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Abstract

Inhibiting the environment pollutions motivated the development of green catalytic systems. The present research proposed a novel model of phase-boundary catalyst by using octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) for the oxidation of styrene by aqueous hydrogen peroxide. The catalytic activities were examined in both stirring and static conditions. The effect of electric current was also studied in static condition. The structural properties of the fabricated catalysts were characterized by X-ray diffractometer, Fourier transformed infrared spectroscopy, field emission scanning electron microscopy, and thermal analysis. Moreover, the influence of PPy and RGO on electrical current of textile was also examined by using four-point probe technique. The catalytic activity of OTS/RGO/CT showed that the RGO could act as the catalytic active site in the oxidation of styrene with aqueous hydrogen peroxide, as indicated by the 21% enhancement in the conversion of styrene when the RGO amount was increased (12 times) in OTS/RGO/CT in stirring condition. Finally, it could be stated that RGO-loaded cotton textile was a promising heterogenous catalyst for the oxidation reaction, specifically for the oxidation of styrene with aqueous hydrogen peroxide.

KEYWORDS

conductivity, graphene oxide, reduction, textile

1 | INTRODUCTION

Nowadays, heterogeneous liquid-phase catalyst systems containing solid catalyst and immiscible liquid phase are widely used. In these systems, stirring and cosolvent are employed to make a homogeneous solution and increase the interaction between the solid catalyst and reactants. However, using cosolvent not only may reduce the selectivity and facilitate the production of by-products and cause leaching of the catalyst but also make problem in the

separation of products from reacting agents. Therefore, in order to solve these problems, a new generation of catalytic systems known as phase-boundary catalyst (PBC) system has been developed. PBC system is a special type of heterogeneous catalyst systems. In this system, the organic phase and liquid phase are immiscible, whereas the solid catalyst is located at the phase-boundary of the two phases. In addition, the PBC system requires no stirring and cosolvent. Therefore, the catalyst at the phase-boundary will increase the interfacial interaction between reactants.¹ The first



reported PBC was modified zeolite with alkylsilane-covered titanium dioxide and placed between an organic and aqueous phase.¹ 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 PBC plays an important role in catalytic behaviours.² PBC systems show good potential in catalytic application due to their unique properties. In this system, no cosolvent and stirring are required to induce the catalytic reactions. In the previous PBC systems, the PBC was in particulate form, which was relatively difficult to handle. It has been reported that the adsorption of the organic molecules can be induced by magnetic field.^{3,4} The present paper proposed a new layered PBC system, where the octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) was synthesized as a layered catalyst. Cotton acted as a layered platform for the attachment of reduced graphene oxide as the active sites, because graphene or graphene-like substances can be applied for catalytic oxidation like oxidation of alcohols, olefins, diarylmethanes, methyl benzenes, thiols, acrolein, and sulfides.⁵⁻⁷ Moreover, it is worth mentioning that remarkable mechanical, electrical, and structural properties of graphene made it as an excellent support in heterogeneous catalysis, which can anchor metallic nanoparticles. Researchers have recently employed reduced graphene oxide sheets as substrate for copper nanoparticles⁸ and also Ni nanoparticles modified by Mo dopant⁵ in hydrogen generation application. The as-prepared nanocatalysts exhibited outstanding catalytic activity towards the hydrolytic dehydrogenation of ammonia borane (NH_3BH_3).

Considering that polypyrrole can enhance the conductivity, so, electric field was applied to this layered catalytic system in order to induce electric current. The effect of electric current in the layered catalytic system was also investigated. Finally, the catalytic activity of PBC system of OTS/PPy/RGO/CT in both static and stirring conditions was evaluated.

2 | EXPERIMENTAL

2.1 | Reagents and materials

All reagents employed were of analytical grade. Graphene oxide was purchased from Sigma-Aldrich. Ethanol (96%) was purchased from QREC. Pyrrole ($\text{C}_4\text{H}_4\text{NH}$, 99.99%), hydrazine hydrate (N_2H_4 , 50–60%), anhydrous sodium

carbonate (Na_2CO_3 , 99.9%), cetyltrimethylammonium bromide “CTAB” ($\text{C}_{19}\text{H}_{42}\text{BrN}$, 99%), and iron (III) chloride (FeCl_3 ; as an oxidation agent in polymerization of pyrrole) were acquired from Sigma-Aldrich. For the characterization, sulfuric acid (H_2SO_4 , 97%), sodium sulfate (Na_2SO_4), and potassium chloride were purchased from QREC. Octadecyltrichlorosilane (OTS) was purchased from Sigma-Aldrich. A piece of nonwoven wiper cloth, with a mass density of 9.623 mg cm^{-2} and 160 fibres per inch, was used. Chemical synthesis of GO/CT, RGO/CT, and OTS/PPy/RGO/CT was carried out as described below.

