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Regenerated cellulose membrane as bio-template for in-situ growth of visible-light driven C-modified mesoporous titania

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ABSTRACT

Visible light driven C-doped mesoporous TiO_2 (C-MTiO_2) nanorods have been successfully synthesized through green, low cost, and facile approach by sol-gel bio-templating method using regenerated cellulose membrane (RCM) as nanoreactor. In this study, RCM was also responsible to provide in-situ carbon sources for resultant C-MTiO_2 nanorods in acidified sol at low temperatures. The composition, crystallinity, surface area, morphological structure, and optical properties of C-MTiO_2 nanorods, respectively, had been characterized using FTIR, XRD, N_2 adsorption/desorption, TEM, UV–vis-NIR, and XPS spectroscopy. The results suggested that the growth of C-MTiO_2 nanorods was promoted by the strong interaction between the hydroxyl groups of RCMs and titanium ion. Optical and XPS analysis confirmed that carbon presence in TiO_2 nanorods were responsible for band-gap narrowing, which improved the visible light absorption capability. Photocatalytic activity measurements exhibited the capability of C-MTiO_2 nanorods in degradation of methyl orange in aqueous solution, with 96.6% degradation percentage under visible light irradiation.

1. Introduction

In recent years, bio-templating techniques with polysaccharides-based material (cellulose, chitosan, lignin, etc.) are actively explored in the fields of metal oxides synthesis due to their environmental friendly process, facile, required low energy and cost effective concerns (Chen et al., 2013; Chen, Kuo, Lu, Hou, & Kuo, 2016; Liang, Liu, & Ni, 2015). However, as compared to other polysaccharides-based materials, cellulose-based materials are the most popular bio-templates used because of their insolubility, which renders them more appropriate for bio-replication than for nanoparticle growth control (Boury & Plumejeau, 2015). For instance, Lu and co-worker had successfully fabricated a millimeter-long TiO_2 fiber with nanostructures using bamboo cellulose fiber as a template (Lu et al., 2013). Moreover, cellulose-based material not only can be employed as a bio-template but also to form organic-inorganic hybrid materials with resultant nanomaterials. In the case of zinc oxide (ZnO), bacterial cellulose (BC) membrane was successfully prepared as a host matrix to promote hybridization with Zn^{2+} ions (Chen et al., 2013). Similar concept was adapted by Zhou and co-worker, where their group has successfully prepared electrospun cellulose acetate supported Ag@AgCl composites (Zhou et al., 2016). The resulting nanocomposites exhibited good mechanical properties and high photocatalytic activity in the degradation of methyl orange.

Recently, there is increasing attention in the development of visible light driven TiO_2 photocatalyst. This is because the traditional TiO_2 possesses relatively large band gap, which means that it can only be activated under UV region. This property limits the practical efficiency for solar applications. Currently, there is increasing attention in the doping of TiO_2 with non-metal atoms since it can avoid deteriorating thermal stability of the TiO_2 lattice structure (Kumar & Devi, 2011). In addition, C-doping of TiO_2 has been reported able to improve its visible light response and photocatalytic activity, and

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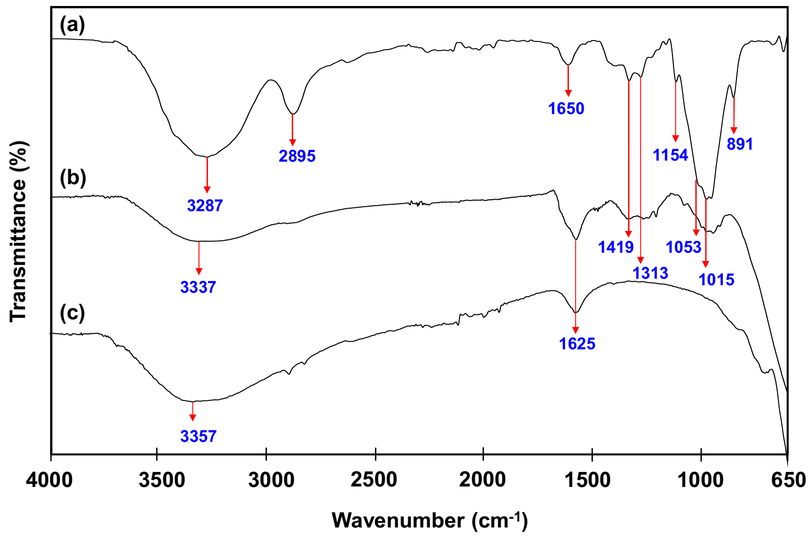

Fig. 1. FTIR of (a) RCM, (b) C-MTiO$_2$ nanorods, and (c) TiO$_2$ P25.

