

SYNTHESIS AND CHARACTERIZATION OF REDUCED GRAPHENE OXIDE-
LOADED COTTON AS PHASE-BOUNDARY CATALYST IN THE
OXIDATION OF STYRENE BY AQUEOUS HYDROGEN PEROXIDE

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To my parents, with love and gratitude

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ABSTRACT

The research described in this thesis is a comprehensive account of the synthesis and characterisation of reduced graphene oxide-loaded textile as a phase-boundary catalyst in the oxidation of styrene with aqueous hydrogen peroxide. A new model of phase-boundary catalyst (PBC) is designed from octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) for the oxidation of styrene by aqueous hydrogen peroxide. Cotton cellulose textile acts as a layered platform where the reduced graphene oxide (RGO) and polypyrrole (PPy) embedded on it. It has been reported that graphene arose as a candidate as a catalyst for oxidation reaction. Cotton textile is chosen owing to the relatively high network surface area, the abundance of hydroxyl functional group and ability to immobilize graphene oxide (GO) on its surface. Polypyrrole is one of conducting polymers capable to increase the conductivity and induced magnetic field. The effect of magnetic field on the selectivity and activity of the PBC has been studied by applying an electric current on the conductive layered catalyst. A well-attached graphene oxide to cotton (GO/CT) composite has been prepared by dipping pristine cotton in GO ink, and followed by the reduction of GO to reduced graphene oxide (RGO) in order to produce RGO/CT. The composite surface was further modified with polypyrrole (PPy) via chemical polymerization to obtain PPy/RGO/CT composite. Finally, the PPy/RGO/CT was functionalized with octadecyltrichlorosilane (OTS) in order to get floated layered catalyst (OTS/PPY/RGO/CT) in the immiscible liquid-liquid system. The catalysts were characterised by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, Field-emission scanning electron microscopy (FESEM), thermal analysis and chemical analysis, followed by X-ray photoelectron (XPS) spectroscopy, while the influence of improving electric current of textile by PPy and RGO was also examined using four-point probe technique. The results from FTIR and XPS spectral analyses proved that the polypyrrole and RGO were successfully attached to the textile. The four-point probe technique proved that the presence of PPy and RGO increased the electrical conductivity of cotton textile. PPy plays an important role in increasing the electrical conductivity compared to RGO since PPy is conducting material and its amount is larger than RGO. Meanwhile, apply electric current did not give significant effect on the catalyst's activity in static condition. The catalytic activity of OTS/PPy/RGO/CT in stirring condition shows that the reduced graphene oxide act as the catalytic active site in the oxidation of styrene with aqueous hydrogen peroxide, as indicated by the 21% increase in the conversion of styrene when the RGO amount was increased (12 times) in OTS/RGO/CT. Meanwhile, main products of the conversion of styrene using reduced graphene oxide-loaded cotton catalyst were styrene oxide and benzaldehyde, with a higher selectivity toward styrene oxide. However, individual graphene materials and PPy before grafting to cellulose fibers were more selective toward benzaldehyde. Lastly, it can be concluded that, based on its properties, reduced graphene oxide-loaded cotton textile is a promising phase-boundary catalyst for the oxidation reaction, specifically for the oxidation of styrene with aqueous hydrogen peroxide.