2.2 | Synthesis of GO/CT and RGO/CT

Graphene oxide was purchased from Sigma-Aldrich. The solution of GO (1 mg ml^{-1}) and de-ionized water was sonicated for 2 hr at 100 W to form a stable dispersion. In the scouring treatment, the cotton textile was boiled for 5 min at 100°C in de-ionized water containing Na_2CO_3 . The first treatment was performed using 10 mg ml^{-1} anhydrous sodium carbonate. After the treatment, the samples were washed with water until the pH was reverted to the neutral range ($\text{pH} = 7$).⁶ The piece of dewaxed cotton textile was dipped into the dispersed GO solution for 30 min under stirring and then dried at 90°C for 1 hr. This step has been repeated 12 times in order to load high amount of GO, followed by washing with de-ionized water and ethanol in order to remove nonattached GO. Finally, the cotton with attached graphene oxide (GO/CT) was dried overnight in a vacuum oven at 40°C . The weight of GO adsorbed on the cotton textile was calculated from the difference in weight before and after attachment. In the next step, the piece of GO/CT was cut to two equal pieces. After that, one piece of GO/CT was given additional treatment of hydrazine ($1\text{ }\mu\text{l}$ for 3 mg of GO, 98% Aldrich)⁷ to convert the GO to reduced graphene oxide on GO/CT (RGO/CT) under 80°C for 12 hr.

2.3 | Synthesis PPy/RGO/CT

Two pieces of GO/CT and RGO/CT were treated by polypyrrole polymerization. Vacuum distilled pyrrole, iron (III) chloride, and surfactants (CTAB) were used for the preparation of PPy/GO/CT and PPy/RGO/CT. The fabric ($80 \times 20\text{ mm}$) samples were immersed in 50 ml of aqueous solution containing pyrrole ($0.14\text{ ml} \approx 2\text{ mmol}$) and surfactants (CTAB) 0.02 M stirred for 30 min before the addition of 0.08-M FeCl_3 solution (50 ml) at $0\text{--}5^\circ\text{C}$ under nitrogen gas flow. The stirring was done for another 4 hr. A dark layer was evident on the surface of the GO/CT and RGO/CT. After polymerization, the resulting fabrics were then immersed in ethanol for 30 min and 1.0-M



HCl for 30 min, rinsed in water, followed by drying in vacuum oven overnight at 40°C. The weight of the polypyrrole attached on the RGO/CT and GO/CT was determined from the difference in weight before and after the attachment and polymerization process.

2.4 | Treatments by OTS

The PPy/RGO/CT pieces were added to a baker containing 22.5- μ l OTS in 100-ml toluene and were left for 5 min to allow chemisorption of OTS. Subsequently, the catalysts were cleaned by rinsing with ethanol and then de-ionized water. The catalysts were dried in vacuum oven at 50°C for 2 hr.

2.5 | Fourier transformed infrared spectroscopy

Fourier transformed infrared spectroscopy was performed using dried KBr powder by Nexus 670 Spectrometer (Nicolet, USA) the samples prepared by KBr pellet method.

2.6 | Field emission scanning electron microscopy

The surface morphologies of the PPy/RGO/CT, PPy/RGO/CT, RGO/CT, and GO/CT composites were analysed using JSM-6701F, with an accelerating voltage of 5 kV. A small amount of the sample was adhered to the sample holder using carbon tape without any further coating of gold on the surface of samples and then analysed by field emission scanning electron microscopy (FESEM).

2.7 | Surface resistivity

The surface resistivity was measured by using Van der Pauw technique [30]. The room temperature resistivity was measured by a Keithley power supply. Four hair-thin copper wires were placed in four equally spaced points on the corners of pieces of cotton textile with dimension of 20 \times 10 mm by using a small amount of silver paste.

2.8 | X-ray crystallography

The structural characterizations were performed by X-ray diffractometer (XRD, D8 Advanced) with CuK α radiations λ = 1.54178 Å at 40 kV and 10 mA. The speed of scanning was set at \sim 2 min⁻¹ with a resolution of 0.011 and 2 θ scanning range from 5° to 40°.

2.9 | Thermal gravimetric analysis

Thermal stability of PPy/RGO/CT, PPy/GO/CT, RGO/CT, and GO/CT was determined by thermogravimetric analysis (TGA, Perkin Elmer, STA 8000). About 20 mg of sample was located in the TGA pan and getting started analysis.

2.10 | Hydrophobicity test analysis

The adsorption of water on the surface of OTS/PPy/graphene/CT was carried out in order to investigate its role in the adsorption capacity. About 1 g of PPy/graphene/CT/OTS sample was dried under vacuum at 100°C overnight. After drying, the sample was subjected to water vapour at room temperature, followed by the determination of the adsorbed water as a function of time. The amount of adsorbed water was determined when it reached its maximum adsorption value.

2.11 | Catalytic application

The catalytic conversion of styrene was conducted in a glass tube reactor. The 5 mmol of styrene, 5 mmol of hydrogen peroxide, and 50 mg of catalyst were placed in the reactor. The reactor was kept in room temperature condition and maintained the room temperature for 24 hr. After completing the reaction, the product was separated by centrifugation and decantation. The organic products were analysed using gas chromatography (GC). The catalytic conversion of styrene was conducted in a special reactor that has been designed by us. The 10 ml of styrene, 10 ml of hydrogen peroxide, and 0.861 g of catalyst were put in the reactor. The reactor was kept in room temperature condition, and a voltage of 25 V was crossed through the layered catalyst, and the reactor was maintained at room temperature for 24 hr. The measured magnetic field was under 0.5 mT. After completing the reaction, the product was separated by centrifugation and decantation. The organic products were analysed using GC.