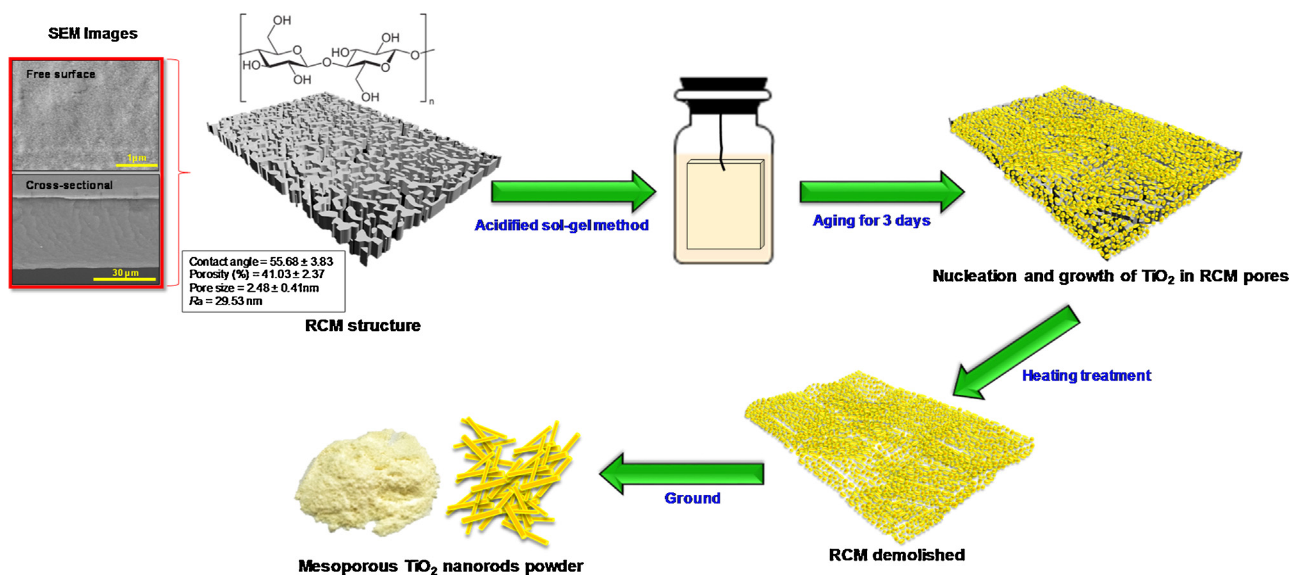

Fig. 2. Schematic illustration of in-situ growth of C-MTiO$_2$ nanorods within RCM matrix.

has been shown to be more effective than other non-metal doping (He, Que, Chen, He, & Wang, 2013). Several compounds have been used as carbon sources for the preparation of C-doped TiO$_2$ including glucose, carbon particle, melamine borate, and oleic acid as well as titanium dioxide precursor such as tetrabutyl orthotitanate Ti(OC$_4$H$_9$)$_4$ (Dong, Wang, & Wu, 2009; Kim, Liu, Nam, & Kim, 2011; Likodimos et al., 2013; Mattle & Thampi, 2013; Xu et al., 2010). However, most of the preparation of C-doped TiO$_2$ are using external carbon sources that prerequisites high temperature treatment between 400 to 600 °C, which are very energy consuming and not economic.

In this case, polysaccharides-based biotemplates have often been considered as in-situ carbon sources for production of C-doped TiO$_2$ for visible light driven photocatalyst. Latest study reported that production of TiO$_2$ with high photocatalytic activity under visible light can be achieved by introducing chitosan as a natural carbon source (Shao et al., 2015). However, to the best of our knowledge, there is yet any research that attempts to prepare C-doped TiO$_2$ nanoparticles by using regenerated cellulose membrane (RCM) as both bio-template nanoreactor and in-situ carbon sources. Recently, our group have successfully fabricated an environmental friendly RCM with low mean pores size of 2.48 ± 0.41 nm by utilizing recycled newspaper as the cellulose source (Mohamed et al., 2015a). It is believed that the resultant RCM can be used as an effective bio-template nanoreactor for the growth of TiO$_2$ nanostructures through its three dimensional porous structures and suitable nano-pore size distribution. Therefore, C-doped mesoporous TiO$_2$ nanorods have been produced by low temperature sol-gel bio-templating method using RCM as nanoreactor, which is environmental friendly, low in cost, energy saving and has facile approach.

2. Experimental

2.1. Materials

Non-printed area of the recycled newspaper was used as the raw material for cellulose source. Sodium hydroxide pallets, iso-propanol, sulphuric acid, and nitric acid were purchased from QReC Malaysia. Sodium chloride (80%) and titanium-*n*-butoxide were