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Three-dimensional graphene networks modified photocatalyst with high performance under visible-light irradiation

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ABSTRACT

Graphene is considered as a promising modifier to improve the photocatalytic performances of TiO_2 due to its excellent electrical property. However, due to the high defect density and low BET area of the widely adopted reduced graphene oxide (RGO), practical performances of the reported RGO-TiO_2 composite photocatalysts are not as good as expected. In this study, three-dimensional graphene networks (3DGNs) prepared by chemical vapor deposition approach is adopted to fabricate composite photocatalyst with TiO_2 (3DGNs-TiO_2). Results manifest that corresponding decomposition rate constant of phenol increases more than 100% and 30% compared to that case of adopting pure TiO_2 and the RGO-TiO_2 under UV-light illumination, respectively. Continuous three-dimensional structure of the 3DGNs provides fast transport channel for electrons (and depresses the recombination of photo-induced electron-hole pairs in the photocatalyst). Moreover, the resulting 3DGNs-TiO_2 displays good catalytic activity under visible-light irradiation due to the sensitization of the 3DGNs.

1. Introduction

Graphene assisted TiO_2 composite photocatalysts have attracted more and more attention due to their expected high properties [1–3]. However, practical performances of the reported graphene-TiO_2 are much lower than theoretical prediction. Firstly, the reported BET areas are smaller than 50 $m^2 g^{-1}$, indicating weak adsorption ability of the resulting photocatalysts [2,4]. Moreover, due to the high defect density and small BET area of the widely adopted reduced graphene oxide (RGO), the recombination rate of photo-induced electron-hole pairs in these photocatalysts is still high. Therefore, further enhancement of catalytic performances for the graphene modified TiO_2 can be achieved after related optimizations.

In order to adsorb more pollutants and inhibit the recombination of photo-induced electron-hole pairs, some attempts on adopting three-dimensional RGO (3DRGO) have been made [5,6]. The resulting catalytic performances are improved evidently, indicating that morphology optimization of the employed graphene is feasible. In fact, compared to that of the 3DRGO, the lower defect density and larger BET area make the three-dimensional graphene networks (3DGNs, prepared by chemical vapor deposition approach) a better photocatalyst modifier. However, the corresponding research is insufficient [7].

In this study, the 3DGNs-TiO_2 composite photocatalyst is prepared and the corresponding catalytic ability is evaluated by decomposition of phenol (avoiding the influence from self-degradation under visible-light illumination when dye pollution is adopted, such as methyl orange and rhodamine B) under UV- and visible-light irradiation. Reasons of the enhanced catalytic performances of the resulting photocatalyst are discussed, and the source of visible-light activity is revealed and confirmed.

2. Materials and methods

Preparation process of the 3DGNs-TiO_2 composite photocatalyst and details of decomposition experiments are shown in Supplementary materials.

3. Results and discussion

SEM images of the 3DGNs-TiO_2 are shown as Fig. 1a and b. The

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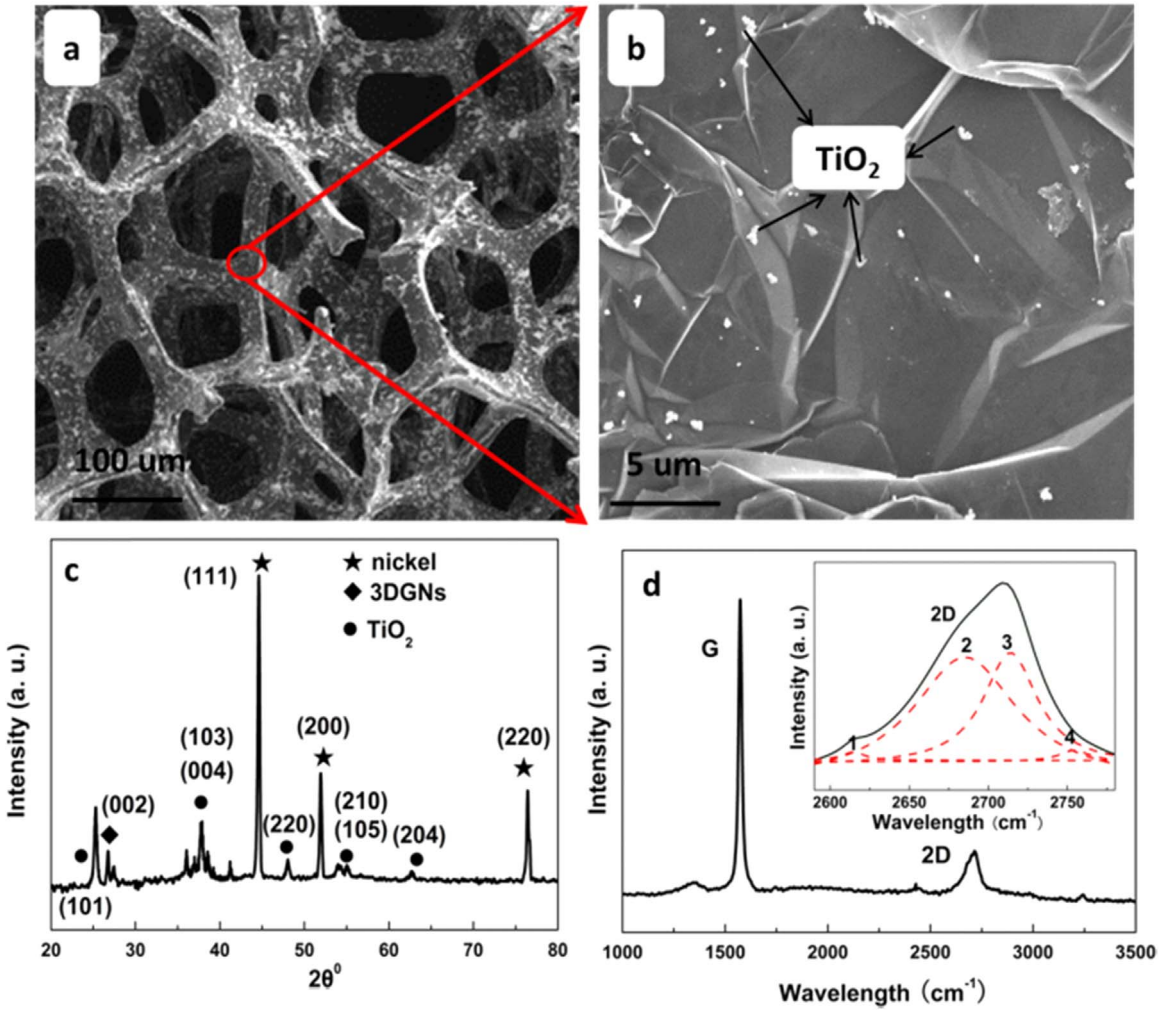