3 | RESULTS AND DISCUSSION

Fourier transformed infrared spectra for the samples synthesized with different PPy and RGO concentrations were presented in Figure 1. For modified fabric samples, the observed absorption peak at 1,552 and 1,427 cm⁻¹ could be related to the C—C and C—N stretching vibrations in the pyrrole ring, respectively.⁹ The bands at 1,319 cm⁻¹ were ascribed to the C—H and C—N in-plane deformation modes, respectively.^{9,10} The other PPy peaks

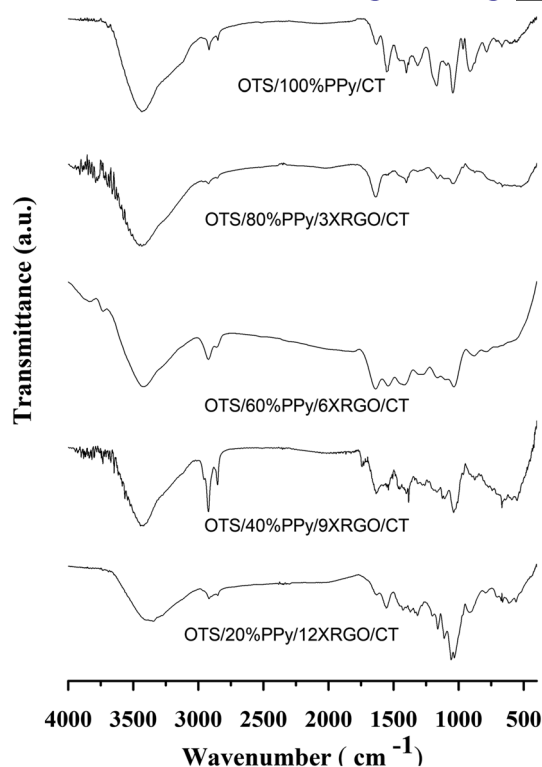


FIGURE 1 Fourier transformed infrared spectra of modified cotton textile

observed at 1,027 and 1,176 cm^{-1} were attributed to the bending vibration for modified cotton fabrics “bipolaron modes” related to N–H deformation and over oxidation, respectively.^{11,12} Attachment of RGO was resulted in a shift in the carboxyl peak towards a higher wavenumber from 1,621 to 1,634 cm^{-1} (Figure 1d,e).¹³ The existence of prominent bands at 1,012 and 1,041 cm^{-1} was related to the functional groups of cellulose, namely, the C–C, C–O, and C–O–C stretching vibrations.¹⁰ The presence of much weaker bands around 2,885 and 2,921 cm^{-1} correlated with the stretching of the C–H bands, proving the attachment of PPy on cotton fabric (Figure 1). The spectra also showed the peak at 2,932 cm^{-1} for antisymmetry stretching and C–H stretching vibrations at 2,860 cm^{-1} for symmetry stretching.¹⁴ These C–H groups came from the alkyl chain of hydrophobic-inducing agent such as OTS.¹⁵

The FESEM images showed the presence of GO, RGO materials, and PPy that were coated on the cotton textile. As showed in Figure 2, surface of the cotton fibres was quite smooth with no evidence of flake and round particles (Figure 2a). The insets of Figure 2b,c displayed the formation of roughness, wrinkles, and frequent grooves on the fibres’ surface, confirming the attachment of GO and RGO sheets onto the cotton fibres. However, the surface of RGO/CT seemed smoother compared with GO/CT. The higher magnification of the modified sample

in Figure 2d revealed the existence of round particles in the case of high amount of PPy loaded on the cotton surface. The increasing of surface roughness in PPy/RGO/CT composites, which could be observed in Figure 2e, was due to the appearance of round particles on the surface of RGO/CT after pyrrole polymerization. However, these nanosized round particles (PPy) were not individually clear in Figure 2e on the surface of RGO/CT as round particles, which could be due to the less concentrated pyrrole added to RGO/CT. A possible reason also might be the penetration of the PPy particles between GO sheet layers and cellulose fibres. Figure 2f,g showed the surface of OTS attached to graphene-coated cotton (OTS/12XRGO/CT) and OTS attached to 20%PPy/12XRGO/C sample. A significant observation in both samples was the increased fibre’s roughness compared with the samples without OTS; however, the graphene and PPy particles were not apparent in these images even at high magnification, which might be due to the OTS attachment.

The FESEM image and EDX analysis of OTS/12XRGO/CT, OTS/20%PPy/12XRGO/CT, and OTS/100%PPy/CT were shown in Figure 3. For the EDX analysis of OTS/12XRGO/CT, three elements (Si, O, and C) could be seen in this composite. However, for the OTS/100%PPy/CT and OTS/20%PPy/12XRGO/CT, five elements (Si, N, O, C, and Cl) were observed after attachment of polypyrrole in the composites.

The composition and hydrophobicity in OTS/PPy/RGO/CT series samples were analysed using TGA in the range of 25–1000°C by applying nitrogen gas. The recorded thermogravimetric plots for all cotton samples showed three degradation steps (Figure 4). The weight loss below 150°C (i.e., the first step) was attributed to the release of water molecules adsorbed on the surface of cotton and modified cotton samples. In addition, this loss might correspond to the breaking of water linkage, which was trapped on the texture of the samples. It has been established that no degradation took place until 200°C. Above this temperature, thermal stability decreased gradually, and fibres were decomposed. The second step (above 200°C) for modified cotton textile may correspond to the degradation of the attached polypyrrole polymer. However, in the case of pure fabric, the second step may be assigned to the thermo-oxidative degradation of the fabrics that transformed to the carbonaceous residues.¹⁶ The second and major weight loss in those samples coated with PPy, such as OTS/20%PPy/12RGO/CT, OTS/40%PPy/9RGO/CT, OTS/60%PPy/6RGO/CT, OTS/80%PPy/3RGO/CT, and OTS/100%PPy/CT, was started around 180°C and continued up to 340°C, which was ascribed to the decomposition of PPy on the top of the composite. However, for the cotton samples modified only by GO and RGO, no significant weight

