogeneous nucleation, which then maintains regular shapes, narrow size distributions and controls the structures [31,32]. Such architectures provide an appropriate optical window for visible light harvesting, short diffusion distance for excellent charge transport, as well as a large contact area for fast interfacial charge separation and photoelectrochemical reactions. In addition, the various  $TiO_2$  nanostructures are stabilized to be prevented from aggregation, which enables  $TiO_2$  to take the most advantages of their structural features in adsorption and photochemical reaction. As a result, the nanojunctions are anticipated to exhibit good photoelectrochemical and photocatalytic activities.

Based on this idea,  $g-C_3N_4$  nanosheets were firstly immersed into a TiCl<sub>4</sub> dilute aqueous solution, TiO<sub>2</sub> nuclei could deposit on  $g-C_3N_4$  surfaces after bath reflux. Then the pre- seeded  $g-C_3N_4$  was dispersed in a given solvent containing Ti precursor, and different TiO<sub>2</sub> nanostructures would grow on the surface of  $g-C_3N_4$  during solvothermal process, according to the related experimental conditions, such as porous structure, facets and low dimensions. The overall synthetic procedure is shown in Section 2. The relationships between the growth parameters, nano and microstructures, and the photoelectrochemical and photocatalytic properties of the hybrids were discussed.

# 2. Experimental

### 2.1. Synthetic procedures

g-C<sub>3</sub>N<sub>4</sub> (CN) nanosheets was prepared by thermopolymerization of urea according to a reported procedure [5]. In a typical synthesis, 10g of urea powder was put into an alumina crucible with a cover, then sealed with aluminum foil, which was heated to 550 °C at a rate of  $10 \circ C \text{ min}^{-1}$  and maintained at 550 °C for 4 h in air. For seeding on the surfaces of g-C<sub>3</sub>N<sub>4</sub> nanosheets (seeded CN), 50 mg of g-C<sub>3</sub>N<sub>4</sub> nanosheets was immersed in 50 mL aqueous TiCl<sub>4</sub> (1  $\mu$ M–1 mM) and stirred at 70 °C for 60 min. After reaction, the product was collected by centrifugation and washed with deionized water several times. Then, the sample was dried at 80 °C in air for 12 h for further synthesis.

To grow Meso-TiO<sub>2</sub> on  $g-C_3N_4$  nanosheets (S-MTO/CN, 0.092 g of seeded CN was first dispersed in 30 mL isopropanol. Then, 0.02 g PVP (MW 8000) and 1.42 g TiOSO<sub>4</sub> solution (15 wt% solution in dilute sulfuric acid, Sigma–Aldrich) were added into the resultant seeded CN solution at room temperature, resulting a molar

ratio of Ti/CN = 1). After stirring 20 min, the above solution was transferred to a Teflon-lined autoclave and treated at 105 °C for 48 h. After reaction, the product was collected by centrifugation and wash with ethanol before being dried at 60 °C in air overnight. The direct grown Meso-TiO<sub>2</sub> on g-C<sub>3</sub>N<sub>4</sub> nanosheets (D-MTO/CN) was synthesized according the above procedure without seeding. The reference Meso-TiO<sub>2</sub> was prepared according to the literature methods with small modification [33].

#### 2.2. Characterization

Powder X-ray diffraction (XRD) data of the products were collected using a Shimadzu XRD-7000, operating at 40 kV, 40 mA for Cu K $\alpha$  radiation ( $\lambda$  = 1.54 Å). Scanning electron microscopy (SEM) images were obtained on a Hitachi S-8020U. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) characterizations were performed with a JEM-2010 operated at 200 kV and Tecnai F30 operated at 300 kV, respectively. Nitrogen adsorption-desorption isotherm measurements were conducted at 77 K using an ASAP 2020. Before analysis, all samples were pretreated by degassing at 200 °C for 6 h to remove any adsorbed species. UV-vis absorption spectra were recorded with a Shimadzu-2550 UV-visible spectrophotometer using BaSO<sub>4</sub> as the background. Photoluminescence (PL) spectra were obtained on an Edinburgh Xe 900. All the spectra were taken at room temperature with an excitation wavelength 385 nm. X-ray photoelectron spectra (XPS) of the samples were measured using a PHI 5300 ESCA system with an Al K $\alpha$  X-ray photoelectron spectrometer at 150W.

