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Hydrothermal synthesis and photoelectrochemical performance enhancement of TiO_2/graphene composite in photo-generated cathodic protection

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ABSTRACT

TiO_2/graphene composites were synthesized through one-step hydrothermal method. The composites show an enhancement in photo-generated cathodic protection as the time-dependent profiles of photocurrent responses has confirmed. XRD data show that a bicrystalline framework of anatase and brookite formed as graphene provided donor groups in the hydrothermal process. The transfer of photoinduced electrons in the biphasic TiO_2 results in effective electron-hole separation. Moreover, graphene lead to a negative shift of the Fermi level as evidenced by Mott–Schottky analysis, which decreases the Schottky barrier formed in the TiO_2 and 304 stainless steel interface and results in the enhancement of photo-generated cathodic protection.

1. Introduction

Titanium dioxide (TiO_2) has received wide attention ever since the discovery of photoinduced water cleavage on a TiO_2 electrode by Fujishima and Honda in the early 1970s [1]. Over the past decades, TiO_2 has found application in many promising areas ranging from photocatalysis, sensors, to photovoltatic [2]. Corrosion-induced costs are very high across the globe. In the past 10 years, research has shown that the photo-voltaic effect of TiO_2 could be achieved for the cathodic protection of metals [3–5], which is named photo-generated cathodic ptotection. The techonology initiates from the generation of electron-hole pairs upon light irradiation. When a photon of energy matches or exceeds the band gap energy (Eg) of TiO_2 (3.2 eV approximately for anatase), an electron is promoted to the conduction band (CB), leaving a hole in the valence band (VB). The photo-excited electrons transfer to the coupled metals, resulting in a potential shift into the corrosion immunity region of the metal. TiO_2 functions as a non-sacrificial photo-anode in the process, which avoids the great waste caused by the sacrifice of conventional metal anodes such as Mg, Zn and Al ones.

While the photo-excited electrons transfer to the coupled metals, the holes migrate to the surface of semiconductor and participate in reactions with electron donors i.e. H_2O. The electron-hole pairs can recombine and release the energy in the form of heat or photon in bulk and/or on the surface region of TiO_2 [6]. The processes are generally viewed as deactivation processes because the photogenerated electrons and holes do not contribute to the cathodic protection.

Graphene with many extraordinary properties such as high electron mobility and large surface area has been extensively investigated with respect to the composites with TiO_2 in the fields of pollutant degradation [7,8], water splitting [9,10], energy device [11], Guo et al. [12] Many studies ascribe the enhancement in photocatalytic performance to the high migration efficiency of electrons [13]. Long rang π-conjugation in graphene yields charge-carrier mobility of 250,000 $cm^2\ V^{-1}\ s^{-1}$ at room temperature [14], which increase the photoinduced electron-hole seperation. However, besides electron mobility, the charge-transfer rate at the interface decides the photoinduced electron-hole recombination rate. The transfer of photoinduced electron from TiO_2 to the coupled metal, which resulted in the photo-generated cathodic protection, is not well known now for TiO_2/graphene composites as the process is not involved in other applications of TiO_2.

In addition, with strong coupling and good interfacial contact in heterojunction, the electron transfer can be ultrafast and even

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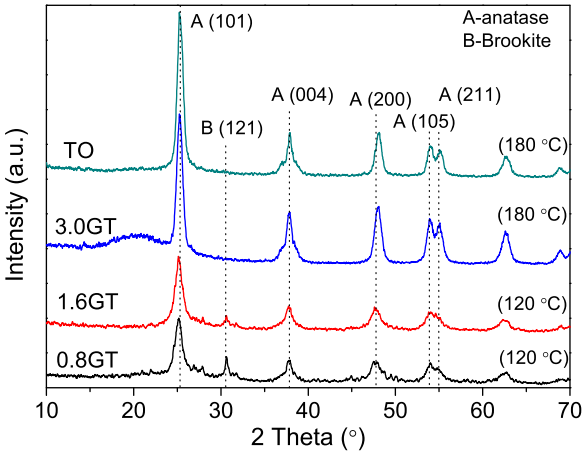

Fig. 1. XRD patterns of the synthesized TiO_2 and TiO_2/graphene composites.

faster than electron-hole recombination with appropriate electron structures [15]. Thus it is of great importance to form maximum interfacial contact between TiO_2 and graphene. graphene consists of graphite sheets covalently bonded with oxygen containing functional groups like hydroxyl and epoxide groups on basal planes and carboxyl groups at the edges. The oxygen functionalities may provide reactive sites for the nucleation and growth of the TiO_2 nanoparticles. This characteristic of graphene was utilized in our synthesis processes, in which a facile route was demonstrated to obtain a TiO_2-graphene composite via a one-step hydrothermal method in the presence of graphene. Because of the unique properties of graphene, it not only improved the separation and transport of photocarriers as other study have reported, but also might cause variation in crystalline structure and electron structure, which influence the charge transfer and electron-hole separation in the photo-generated cathodic protection.