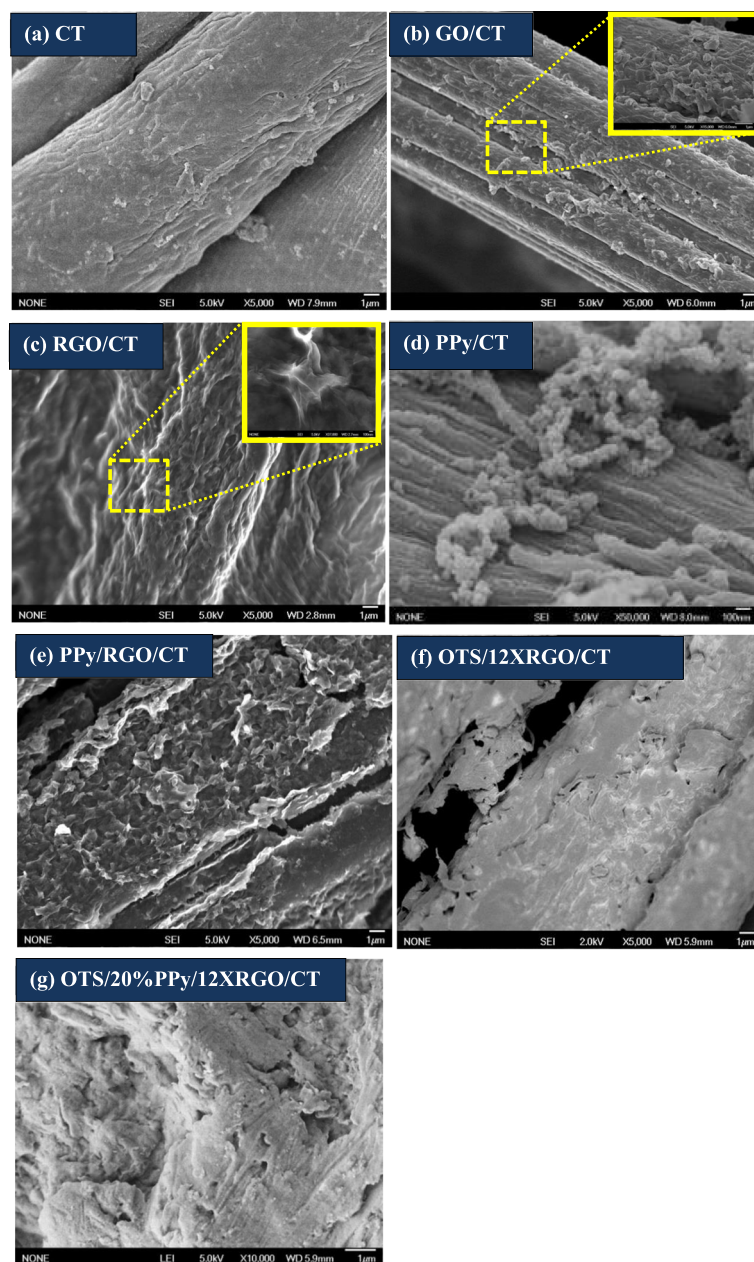


FIGURE 2 Field emission scanning electron microscopy images of samples (a) CT, (b) GO/CT, (c) RGO/CT, (d) PPy/CT, (e) PPy/RGO/CT, (f) OTS/12XRGO/CT, and (g) OTS/20%PPy/12XRGO/CT composites

loss was observed in the range of 180–340°C. The highest weight loss of these samples happened in the range of 320°C up to 380°C. On the other hand, weight loss around 320°C was related to the decomposition of the oxygen functional groups in GO and RGO. Furthermore, the degradation rate for composite textiles possessing PPy and RGO was also lower than pure cotton or those samples coated only with RGO or GO. For samples of OTS/20%PPy/12RGO/CT, OTS/40%PPy/9RGO/CT, OTS/60%PPy/6RGO/CT, OTS/80%PPy/3RGO/CT, and OTS/100%PPy/CT, the second weight loss stage was around 57%, 42%, 32%, 29%, and 28%, respectively, which was due to the first degradation of polymer. However, for the 12RGO/CT and 12GO/CT samples, the most weight loss between 320°C and 340°C was 71% and 75%,

respectively. PPy in the OTS/PPy/RGO/CT composites system may have hindered the heat accumulation between RGO layers. Therefore, by increasing the amount of PPy, the rate of degradation and weight loss of the composites were decreased. The TGA patterns of samples before and after treatment with OTS were almost the same, which could be due to the less amount of OTS being loaded on the samples, considering that the amount of OTS was optimized to the lowest quantity in order to prevent damage to the modified samples. In conclusion, the sample treated with GO and PPy had a different TGA weight loss curve compared with pure cotton sample. These results suggested that PPy, GO, and RGO acted as a retardant and the thermal stability of the all samples increased after modification. However, the curves showed