#### 2.3. Photoelectrochemical measurements

Photoelectrochemical measurements were performed on a CHI 660B electrochemical system (Shanghai, China) operated in a standard three-electrode configuration with an FTO electrode deposited with the sample as a photoanode, a Pt wire as counter electrode, and a standard calomel electrode as the reference electrode. 0.1M Na<sub>2</sub>SO<sub>4</sub> was used the electrolyte. The photoanode was prepared as follow: 50 mg of the as-prepared photocatalyst was suspended in 0.5 mL of ethanol to produce a slurry, and then coated onto fluorine-doped tin oxide (FTO) glass substrate via the doctor blading method to ensure that all investigated working electrodes were of similar thickness. The side part of the FTO glass was previously protected using Scotch tape to reserve an area of 3.6 cm<sup>2</sup> (1.8 cm × 2 cm rectangle). The electrodes were dried in air at 50 °C for 10 h to eliminate ethanol and subsequently sintered at 200 °C for 5 h with 1 °C min<sup>-1</sup> ramp rate.

Electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential. A sinusoidal AC perturbation voltage amplitude of 5 mV was applied to the electrode over the frequency range 0.05–105 Hz.

#### 2.4. Photoactivity measurements

The photocatalytic activities were evaluated by measuring the degradation of MO and phenol, respectively, in an aqueous solution under visible light irradiation. The reaction solution contained 50 mg as received photocatalyst mixed with 50 mL aqueous solution of  $10 \text{ mg L}^{-1}$  in an 80 mL cylindrical quartz photochemical reactor with water circulation facility. The pH of the above solution was adjusted to 2.9–3.0 using H<sub>2</sub>SO<sub>4</sub> solution to ensure its characteristic wavelength  $\lambda_{max}$  unchanged during measurement. The photocatalytic test was conducted by low intensity irradiation with LED lamps (3W × 2, 420–425 nm, about 8.0 mW cm<sup>-2</sup>), which was located at 5 cm away from the surface of reaction solution. The concentration of dye during the degradation was monitored using a UV–vis spectrometer. Prior to irradiation, the suspension was



**Fig. 1.** FESEM and TEM images of (a) as synthesized g-C<sub>3</sub>N<sub>4</sub> nanosheets, (b) seeded g-C<sub>3</sub>N<sub>4</sub>, insets are EDS spectra showing a weak Ti signal after seeding. (c and d) shows the seeded grown S-MTO/CN hybrid, indicating the high dispersity and pores arising from gaps among Meso-TiO<sub>2</sub> microspheres that are sandwiched and covered by g-C<sub>3</sub>N<sub>4</sub> nanosheets.

continuously stirred in darkness for 1 h to ensure the establishment of an adsorption-desorption equilibrium. At a given time interval, 2 mL suspension were sampled and separated through centrifugation at 10,000 rpm. The supernatants were extracted to examine the degradation of MO at 505 nm and phenol at 270 nm on a UV-vis spectrophotometer, respectively.