2. Material and methods

2.1. Preparation of TiO_2-graphene composites

A one-step hydrothermal method was introduced to synthesize well-dispersed TiO_2 nanoparticles on the surface of graphene. Aqueous colloidal suspension of graphene oxide without stabilizers was purchased from Hengqiu Graphen Techonogy (Suzhou) Co. Ltd. All chemicals used in the experiments were in analytical reagent grade. Tetraethyl orthotitanate ($Ti(OC_2H_5)_4$) was used as the precursor of TiO_2 and diethanolamine (DEA) as the catalytic agent. $Ti(OC_2H_5)_4$ was added dropwise into the mixed solution of DEA, ethanol and de-ionized water with the volume ratio of 1/10/1 under vigorous stirring [16]. Then, this solution was added into graphene suspension and the mixture was magnetically stirred for 1 h. The suspension was sealed into a Teflon®-lined autoclave and maintained at 120 °C and 180 °C for 12 h. Finally, the resulting samples were collected after the autoclave was cooled to room temperature naturally and washed with de-ionized water several times to remove any impurities an dried at 60 °C.

It has been demonstrated that the dosages of graphene in graphene-involed semiconductor photocatalysts are usually very little, for some inherent negative problems aroused such as light shield or/and scatting along with the increase usage of graphene, which in return affect the photocatalysis properties of these composites [17]. We prepared TiO_2-graphene composite with 0.8 wt%, 1.6 wt% graphene heated at 120 labled 0.8GT and1.6GT respectively and 3.0 wt% graphene at 180 °C labled 3.0GT in this paper. Pure TiO_2 (TO) nanoparticles were also prepared through the hydrothermal method with the same parameters.

2.2. Characterization

The crystalline phase composition of the TiO_2-graphene samples was characterized by X-ray diffraction (XRD, D/max-RB) with

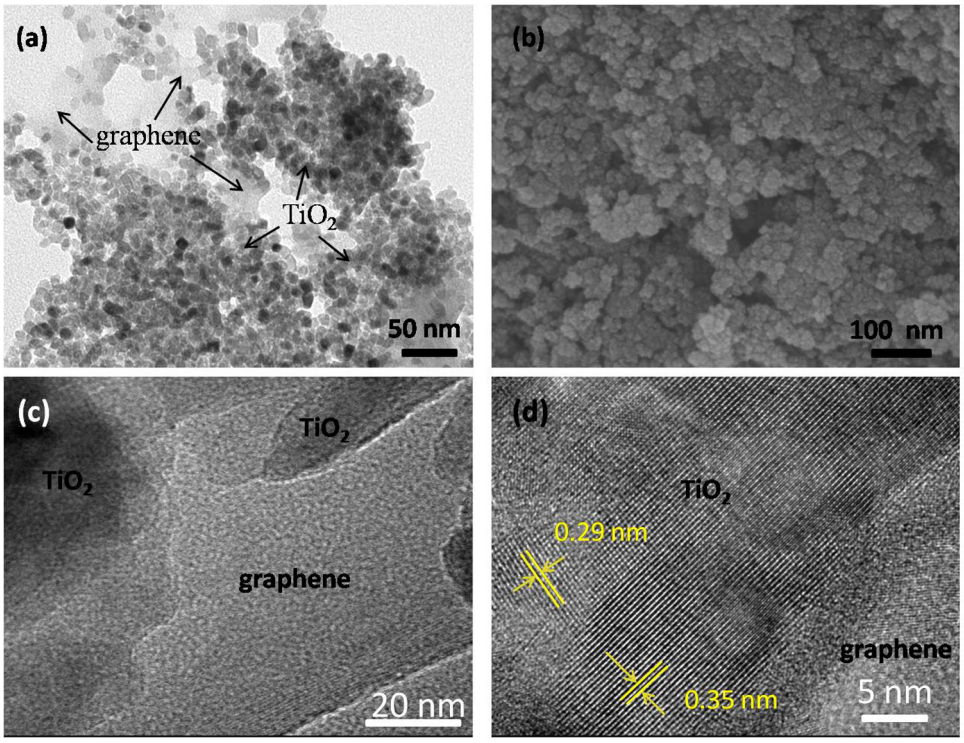

Fig. 2. Morphologies of the synthesized TiO_2/graphene 1.6GT composites: (a) TEM image of the TiO_2/graphene composites; (b) SEM image of the TiO_2/graphene composites; (c) and (d) HRTEM image of the TiO_2/graphene composites.