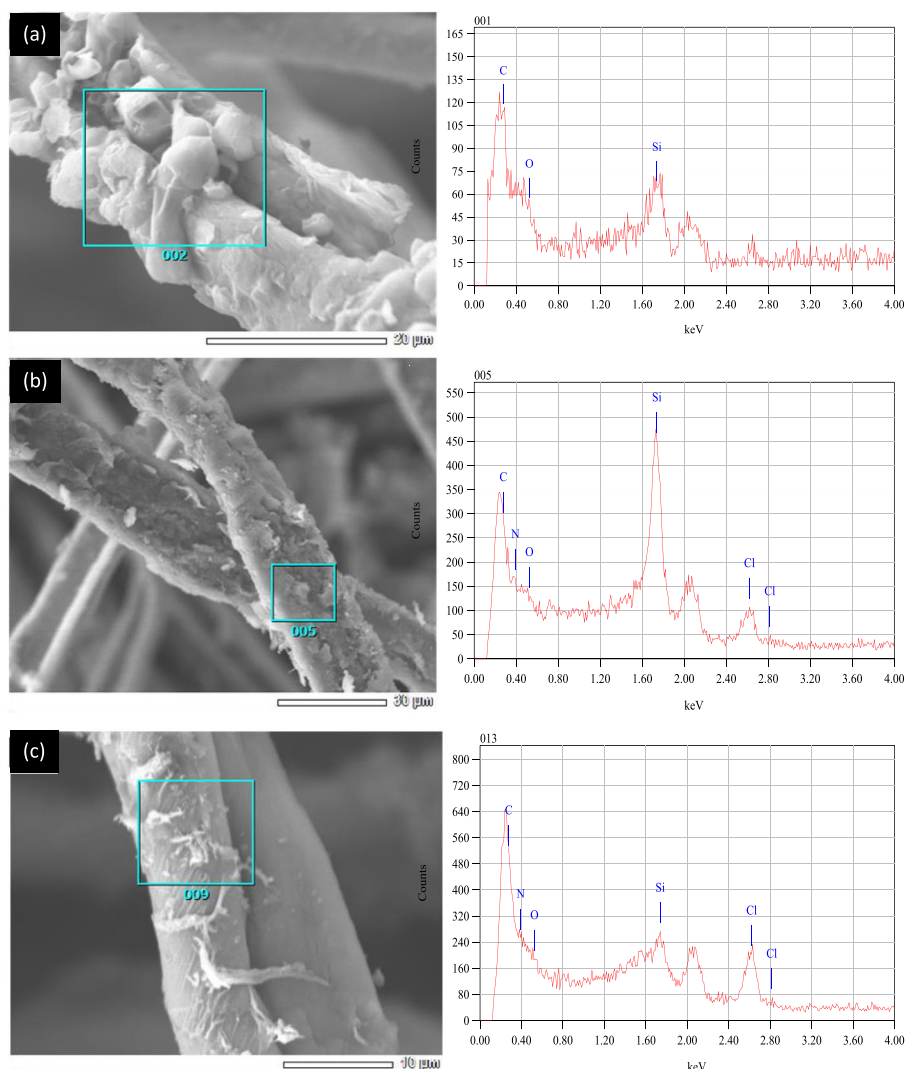


FIGURE 3 EDX images of (a) 12XRGO/CT/OTS, (b) 20%PPy/12XRGO/CT/OTS, and (c) OTS/100%PPy/CT composites

that the retardant property of PPy was more than GO and RGO due to lack of oxygen functional groups attached to aromatic carbon structure. In this regard, the highest thermal stability was obtained in samples with higher loading of PPy.

Figure 5 showed the XRD pattern of textile modified by polypyrrole, reduced graphene oxide, and OTS at 2θ value of 5° – 40° . The pristine cotton had three diffraction peaks at 15° , 16.4° , and 22.6° , which were assigned to 101, 102, and 200 planes, respectively.^{17,18} XRD results showed reduction in fibre crystallinity after treatment with polypyrrole and OTS.¹⁸ Studies showed that the PPy powder exhibited a weak and broad diffraction peak at $2\theta = 25.9^{\circ}$, which indicated the amorphous structure of PPy particles.¹⁹ It is difficult to find the characteristic peak of GO in the patterns of modified cotton fabrics due to the low amount of GO loaded.²⁰ The crystallinity of the cotton was reduced in polypyrrole-coated cotton. Amorphous polypyrrole showed only a reflection at 21° .

The relationship between catalytic activity and the crystallinity of the composite especially in inorganic compound was reported in another study.²¹ They found that the crystallinity of the specimen strongly affected the catalytic activity of ZrO_xN_y and TaO_xN_y . However, there is no report on the relation between graphene materials, crystallinity, and their catalytic activity.

Figure 6 showed the water adsorption capacity within 6 hr and also the weight gain of catalysts that were measured initially every 30 min and followed by every 1 hr till 5 hr. It was interesting that Langmuir isotherm was observed with first-order kinetic reaction, showing that the water molecules adsorbed to a maximum of one monolayer on the solid surface. The maximum percentage of water adsorption was achieved for OTS/12RGO/CT, where increasing amount of PPy components led to decrease of 25% at 5 hr. OTS/12RGO/CT had the highest water adsorption capacity of around 37%, and this implied that the composite functionalized with reduced