## 3. Results and discussions

## 3.1. Morphology and structure

Because of the ammonia-based bubbles formed during the pyrolysis process of urea, the as synthesized g-C<sub>3</sub>N<sub>4</sub> is porous and consists of many curved nanosheets with lamellar morphology [34], approximately 16 nm in thickness (Fig. 1a and b and Fig. S1). After seeding with dilute TiCl<sub>4</sub> aqueous solution, the interconnection and overlapping of the curved g-C<sub>3</sub>N<sub>4</sub> (denoted as CN) nanosheets were partially unfolded, and the nanosheets became slightly thinner probably caused by the exfoliation of g- $C_3N_4$  in water [7]. EDS result shows that a weak but clear Ti element signal is detected in seeded CN although no trace of titania could be observed by either FESEM or TEM (inset Fig. 1a and b), suggesting the seeds are of extremely small TiO<sub>2</sub> clusters. 3D disordered mesoporous single crystal-like TiO<sub>2</sub> nano-/microspheres (denoted as Meso-TiO<sub>2</sub>) formed by self-assembled primary anatase nanocrystals (5-8 nm) with mesopores among them after hydrothermal treatment together with CN, which was confirmed by XRD and HRTEM (See below). For S-MTO/CN with appropriate seed concentration, Meso-TiO<sub>2</sub> nanospheres are wrapped

and isolated each other by curved CN to produce well-dispersed 3D/2D Meso-TiO<sub>2</sub>/CN nanojunctions and intimate interfacial contact, which is beneficial for fast charge transfer across the interface (Fig. 1c and d). For D-MTO/CN using a similar approach but in the absence of seeding, on the other hand, there are significant disengagement between CN and larger-sized Meso-TiO<sub>2</sub> microspheres (mainly within 600-1000 nm) (Fig. S2), similar to the material obtained by physically mixing Meso-TiO<sub>2</sub> and CN. Note that the dispersion and the size of Meso-TiO<sub>2</sub> was improved by increased seed concentration, and in a range of 30-60 µM wellgrown and highly dispersity were achieved. Further increasing the seed concentration restrained the self- assembly of Meso-TiO<sub>2</sub> nanospheres, and would lead to complete suppression of the formation of Meso-TiO<sub>2</sub> nanospheres after 1 mM of seeding, forming a 0D/2D type hybrid (Fig. 2). These results reveal that the seeding exerts great influence in anchoring TiO<sub>2</sub> during solvothermal growth and narrowing their distribution, which depends on the domination of homogeneous nucleation growth or heterogeneous nucleation growth. Further information about the microstructure of the S-MTO/CN hybrid was obtained from high-resolution TEM (HRTEM) images. From a single Meso-TiO<sub>2</sub> nanosphere to observe, the inner microstructure consists of disordered mesopores and the selected area electron diffraction (SAED) pattern give clear diffraction spots, suggesting a single-crystal-like nature along the anatase (001) zone axis (Fig. 3a and b). The orientation of (001) facets is due to the preferable adsorption of  $SO_4^{2---}$  onto (001) surfaces during crystallization [33]. The HRTEM image of the edge of a Meso-TiO<sub>2</sub> nanosphere also shows the characteristic lattice fringe of (001) and (101) facets (Fig. 3c). These are consistent with that



Fig. 2. TEM images of S-MTO/CN at different seed concentration. (a) 5  $\mu$ M, (b) 30  $\mu$ M, (c and d) 60  $\mu$ M, (e and f) 240  $\mu$ M and (g and h) 1 mM, showing the improved dispersion and smaller particle size of Meso-TiO<sub>2</sub> with the increased seed concentration.



Fig. 3. HRTEM images and SEAD pattern of S-MTO/CN, suggesting the mesopores caused by self-assembly of component TiO<sub>2</sub> nanocrystals with exposed (001) facets and the intimate contact between Meso-TiO<sub>2</sub> and CN. Seed concentration, 30  $\mu$ M.



Fig. 4. (a) XRD patterns, (b) XPS spectra, (c) low-angle X-ray diffraction and (d) nitrogen adsorption-desorption isotherm results of CN, Meso-TiO<sub>2</sub>, D-MTO/CN and S-MTO/CN.



Fig. 5. Representative TEM images of morphology evolution of S-MTO/CN with the increased solvothermal reaction time. Scale bar, 100 nm.