ABSTRAK

Penyelidikan yang dilakukan dalam tesis ini merupakan laporan yang menyeluruh terhadap sintesis dan pencirian tekstil termuat grafina oksida sebagai mangkin sempadan fasa dalam pengoksidaan stirena dengan hidrogen peroksida akueus. Model baru mangkin sempadan fasa (PBC) ini direka bentuk dengan menggunakan polipirol/grafina oksida terturun/kapas (OTS/PPy/RGO/CT) untuk pengoksidaan stirena oleh hidrogen peroksida akueus. Tekstil selulosa kapas bertindak sebagai penyokong berlapis yang di dalamnya tertanam grafina oksida terturun (RGO) dan polipirol (PPy). Telah dilaporkan bahawa grafina muncul sebagai calon mangkin untuk tindak balas pengoksidaan. Kain kapas telah dipilih disebabkan mempunyai luas permukaan rangkaian yang relatif tinggi, kelimpahan kumpulan hidroksil dan kebolehan untuk memegunkan grafina oksida (GO) di permukaannya. Polipirol merupakan salah satu polimer konduksi yang mampu meningkatkan kekonduksian dan medan magnet teraruh. Kesan medan magnet terhadap kepilihan dan aktiviti PBC telah dikaji dengan menggunakan arus elektrik pada mangkin lapis konduksian. Grafina oksida yang terlekat dengan baik di atas komposit kapas (GO/CT) telah disediakan secara mencelup kapas asli dengan menggunakan dakwat GO, dan diikuti dengan penurunan GO kepada grafina oksida (RGO) bagi menghasilkan RGO/CT. Permukaan komposit selanjutnya telah diubahsuai dengan polipirol (PPy) melalui pempolimeran kimia untuk memperoleh komposit PPy/RGO/CT. Akhirnya, PPy/RGO/CT difungsikan dengan oktadesiltriklorosilana (OTS) untuk mendapatkan mangkin lapis terapung (OTS/PPY/RGO/CT) dalam sistem cecair-cecair tak terlarutcampurkan. Mangkin telah dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi ultralembayung-nampak (UV-Vis), mikroskopi elektron pengimbasan pancaran medan (FESEM), analisis terma dan analisis kimia, diikuti oleh spektroskopi fotoelektron sinar-X (XPS), manakala pengaruh peningkatan arus elektrik tekstil oleh PPy dan RGO turut dikaji dengan menggunakan teknik prob empat titik. Keputusan analisis spektrum FTIR dan XPS membuktikan bahawa polipirol dan RGO telah berjaya melekat di tekstil. Teknik prob empat titik membuktikan bahawa kehadiran PPy dan RGO telah meningkatkan kekonduksian elektrik tekstil kapas. PPy memainkan peranan penting dalam meningkatkan kekonduksian elektrik berbanding dengan RGO memandangkan PPy ialah bahan konduksi dan jumlahnya lebih besar daripada jumlah RGO. Manakala, ours elektrika yang digunakan tidak memberi kesan yang signifikan kepada aktiviti mangkin dalam keadaan statik. Aktiviti pemangkinan OTS/PPy/RGO/CT dalam keadaan dikacau menunjukkan bahawa grafina oksida terturun bertindak sebagai tapak aktif mangkin dalam pengoksidaan stirena dengan hidrogen peroksida akueus, seperti yang ditunjukkan oleh pertambahan sebanyak 21% penukaran stirena apabila jumlah RGO ditingkatkan (12 kali) dalam OTS/PPy/RGO/CT. Sementara itu, produk utama penukaran stirena menggunakan mangkin kapas tercangkuk grafina oksida ialah stirena oksida dan benzaldehid dengan kepilihan yang lebih tinggi terhadap stirena oksida. Walau bagaimanapun, bahan grafina dan PPy individu sebelum pencangkukan serat selulosa adalah lebih selektif terhadap benzaldehid. Akhirnya sekali, maka dapat disimpulkan bahawa, berdasarkan sifatnya, tekstil kapas termuat grafina oksida adalah mangkin sempadan fasa yang berpotensi untuk tindak balas pengoksidaan, khusus untuk pengoksidaan stirena dengan hidrogen peroksida akueus.

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OTS/100%PPy/CT

LIST OF ABBREVIATIONS

FTIR	-	Fourier Transform Infrared
EDX	-	Energy dispersive X-ray
XRD	-	X-ray diffraction
FESEM	-	Field emission scanning electron microscopy
GO	-	Graphene oxide
FWHM	-	Full width at half maximum
CT	-	Cotton
PBC	-	Phase-boundary catalytic (system)
RGO	-	Reduced graphene oxide
SEM	-	Scanning electron microscope
XRD	-	X-ray Diffraction
TGA	-	Thermogravimetric analysis
OTS	-	Octadecyltrichlorosilane
XPS	-	X-ray photoelectron spectroscopy
GC	-	Gas chromatography
PPy	-	Polypyrrole
GO/CT	-	Graphene oxide/Cotton
RGO/CT	-	Reduced graphene oxide/Cotton
PPy/CT	-	Polypyrrole/Cotton
PPy/RGO/CT	-	Polypyrrole/reduced graphene oxide/Cotton
OTS/PPy/RGO/CT	-	OTS/Polypyrrole/reduced graphene oxide/Cotton