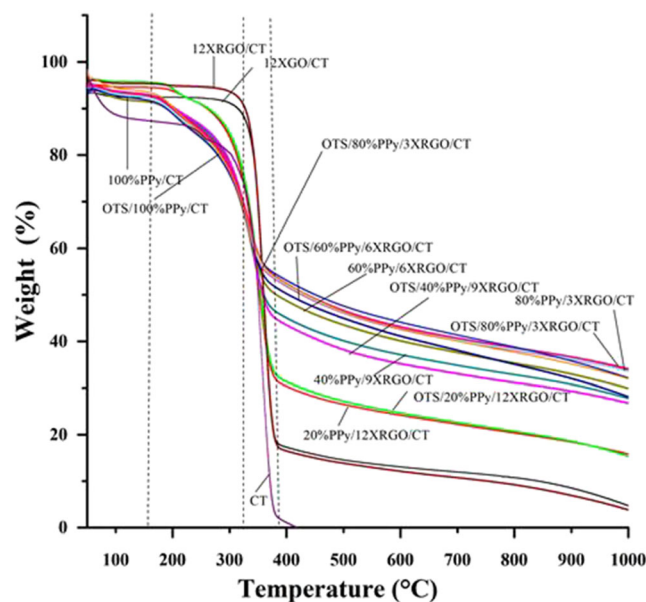


FIGURE 4 Thermogravimetric analysis curves of CT, 12GO/CT, 12RGO/CT, OTS/20%PPy/12RGO/CT, OTS/40%PPy/9RGO/CT, OTS/60%PPy/6RGO/CT, OTS/80%PPy/3RGO/CT, and OTS/100%PPy/CT composites

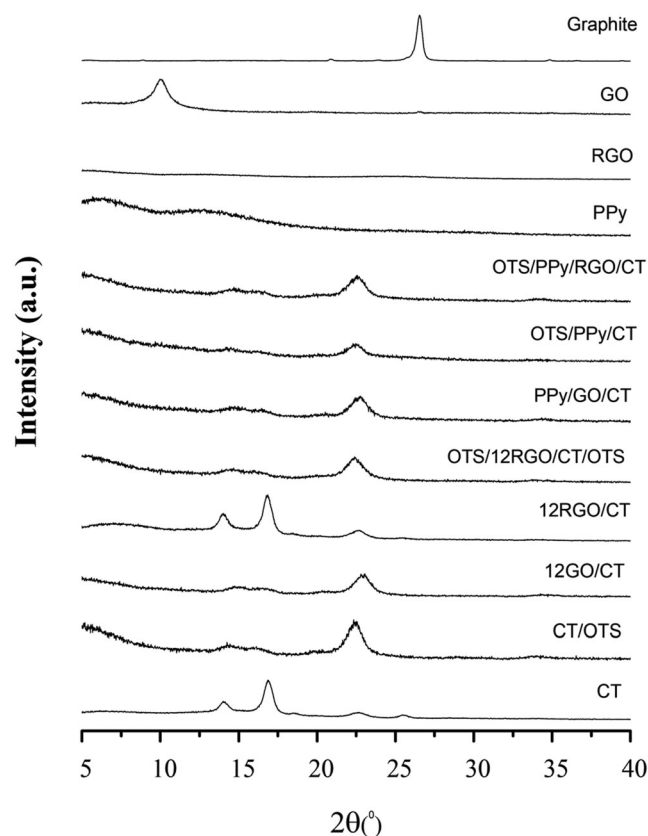


FIGURE 5 X-ray diffractometer patterns for CT, OTS/CT, RGO/CT, OTS/RGO, PPy/GO/CT, OTS/PPy/CT, and OTS/PPy/RGO/CT

graphene oxide was highly hydrophilic. As reported in Figure 6, the water adsorption capacity of the samples gradually increased by increasing the amount of RGO.

The presence of PPy on the top of composite increased the hydrophobicity. However, the hydrophilic effect of the RGO was more than the hydrophobic effect of PPy. Therefore, the hydrophobicity of the catalyst was evidently decreased. The observations indicated that water capacity of all the samples was almost constant, which could be related to the water saturation of the superficial reduced graphene oxide and PPy groups. However, the GO showed hydrophobic effect that may be due to its unsmooth surface and abundant of oxygen functional group (steric hindrance).

3.1 | Catalytic oxidation of styrene in stirring condition by using OTS/PPy/RGO/CT as the catalyst (stirring condition)

The oxidation of styrene was conducted at room temperature in a glass vessel, with acetonitrile as the solvent and hydrogen peroxide as the oxidant. The oxidation products were analysed by GC. The products of styrene oxidation were benzaldehyde, styrene oxide, and phenylacetaldehyde, which was in agreement with previous study.²² Meanwhile, the commercial compounds that might be produced in this reaction were also characterized by GC. The retention time of the chemical compounds in this analysis was summarized in Table 1. In a blank experiment (Figure 7), the conversion of styrene was relatively low in the absence of any catalyst, and the results showed that trace activity around 3% was observed over a 24-hr run. When graphene oxide was used as catalyst for the styrene oxidation, a moderate conversion was obtained. Moreover, the selectivity towards benzaldehyde was almost 99%, with no side product. However, when reduced graphene oxide-coated textile and the graphene oxide-coated textile catalyst were used in this reaction, benzaldehyde and styrene oxide were found to be the main products in the styrene oxidation. A relatively high styrene conversion of 21% and 17% was observed, whereas the selectivity towards styrene oxide dramatically increased to 72% and 80%, respectively. Similar to titanium containing zeolite,²³ graphene is able to decompose H_2O_2 .²⁴ We believe that this characteristic explains the catalytic oxidation activity of the graphene catalyst. Typically, oxidation of alkanes/alkenes/aromatics followed the Langmuir-Hinshelwood mechanism.²⁵ Accordingly, it was proposed that styrene oxidation was initiated with concurrent adsorption of H_2O_2 and styrene over the surface of the catalyst. This was in the same direction with the study reported by Yang et al.²⁴ The formed surface oxygen species and the H_2O_2 active intermediates would interact with nearby adsorbed styrene upon the surface of RGO in a way to create the