Fig. 6. XRD patterns of S-MTO/CN vs solvothermal time. Seed concentration, 30 µM.

of pure Meso-TiO<sub>2</sub>, indicating neither CN nor seeding influence the formation of Meso-TiO<sub>2</sub>. Additionally, an intimate contact between Meso-TiO<sub>2</sub> and CN sheets is clearly observed (Fig. 3d). With comparison to direct-grown process, seed-induced growth not only inherits the structural features of Meso-TiO<sub>2</sub>, but also produces more homogenous dispersities, which enable better separation of photogenerated electron-hole pairs and more efficient electron transfer within the hybrid structure.

The crystal structure of the obtained samples was investigated by X-ray diffraction (XRD) (Fig. 4a). The as-prepared CN presents characteristic (100) and (002) peaks at  $12.91^{\circ}$  (d=0.685 nm) and  $27.8^{\circ}$  (d = 0.320 nm), corresponding to the in-plane structural packing motif and interlayer stacking of  $\pi$ -conjugated aromatic systems, respectively [5]. The distance is slightly smaller than the size of the tris-s-triazine unit (ca. 0.73 nm), which presumably can be attributed to the presence of small tilt angularity in the structure [35]. No difference was detected between pure and seeded CN, suggesting the layered structure of CN remained unchanged undergoing TiO<sub>2</sub> seeding procedure. For S-MTO/CN, all peaks are unambiguously assigned to  $g-C_3N_4$  and anatase TiO<sub>2</sub> (JCPDS 37-1492) and no parasitic crystalline phase is observed. XPS (X-ray photoelectron spectroscopy) survey spectrum shows the presence of C, N, Ti and O elements with C/N and Ti/O atomic ratio of approximately 3:4 and 1:2, respectively, agreeing with the nominal atomic composition of C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> (Fig. S3). As further revealed in Fig. 4b, the high resolution C 1s spectrum displays two peaks centering at 284.98, and 288.48 eV. The peak at 284.98 eV may be attributed to contaminated carbon and surface carbon, and the peak at 288.48 eV can be assigned to C–(N)3 groups of g-C<sub>3</sub>N<sub>4</sub> [36]. The corresponding spectrum of N 1s can be deconvoluted into three peaks at 399.08, 400.58 and 404.58 eV, ascribable to sp<sup>2</sup>-hybridized nitrogen (C–N=C), tertiary nitrogen (N–C3) and the charging effects, respectively. The binding energy of O 1s at 529.98 eV can be ascribed to O<sub>2</sub><sup>---</sup> of TiO<sub>2</sub> and 531.28 eV to surface hydroxyl. The binding energy of Ti  $2p^{3/2}$  (458.78 eV) and Ti  $2p^{1/2}$  (464.28 eV) demonstrate the Ti<sup>4+</sup> species in the form of TiO<sub>2</sub> clusters [37]. In addition, no fitted peak is related to the Ti–C or Ti–N bonds, suggesting no chemical reaction occurs between g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> during synthesis.

Fig. 4c depicts the low-angle powder XRD patterns of Meso-TiO<sub>2</sub>, D-MTO/CN and S-MTO/CN. Each of them has an evident diffraction peak, which is a characteristic of disordered mesoporous structure. It is worth noting that S-MTO/CN exhibits stronger diffraction and slight shift toward lower 2 theta angle, giving more distinct mesoporous structural characteristic and larger mesopore, possibly caused by the confinement of CN against self-assembly of small component TiO<sub>2</sub> nanocrystals to a certain extent. To clarify this issue further, N<sub>2</sub> adsorption-desorption isotherm measurements were employed (Fig. 4d). All the tested Meso-TiO<sub>2</sub>, CN and g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> hybrids demonstrate type IV isotherm with a H3-type hysteresis loops, confirming the presence of mesopores. The isotherm of S-MTO/CN hybrid displays the highest adsorption at the high relative pressure  $(P/P_0)$  of approaching 1, indicating the coexistence of large mesopores and macropores [37]. Correspondingly, two peaks are observed from the pore distribution curve (inset in Fig. 4d), one at 4 nm is attributable to the confined self-assembled TiO<sub>2</sub> component nanoparticles, in accordance with the low-angle X-ray diffraction result (Fig. 4c). The other broad peak centering at 50 nm is probably formed from gaps between entangled CN nanosheets and Meso-TiO<sub>2</sub>, caused by the steric confinement of crumpled and entangled nanosheet structure of seeded CN against Meso-TiO<sub>2</sub> growth. This is in good agreement with the SEM and TEM observations. The as obtained hierarchically macromesoporous structure is expected to improve the penetration and adsorption of pollutants and to allow quick transport of reaction species onto the active sites [38].