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Catalytic reactions carried out by using heterogeneous catalysts are preferable than those of homogeneous catalysts, due to the disadvantages posed by homogeneous catalysts. The main disadvantage of homogeneous catalyst is in the separation of product from the catalyst because both (catalyst and reagents) exists in the same phase. Due to this problem, purification of product needs several processes and increases the manufacturing cost. However, the catalytic activity of homogeneous catalyst was reported to be higher than that of heterogeneous catalyst. Heterogeneous catalyst are still preferred owing to ease of separation from final products. They are also reusable, therefore it requires lower cost. From an economic point of view, which is usually the main concern, heterogeneous catalysts are very useful to convert precursors into valuable substance that are low cost, environmental friendly and efficient (Ertl, 2008; Rase, 2000). Typically, solid materials such as metals or metal oxides are applied as heterogeneous catalysts and utilized in reactions of liquid-liquid phases and liquid-gas (Ertl, 2008).

During a heterogeneous catalytic reaction, the phase in which the catalyst exists is different from the phase in which the reactant(s) are. In general, solid catalysts are embedded in the reacting species that are normally in gaseous or liquid phase. As a result, essentially, the reaction rate depends on the mass transfer or diffusion between the phases (Klaewkla *et al.*, 2011). Therefore, mass transfer is an important phenomenon in a heterogeneous catalytic system (Bond, 1987).

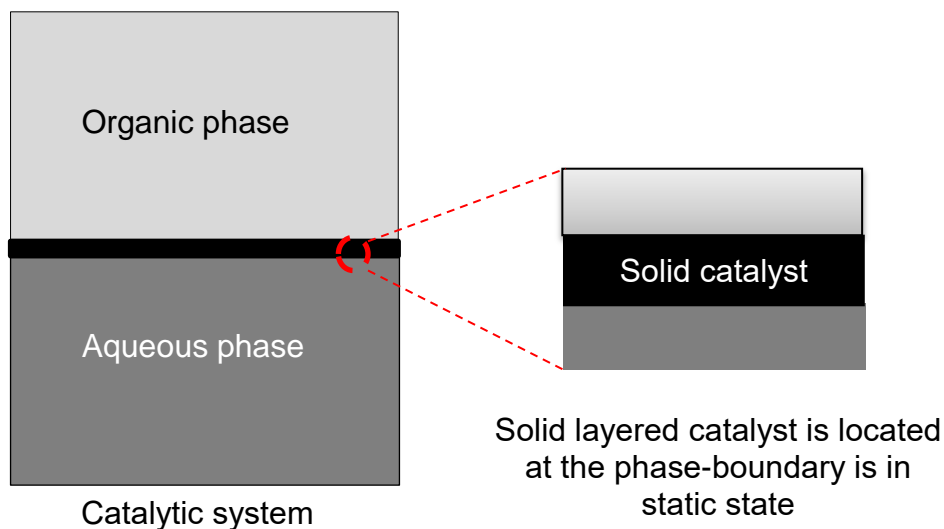


Figure 1.1 The illustration of PBC system

Nowadays, heterogeneous liquid-phase systems that include solid catalyst and immiscible liquid phase are widely utilized. In this system, stirring and co-solvent are used in order to make a homogeneous solution and to increase the interaction between the solid catalyst and reactants. However, this kind of heterogeneous catalytic system suffers from some problems. In order to solve these problems, a new generation of catalytic systems known as phase-boundary catalytic (PBC) system has been developed (Nur *et al.*, 2000) (Figure 1.1).

PBC system is a special type of heterogeneous catalyst system. In this system, the organic phase and liquid phase are immiscible, while the solid catalyst is located at the phase-boundary of the two phases. In addition, the PBC system requires no stirring and co-solvent. Therefore, the catalyst at the phase-boundary will increase the interfacial interaction between reactants (Nur *et al.*, 2000).

The first PBC reported was modified zeolite with alkylsilane-covered titanium dioxide and placed between an organic and aqueous phase (Nur *et al.*, 2000). It was used as catalyst for the epoxidation of 1-octene to give 1, 2-epoxyoctane. This PBC allows the mass transfer from liquid phases (reactants) to the solid catalyst phase without stirring. The amphiphilic solid catalyst led to mutual attraction in both organic and aqueous phases and also improved the catalytic

reaction. Therefore, it can be concluded that the amphiphilic structure of the phase-boundary catalyst plays an important role in catalytic behaviors (Nur *et al.*, 2000).