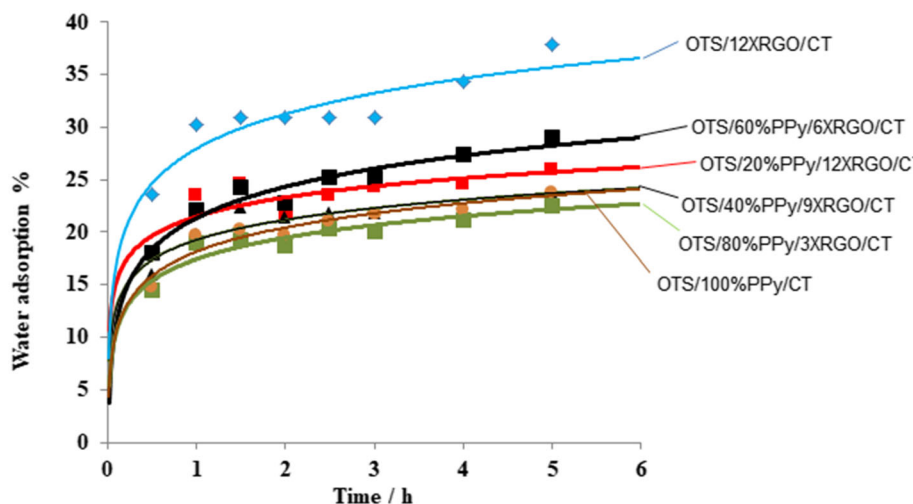


FIGURE 6 Water adsorption capacity (%) of modified cotton textiles

TABLE 1 The retention times of acetonitrile and styrene and its derivatives

No.	Compound	Retention time (min)
1	Acetonitrile (solvent)	0.907
2	Styrene	1.885
3	Benzaldehyde	2.326
4	Phenylacetaldehyde	2.530
5	Styrene oxide	3.825

desired oxidized products. The present research showed that GO, if not reduced to RGO and kept in its oxidized form, demonstrated still an appropriate selectivity towards benzaldehyde. When coated to the cotton, the activity increased, but it showed higher selectivity towards styrene oxide instead of benzaldehyde.

To make a deeper insight into this phenomenon, further research was carried out on transformation of H_2O_2 to the active oxygen species over a series of catalysts.²⁴ As shown in previous studies, it could be observed that di-oxygen was formed on RGO and GO catalysts, with a slower decomposition rate for GO compared with that of RGO.²⁴ As they found, higher oxygen species from H_2O_2 transform rate was directly related to the π character of reduced graphene oxide and graphene oxide^{26,27}; however, the two substances possess similar surface areas. On GO, oxidation partly destroyed the π system of graphene. A considerable disruption occurred to the π system because the oxygen-functional groups were introduced on the GO surface. C/O ratio of RGO, which was computed using XPS, was 3.11, whereas that of GO was 2.0. It changed the sp^2 carbon in the graphene network to sp^3 hybridized carbon. On the contrary, upon those catalysts that had lower catalytic performance

(i.e., GO), fewer surface sites existed for styrene adsorption because of imperfect π system or confined surface area. Reasonably, when more sites exist for styrene adsorption, the probability of contact and interaction of the adsorbed styrene with the transient reactive surface oxygen species increases; meanwhile, styrene would be oxidized more probably.

Over the catalyst, an improvement occurred in the oxidation of styrene with benzaldehyde, and the styrene oxide would be the most important product. As demonstrated in Figure 7, when no cellulose and cotton fabrics were present in the catalysts, the selectivity towards benzaldehyde was increased. On the other hand, by enhancing the loading of GO, RGO, and PPy, the catalytic selectivity towards benzaldehyde was increased too. Moreover, for selectivity of styrene oxide, this trend was reversed. When the cellulose fabrics were attached to the GO and RGO materials, the catalytic selectivity towards styrene oxide was increased, whereas the selectivity for phenylacetaldehyde was low, and this product appeared only when the catalyst contained cellulose fabrics.

Cotton was chosen as it has relatively high network surface area, abundance of hydroxyl functional group, and ability to immobilize graphene and graphene oxide on its surface. The immobilization of graphene and graphene oxide is important to prevent wrinkling and agglomeration of graphene. In this regard, the graphene oxide-coated cotton catalyst showed higher catalyst activity compared with the graphene oxide. Same phenomena happened for reduced graphene oxide too. This was due to the increase in the surface area of OTS/12XGO/CT and OTS/12XRGO/CT compared with the pure powder ones and also the prevention of agglomeration. However, the conversion of the OTS/12XGO/CT increased in the oxidation of the styrene, but the selectivity was towards styrene oxide. It was observed that RGO/CT had higher