#### 3.2. Growth mechanism

To understand the substantial role of "seeding" in growing  $TiO_2$  nanostructures, products were collected at designated growth stages and their TEM images are given in Fig. 5, respectively. For S-MTO/CN,  $TiOSO_4$  (Ti precursor) first precipitates due to the insolubility with isopropanol, forming sphere-like particles randomly distributing from 50 nm to 10  $\mu$ m in diameter.  $TiOSO_4$  was



Fig. 7. TEM images of seed-induced grown (a) TiO<sub>2</sub> nanowire/CN (S-TONW/CN) and (b) TiO<sub>2</sub>(B) nanosheet/CN (S-TOB/CN).



Fig. 8. (a) UV-vis spectra, (b) photoluminescence spectra, (c) transient photocurrent density vs time and (d) EIS Nyquist plots.



Scheme 1. Schematic illustration of growing Meso-TiO<sub>2</sub> on seeded g-C<sub>3</sub>N<sub>4</sub>.



Fig.9. Photocatalytic activity of S-MTO/CN at different seed concentration for degradation of MO upon visible light.

verified through EDS analysis but Ti-contained crystalline phase is undetectable from XRD (Fig. 6). In this step amorphous TiOSO<sub>4</sub> microspheres remain a precursor and spatially separate from preseeded CN, and this status changes gradually with solvothermal time [33]. With respect to the initially smooth surface of seeded CN, 1 h-solvothermal treatment leads to cavitation in some precursor nanospheres and rough-edged CN (inset in Fig. 5), implying hydrolysis of Ti precursor and heterogeneous nucleation synchronize. Some particles 30-50 nm in size have grown on the CN after 6 h, which are composed of finite number of clusters. These welldispersed nanoparticles are confirmed to be TiO<sub>2</sub> by XRD pattern, in which the slight bulge around 25.3° arising from the anatase TiO<sub>2</sub> (101) diffraction is observable and other diffraction peaks are not appearing due to the low crystallization. The seeds, as the heterogeneous nucleation sites, can induce primary TiO<sub>2</sub> clusters growing on CN so that the agglomeration may be avoided. However, the number of anatase particles per unit area is much low owing to the incomplete hydrolysis of Ti precursor. With the increase of time to 12 h, the precursor has completely disappeared and the subsequent self-assembly of TiO2 component nanoparticles around the pre-anchored nuclei particles contributes to the formation of olive-shaped anatase TiO<sub>2</sub> nanoparticles, 50-80 nm in size. In this step, initial mesoporous structure has already formed in those nano ellipsoids. Due to the competitive growth of surviving particles subject to Oswald ripening, final mesoporous nanospheres with size 50-200 nm formed. The driving force for the component TiO<sub>2</sub> nanoparticles toward nanosphere is to reduce the total

Table 1

Kinetic constant of photocatalysis for different photocatalysts under visible light irradiation.

Sample	$k (min^{-1})^a$	
	МО	Phenol
CN	0.0034	0.0027
Meso-TiO <sub>2</sub>	0.0070	0.0005
D-MTO/CN	0.0234	0.0157
S-MTO/CN <sup>b</sup>	0.1014	0.0387
S-TOB/CN <sup>b</sup>	0.0446	-
S-TONW/CN <sup>b</sup>	0.0412	-

<sup>a</sup> The kinetic constant k was obtained from the slope of Ln  $(C_0/C)$  vs irradiation time.