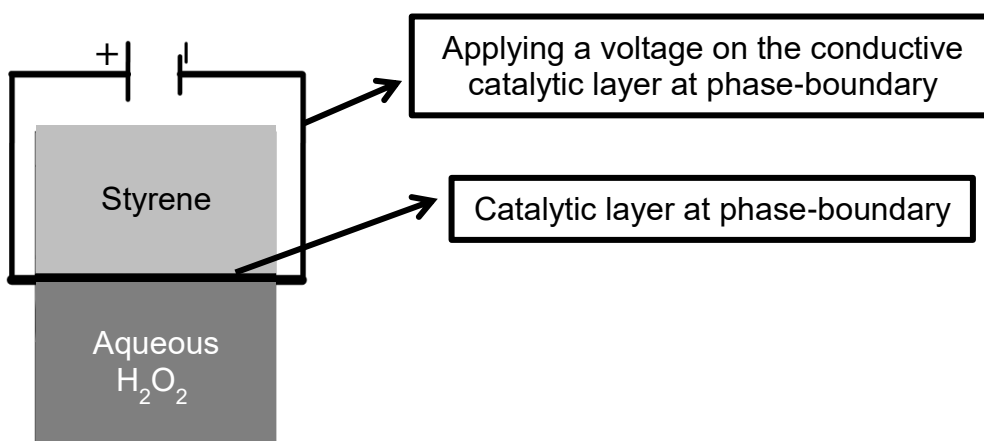


Figure 1.2 The application of current through catalyst in order to increase catalytic activity and selectivity

PBC system is desirable as it omits the need of stirring during reaction and ease in separation between product and catalyst. Previously, temperature controlled selectivity of alkylsilylated-Ti(IV) salicylaldehyde complex as catalyst in oxidation of 1-octene by using aqueous hydrogen peroxide (H_2O_2) in phase-boundary catalytic system have been examined (Yuan *et al.*, 2013). The results showed that two properties made the selectivity of reaction temperature-controllable in phase-boundary catalytic system. First property was due that the catalyst have ability to locate between liquid–liquid boundary. Second, the catalyst can be well-disperse and fix after 24 h at 90 °C in the consolute layer of the liquid–liquid phase owing to an enhancement in the miscibility between liquid–liquid boundary at relatively high temperature. In temperature-controllable reaction, the rate of hydrogen peroxide decomposition depends mainly on two issues: the reaction temperature and the type of catalyst. However, the oxidation reaction has been performed in relatively high temperature. Therefore, in this case, both the catalytic system and temperature can affect on decomposition rate of H_2O_2 . The catalytic activity increased by increasing the temperature up to 90 °C. However the best selectivity has been achieved at low temperature.

In this research, a new model of phase-boundary catalytic system has been designed by using octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) in the oxidation of styrene. Cotton acts as a layered platform, where reduced graphene oxide (active site) and polypyrrole are embedded on. Cotton is chosen as the support as it has relatively high surface area network, abundance of hydroxyl functional group and the ability to immobilize reduced graphene oxide (RGO) on its surface. The immobilization of RGO is important to prevent wrinkling and agglomeration of RGO. Besides that, RGO can also help to balance the decomposition rate of H_2O_2 and the oxidation rate of styrene. Thus, the catalytic activity can be improved. Apart from that, RGO has active sites for the oxidation of styrene to produce benzaldehyde. The abundance of π -system in graphene may increase the interaction of guest-graphene, therefore, leading to an increase in catalytic efficiency, particularly for those reactants with π -system (Yang *et al.*, 2013). Polypyrrole is used as the conductive material to improve and conduct electric current. The electric current then may induce decomposition of H_2O_2 . Octadecyltrichlorosilane is attached as the last material on the layered catalyst in order to increase the hydrophobicity of the catalytic system that allows the catalyst to be in the between of aqueous and organic phases. Therefore, the activity and selectivity of the catalytic reaction can be increased (Figure 1.2 and 1.3).

Graphene is an ideal nanosheet material for hosting a wide range of functionalities via noncovalent or covalent modification interaction (Su and Loh, 2012). Furthermore, in cases where there are the giant π -system, the guest-graphene interaction may be increased and the catalytic performance can be improved, especially for those reactants that have a π -system.