Fig. 1. (a) Low and (b) high magnification SEM images of 3DGNs-TiO_2, (c) XRD curve of the 3DGNs-TiO_2, (d) Raman curve of the 3DGNs, the detail of 2D peak is shown as inset.

uniformly distributed TiO_2 nanoparticles can be identified clearly on the surface of 3DGNs (the sparse distribution of TiO_2 nanoparticles is in favor of high catalytic performance) [7], indicating isotropy of the 3DGNs substrate. The sizes of TiO_2 nanoparticles range from 20 nm to 50 nm. Corresponding X-ray diffraction profile of the photocatalyst is displayed as Fig. 1c, and thickness of the adopted 3DGNs can be determined by the shape of 2D peak from its Raman curve (Fig. 1d). Four Lorentz components can be found after careful fitting, manifesting two-layer structure of the employed 3DGNs [8]. In fact, two-layer thickness is a proper choice because the integrity and continuity of monolayer 3DGNs are difficult to ensure, while the thicker 3DGNs sample (more than three-layer) could not further improve the resulting performances (only surface graphene plays as a holder for the TiO_2 nanoparticles).

Under UV-light illumination, the decomposition of phenol by using pristine TiO_2, 3DGNs and 3DGNs-TiO_2 are recorded, and evident distinctions can be seen (Fig. 2a). For 3DGNs-TiO_2, more than 90% phenol degrades after 4 h irradiation, whereas for pristine TiO_2 more than 30% phenol still remains under identical conditions. Moreover, no obvious change can be seen from phenol concentration by using the original 3DGNs. The above results demonstrate that only TiO_2 plays as effective ingredient to decompose pollution, while the presence of 3DGNs acts as an enhancer rather than a catalyst. Three major reasons can lead to the improved catalytic performance. Firstly, large BET area of the 3DGNs makes it an excellent scaffold to load TiO_2 nanoparticles and adsorb more pollution molecules. BET area of the prepared 3DGNs-TiO_2 is 9.8 times higher than that of pristine TiO_2 (and more than 2.6 times higher than previous reported 3DRGO-TiO_2), which leads to the higher decomposition rate constant of phenol (Table S1 of Supplementary Materials). Secondly, according to previous report, Fermi level of graphene is lower than conduction band of TiO_2 [9]. Thereby, the presence of 3DGNs achieves effective separation of photo-induced electrons and holes in the composite photocatalyst. The depressed recombination of electron-hole pairs in the 3DGNs-TiO_2 is confirmed by photoluminescence curves (inset of Fig. 2a). Thirdly, the continuous structure and high electron mobility of the 3DGNs make it a better electron sink (better than 3DRGO) to further promote the utilization efficiency of photo-generated electrons.

Besides the photocatalytic activity under UV-light illumination, corresponding performance of the 3DGNs-TiO_2 under visible-light irradiation is also measured because developing new photocatalysts with visible-light activity is significant to utilize the sunlight adequately. Different from the case of UV-light illumination, the phenol concentration is almost invariant by using pure TiO_2 under visible-light irradiation due to its wide band gap (~3.2 eV, excitation wavelength is ~380 nm). Contrarily, the 3DGNs-TiO_2 shows a well catalytic activity under identical condition, and 67% phenol decomposes after 5 h irradiation (Fig. 2b). As we known, two approaches including doping and adding sensitizer can endow visible-light activity for wide band-gap semiconductor. For the former, the band gap of TiO_2 would decrease due to the presence of impurity level. However, the recombination of electron-hole pairs would enhance because of the induction effect of impurity atoms. Based on UV–visible diffuse scattering spectrum, absorption edges of the pure TiO_2 and 3DGNs-TiO_2 are identical (inset