 $^{b}\,$  Seed concentration, 60  $\mu M$ 

surface energy of TiO<sub>2</sub> crystals. Largely thanks to proper amount of nucleation site on CN and steric confinement caused by the limited space between CN nanosheets as well, the overlarge microspheres can be avoided, in contrast to the case where there is no seeding [31]. Increase of seed density on the surface of CN can improve the dispersity of Meso-TiO<sub>2</sub> in hybrid, while impede the self-assembly (Fig. 2). The optimum seeding solution concentration in the experimental should be 30–60 µM at a given Ti precursor proportion ranging from 0.2 to 1.0 (Ti/CN molar ratio), and more or less than this seeding density scope would either completely suppress the self-assembly of component TiO<sub>2</sub> nanocrystals or cause microspheres agglomeration. The overall growth process follows the "hydrolysis – seed-induced growth (crystallization) – self-assembly" process that is summarized in Scheme 1. This is a little different from the growth of Meso-TiO<sub>2</sub> on GO, because the surface functional groups such as hydroxyl on GO may act as favorable nucleation sites for guest materials [39], which enables the control of heterogeneous nanostructures loaded on GO without seeding [40–42]. Unlike GO, g-C<sub>3</sub>N<sub>4</sub> through thermal polymerization route is endowed with amine and/or imino groups located in defects [5], these are not adequate as nucleation sites for metal ions under wet chemical conditions, except that those which have well- matched lattice parameter can form intimate contact with g-C<sub>3</sub>N<sub>4</sub> [43,44]. Homogeneously dispersed anatase TiO<sub>2</sub> nanowires and TiO<sub>2</sub>(B) ultrathin nanosheets on CN were also obtained based on the seeded growth process, just employing the specific solvents and templates for 1D and 2D TiO<sub>2</sub>, respectively, as confirmed with Fig. 7 and Fig. S4 [45,46]. On the basis of the above data, it can be concluded that the addition of CN has no impact for the formation of various TiO<sub>2</sub> nanostructures in different medium systems, therefore, we predict this method could be extended to synthesize other family of oxide/CN hybrids with well-dispersed and controllable nanostructure.



Fig. 10. Phtodegradation profile of (a) MO and (b) phenol vs time for different photoactive materials under visible irradiation. Seed concentration, 60  $\mu$ M.



**Fig. 11.** The effect of various scavengers on kinetic constant of photocatalysis for (a) S-MTO/CN and (b) g-C<sub>3</sub>N<sub>4</sub>, using MO as the probe pollutant. All the experiments were performed by adding 1 mmol scavenger. N<sub>2</sub> were bubbled for 0.5 h before and through photocatalysis.

#### 3.3. Optical and photoelectrochemical properties

The optical properties of the samples were studied by UV-vis absorption spectroscopy (Fig. 8a). Pure CN nanosheets exhibit an absorption edge at 439 nm, indicating the band gap of 2.82 eV, which is slightly wider than bulk  $g-C_3N_4$  (2.7 eV) owing to the quantum confinement [47,48]. The TiO<sub>2</sub> incorporation does not change the absorption edge but enhances the UV light absorption, which is a result of absorbance superposition of CN and  $TiO_2$ , suggesting no doping into the lattice, in line with XPS results. In addition, the absorbance feature of S-MTO/CN shows a flat but evident absorption over the range of wavelengths investigated longer than 439 nm, which demonstrate the hybrid may be able to absorb more light and thus favor the catalysis [49]. Remarkable quenching of photoluminescence intensity of CN was observed after TiO<sub>2</sub> incorporation (Fig. 8b), implying that the photogenerated electrons and holes have better separation in the S-MTO/CN. The low photoluminescence intensity may correlates with the efficient charge transfer between CN and TiO<sub>2</sub>, which confirms the preventing from the direct recombination of electrons and holes [22].