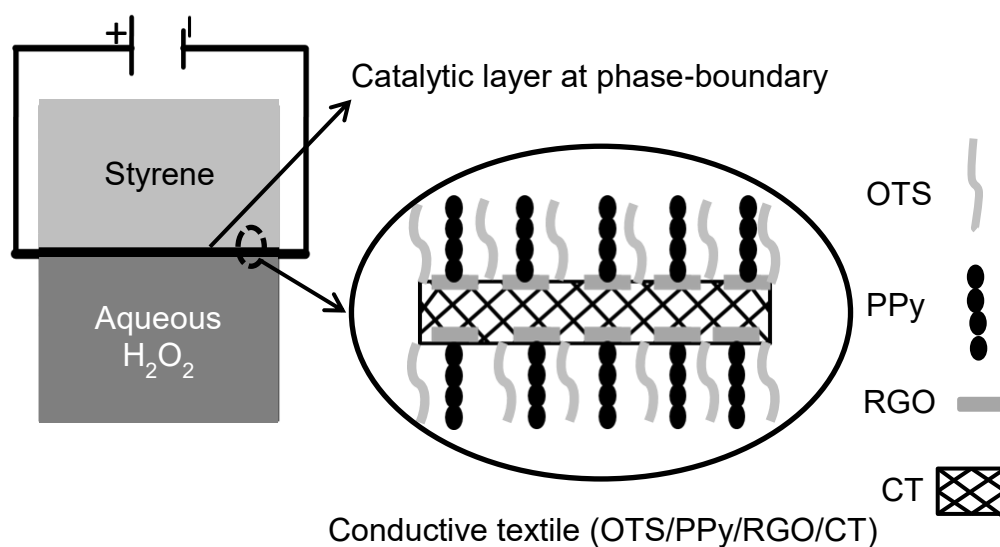


Figure 1.3 A new model for PBC system

According to some studies in the literature, graphene or graphene-like substances can be applied to organic synthesis, catalytic oxidation like oxidation of alcohols, olefins, diarylmethanes, methyl benzenes, thiols, acrolein and sulphides (see Dreyer and Bielawski, 2011; Dreyer *et al.*, 2010; Huang *et al.*, 2012). Similar to titanium modified zeolite, graphene is also able to activated H₂O₂ (Song *et al.*, 2010). It is believed that this specification explains catalytic oxidation activity of the graphene catalyst. This is acknowledged that the oxidation of alkanes/alkenes/aromatics is commonly followed by the Langmuir-Hinshelwood mechanism. In this regard, it is proposed that the styrene oxidation reaction initiates with the simultaneous adsorption of H₂O₂ and styrene over the surface of the catalyst, similar to mechanism of benzene oxidation reported by Yang *et al.* (2013). Beside that the existence of Lewis acid in graphene was investigated and proven by Peng (Su and Loh, 2012). They reported the location of active site is at the activated defects on the basal of graphene oxide and chemically converted graphene. It has been reported from previous studies that the oxidation reaction can be catalysed by Lewis acids sites (Corma and Garcia, 2003). Therefore it can be concluded that the formed surface oxygen species, will then react with adjacent adsorbed styrene on the defect active site of graphene surface as Lewis acids to generate the desired oxidized products. Because of this, it is suggested that chemically converted graphene can act

as a catalyst in the oxidation of styrene to benzaldehyde and others oxidized products (Figure 1.4).

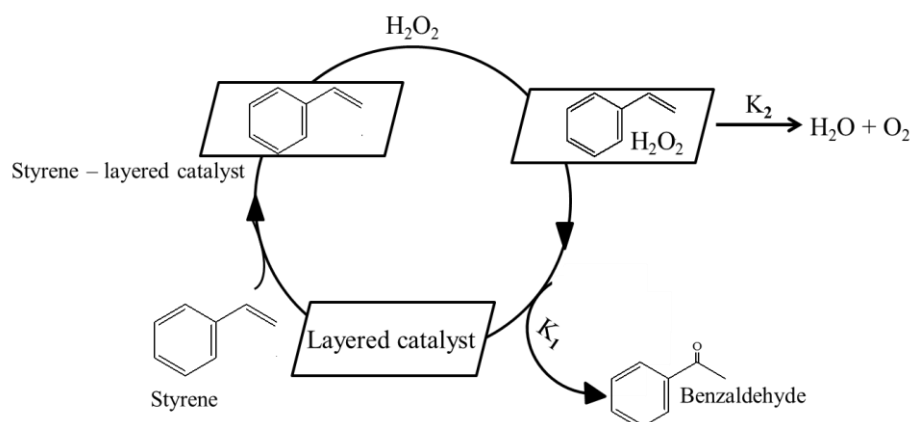


Figure 1.4 The proposed mechanism of the oxidation of styrene on layered catalyst (K_1 : the rate of styrene reaction with formed surface oxygen species, K_2 : the rate of H_2O_2 decomposition) (Yang *et al.*, 2013)

1.2 Statement of problem

In heterogeneous catalytic system to speed up the reaction, vigorous stirring is needed in order to transfer liquid reactants molecule into solid active site particles. However, stirring increases the energy consumption in industry. Hence, critical demand for a new heterogeneous catalytic system without stirring is needed to reduce energy consumption in industrial sector (Bond, 1987). In addition, the use of co-solvent can cause problem in the separation of products from the mixture reaction. On the other hand, the use of co-solvent can decrease the selectivity, and drive the reaction to produce by-products and causes leaching of the catalyst. In order to solve these problems, a new generation of catalytic systems known as phase-boundary catalytic (PBC) system has been developed (Nur *et al.*, 2000). In this system, no co-solvent and stirring are required to induce the catalytic reaction. However, previous PBC were in particulate forms, which suffered from drawbacks such as difficulty in handling, aggregation of particles, poor reusability and also mobilization of catalytic particles in consolute layer (Yuan *et al.*, 2013). Therefore, a new model of

conductive layered PBC system is proposed which can solve the drawback of using of co-solvent and stirring. Also the layered property of this novel catalyst can simplify the catalyst handling. In this new approach, the effect of electric current on the selectivity and activity of the PBC system has been investigated by applying a current on the conductive layered catalyst. The current can induced the magnetic field. It has been reported that the adsorption of the organic molecules can be induced by magnetic field (Spaldin, 2010; Yamamoto *et al.*, 2002), since the adsorption is the most important step in catalytic reactions. One expects that magnetic field induced by applying the electric current in layered catalyst can improve the catalytic activity.

1.3 Objective of the research

The objectives of this research are as the followings;

- To synthesize and design layered catalysts of modified RGO/CT as phase-boundary catalyst (PBC).
- To study the physical and chemical properties of the modified RGO/CT using spectroscopy, microscopy and thermal analysis techniques.
- To test the catalytic activity/performance of the modified RGO/CT as phase-boundary catalyst (PBC) in the oxidation of styrene using aqueous H₂O₂.
- To investigate the effects of electric current on the catalytic activity and selectivity of modified RGO/CT.

1.4 Significance of the study

The novelty of this study is the design of octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) layered catalyst in

PBC system of converting styrene to benzaldehyde. Besides that, there are no reports about the effect of the electric current in the PBC system towards increasing the selectivity of the catalytic reaction. Thus, this is the initial study of the catalytic conversion of styrene by using OTS/PPy/RGO/CT layered catalyst in PBC system to improve the activity and selectivity of the catalytic reaction. Finally, the ultimate goal of this research is to study structure-property relationship of the layered catalyst in order to achieve good performance in the catalytic activity and selectivity for organic catalytic reaction by electric current without stirring.

1.5 Scope of the research

The scope of this study can be divided into four parts which are the synthesize and design layered catalysts of modified RGO/CT as PBC, study the physical and chemical properties of the modified RGO/CT using spectroscopy, microscopy and thermal analysis techniques, test the catalytic activity/performance of the modified RGO/CT as phase-boundary catalyst (PBC) for the oxidation of styrene using H_2O_2 and lastly investigation the effects of electric current on the catalytic activity and selectivity of modified RGO/CT.

First, modified RGO/CT is synthesized by dip coating of cotton textile in graphene oxide solution. Then graphene oxide reduced by hydrazine. Second, in order to investigate the physical and chemical properties of the modified RGO/CT, the samples were analysed by different techniques such as Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis, UV-vis spectroscopy, Raman spectroscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM), field-emission scanning electron microscope (FESEM), and X-ray photoelectron spectroscopy (XPS), Van der Pauw techniques and Raman spectroscopy. Third, in order to investigate the catalytic activity of modified RGO/CT composite as PBC system with layered catalyst, the catalytic performance in the oxidation of styrene with aqueous H_2O_2 has been carried out under electric current in ambient temperature to observe the effect of current toward the catalytic activity. The catalytic activity has been carried out in ambient temperature (25 °C).