Fig. 8c exhibits the transient photocurrent responses via repeated on/off visible light irradiation cycles of CN based electrodes and the contrast materials, which can demonstrate the separation and migration efficiency of photogenerated carriers between CN and TiO<sub>2</sub> [15]. All of the samples exhibit reversible photocurrent responses on each illumination. The transient photocurrent density of the direct-grown D-MTO/CN is higher than 0.91  $\mu$ A cm<sup>-2</sup>, whereas that of the CN is 0.37  $\mu$ A cm<sup>-2</sup>. It is worth noting that the seed-induced S-MTO/CN hybrid exhibits the highest transient photocurrent density reaches 2.21  $\mu$ A cm<sup>-2</sup>, which is 2.43 and 5.97

fold larger than those of D-MTO/CN and CN, respectively. This result confirms that the well-constructed  $TiO_2/CN$  nano-architectures have a significant improvement in suppressing charge recombination and transferring the photogenerated electrons from CN.

To further investigate the charge transport behavior in the  $TiO_2/CN$  hybrid system, we conducted electrochemical impedance spectroscopy (EIS) measurements (Fig. 8d). In the Nyquist diagram, the radius of each arc is related to the charge transfer process at the electrode/electrolyte interface. Where is smaller radius, there is lower charge transfer resistance for the corresponding electrode/electrolyte [44]. The S-MTO/CN exhibits the smallest charge transfer resistance among all CN-based electrodes before and after visible light irradiation, which illustrates the effective charge transfer between the electrode and the electrolyte, owing to the well-constructed heterojunction.

# 3.4. Photocatalytic activity

The global photocatalytic activities of the samples were evaluated by degradation of methyl orange (MO) and phenol in aqueous solution under visible light irradiation. Among loaded nanostructures, mesoporous TiO<sub>2</sub> crystals exert the greatest influence in photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> (Table 1). Meanwhile, the photocatalytic activity of S-MTO/CN is highly depending on the employed seed concentration, which was enhanced and achieved the optimized performance at 30–60  $\mu$ M of seeding, as shown in Fig. 9. When further increasing the seed concentration, the photocatalytic activity was gradually decreased, probably due to the degradation of self-assembly of Meso-TiO<sub>2</sub>, although maintaining a high dispersity of TiO<sub>2</sub> nanoparticles loaded on CN (Fig. 2). Fig. 10 show



Scheme 2. Schematic for the energy band structure of the S-MTO/CN, g-C<sub>3</sub>N<sub>4</sub> and proposed mechanism for charge transfer.

the time profiles of  $(C/C_0)$ , where  $C_0$  represents the concentration at the adsorption-desorption equilibrium of the photocatalyst before illumination and C the concentration at the illumination time. Although pure CN possesses a high specific surface area (Table S1), near does the D-MTO/CN, the kinetic constants for the degradation of MO and phenol are, respectively, increased almost 6.9 and 5.8 times vs the pure CN nanosheets, although Meso-TiO<sub>2</sub> cannot respond to visible light. In addition, the higher degradation efficiency toward MO than that toward phenol is connected with a contribution of photosensitization mechanism. When D-MTO/CN was replaced with the S-MTO/CN as photocatalyst, the corresponding kinetic constants were further enhanced, respectively, by 333 and 146%. These results can be attributed to the well-constructed heterojunctions of Meso-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, as well as the much enhanced MO adsorption (Table S1), owing to the large BET area and surface charges of the hierarchical macromesoporous S-MTO/CN hybrid. The photocatalytic performance remained almost unchanged after 5-cycle photocatalysis, indicating its chemical and structural stability (Fig. S5).

It has been recognized that the hydroxyl radicals (•OH), photo induced holes and superoxide radicals  $(O_2^{\bullet})$  are the potential species for the photocatalytic oxidation of organic molecules, which stem from the conduction band (CB) and valence band (VB), respectively [50]. In order to reveal the photocatalytic mechanism and the underlying reasons of enhanced photocatalytic activity for the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrids, the main species involved in MO photodegradation over S-MTO/CN and pure CN nanosheets were monitored through the radicals and holes quenching experiments [51,52]. As is shown in Fig. 11, the addition of ammonium oxalate (AO) as a holes scavenger markedly inhibits the degradation of MO, about 76.3% reduction of reaction rate, which confirms that holes are the dominant active species in the hybrid system. At the same time, injecting tertbutanol (TBA, a scavenger for •OH) and the N<sub>2</sub> purging (a scavenger for  $O_2^{\bullet-}$ ) retard the rate by 29.8% and 37.8%, respectively, which indicates both •OH radicals and dissolved oxygen are also involved in the MO photooxidation process and share a similar portion in this process. For pure CN nanosheets, on the contrary,  $O_2^{\bullet-}$ radicals contribute about 76.5% of MO degradation efficiency while holes contribute a lower portion, ca. 23.5%. Additionally, •OH scavenger has almost no contribution in degradation of MO, only a slight depress (ca. 2.9% of reaction rate) was detected. These results suggest that the trigger of the photocatalysis switched from CB alone toward VB as well as CB after Meso-TiO<sub>2</sub> was elaborately incorporated. On the basis of charge transfer mechanism of the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction together with above quenching experiments, we proposed a possible photocatalytic mechanism (Scheme 2). Owing to the wide band gap of Meso-TiO<sub>2</sub> ( $E_g$  = 3.2 eV), only g-C<sub>3</sub>N<sub>4</sub> can capture incident photons of visible light. Thanks to the band alignment and the potential difference, the photogenerated electrons at the CB (LUMO) of CN nanosheets can fast migrate to the CB of Meso-TiO<sub>2</sub>. Since the photoinduced holes could not lead to the generation of •OH radicals caused by the more negative VB (HOMO) position of  $g-C_3N_4$  (1.57 eV vs NHE) in contrast to  $\bullet$ OH/OH $^-$  (1.99 eV vs NHE) [28], the accumulated holes may directly react with the MO. Meanwhile, the photoinduced electrons can react with dissolved O<sub>2</sub> in the aqueous solution to form  $O_2^{\bullet-}$ , and further reactions produce •OH radicals, both which are effective active species to oxidize MO. Therefore, photoinduced holes,  $\text{O}_2^{\bullet-}$  and  $^\bullet\text{OH}$  are all involved in the oxidation of MO, and the holes are the biggest contributor of them. For pure g-C<sub>3</sub>N<sub>4</sub> nanosheets, however, it could hardly produce •OH radicals under visible light illumination and only O2•as well as holes are ready for reaction. Due to the large difference in migration rate between photogenerated electrons and holes, it can be understand that the formation of O<sub>2</sub>•- and subsequent reaction with MO are much quicker than the oxidation of MO directly by holes. On the other hand, for S-MTO/CN hybrid, Meso-TiO<sub>2</sub> can efficiently trap electrons at its CB, at the same time, holes are leaven at the VB of CN, spatially separating electron-hole pairs, which provides more chances for accumulated holes to be involved in the reaction with MO instead of recombination.

#### 4. Conclusions

Pre-seeded g-C<sub>3</sub>N<sub>4</sub> was endowed with abundant anchoring sites toward the heterogeneous nucleation growth of TiO<sub>2</sub>. On this basis, it enables one to construct various TiO<sub>2</sub> nanostructures on g-C<sub>3</sub>N<sub>4</sub> surfaces with highly dispersion. After incorporation of TiO<sub>2</sub>, the TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid photocatalyst exhibited significantly enhanced photocatalytic activity under visible light irradiation. This enhancement has been demonstrated to be due to the great contribution of photoinduced holes caused by adequate separation and fast transfer of photogenerated electron at the heterojunction interfaces derived from the well- constructed nano-architectures and well matched energy level between the TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. This strategy is significant to construct fantastic nanostructures of metal oxides on 2D surfaces and to form homogeneously dispersed composite photocatalysts.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat. 2015.03.006.

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