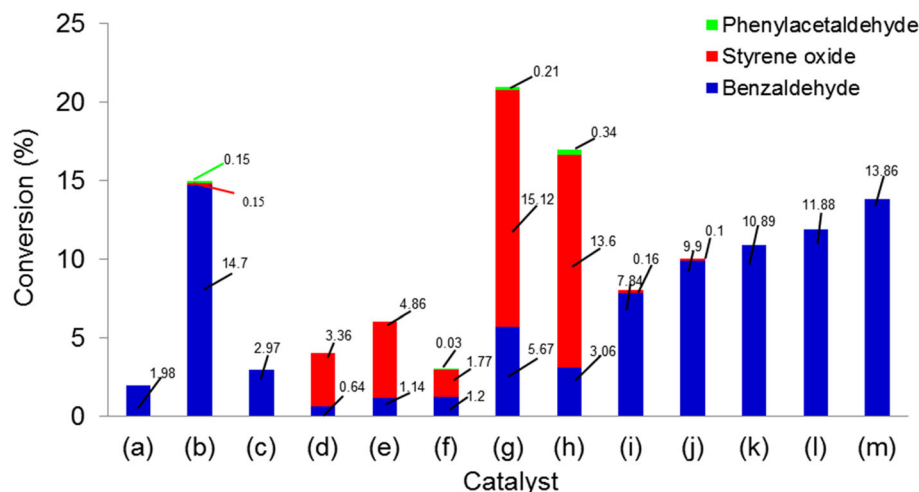


FIGURE 7 Oxidation of styrene by hydrogen peroxide using octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) as catalyst at room temperature for 24 hr. (a) Blank, (b) GO, (c) PPy, (d) CT, (e) OTS/CT, (f) cellulose, (g) OTS/12XRGO/CT, (h) OTS/12XGO/CT, (i) OTS/20%PPy/12XRGO/CT, (j) OTS/40%PPy/9XRGO/CT, (k) OTS/60%PPy/6XRGO/CT, (l) OTS/80%PPy/3XGO/CT, and (m) OTS/100%PPy/CT

conversion of styrene and selectivity of styrene oxide compared with OTS/12XGO/CT.

More effort has been made to study the catalytic activity and selectivity of the OTS/PPy/RGO/CT series catalysts. The catalyst activity after the attachment of RGO/CT with 20%PPy decreased. However, the selectivity towards benzaldehyde increased. By attaching more PPy and reducing the amount of RGO, simultaneously, in OTS/PPy/RGO/CT series samples, the most effective active site towards benzaldehyde was changed to N^+ functional group inside the polypyrrole structure, which was located on top of the composite. Therefore, by increasing the amount of PPy active sites on the top of the modified cotton composite, the catalyst selectivity towards benzaldehyde was increased. However, the best catalyst in terms of styrene conversion was found to be OTS/12XRGO/CT with the maximum amount of graphene. In the catalyst's selectivity point of view, it could be seen that the selectivity towards styrene oxide for all the catalysts was higher than that for benzaldehyde, whereas graphene and graphene oxide were attached to the cotton material, and there was no PPy attached on the top of cotton. On the other hand, cellulose increased the selectivity towards styrene oxide. In contrast, when GO, RGO, and PPy were applied as the catalyst, the selectivity was towards benzaldehyde.

One would expect that the mentioned catalysts (GO, RGO, and PPy) and also the cellulose fibres grafted by polypyrrole favoured the carbon-carbon bond cleavage. Consequently, when PPy particles increase, bond scission reaction was preferred, which caused the creation of more benzaldehyde (path I, Figure 8). This concept was in the same agreement with the reported work by Nur

et al.¹⁵ where highest loading amount of TiO_2 generated more benzaldehyde in comparison with the styrene oxide. Another pathway for the synthetization of styrene oxide from styrene was through oxidation reaction to form styrene oxide (path II, Figure 8). Figure 8 displayed a schematic picture of the conceivable pathway in styrene oxidation. The two different pathways may occur in parallel; however, in case of this catalyst, O—H group of cellulose and fabrics had a great impact on promoting the oxidation of styrene by path II, through increasing the adsorption of H_2O_2 with the help of abundant hydroxyl groups on the surface of cellulose structure. In contrast, the π - π character inside PPy, GO, and RGO was responsible for helping the oxidative cleavage of bond in styrene (path I, Figure 8).

3.2 | Catalytic activity of OTS/PPy/RGO/CT series catalyst induced by electrical current in static condition

Catalytic activity of OTS/PPy/RGO/CT series catalysts in the oxidation of styrene with H_2O_2 was performed at room temperature for 24 hr induced by electrical current.

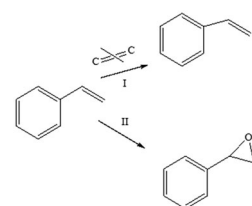


FIGURE 8 Pathway in styrene oxidation reaction



The reaction mixture containing styrene (10 ml) and H_2O_2 (10 ml) was put in the customized reactor, which was made for special application of electrical current on layered catalyst. The prepared catalyst (0.861 g) was able to float between the organic and aqueous phase. The reaction was carried out in the customized reactor under 25 V of electric voltage. The products of the reaction were analysed by a Shimadzu gas chromatograph using a hydrophobic column. For this series of catalysts, OTS/20%PPy/12XRGO/CT, OTS/40%PPy/9XRGO/CT, OTS/60%PPy/6XRGO/CT, OTS/100%PPy/3XRGO/CT, and OTS/100%PPy/CT had the ability to conduct electrical current. Due to this property, the idea to replace stirring was emerged. These series of reaction were performed without help of any stirring and in static condition, and the conductivity of this catalyst series was measured by Van der Pauw method. Figure 10 showed the conductivity results of composite series with various amount of RGO and PPy. It was found that the role of PPy on textile conductivity was more effective than RGO as shown in Figure 9. OTS/20%PPy/12XRGO/CT and OTS/40%PPy/9XRGO/CT samples, with moderate conductivity of 4.47 and 15.58, respectively, achieved higher catalytic activity due to the RGO active sites inside these samples. However, no catalytic activity was recorded when no electrical current was used and in static condition. These results suggested that the high

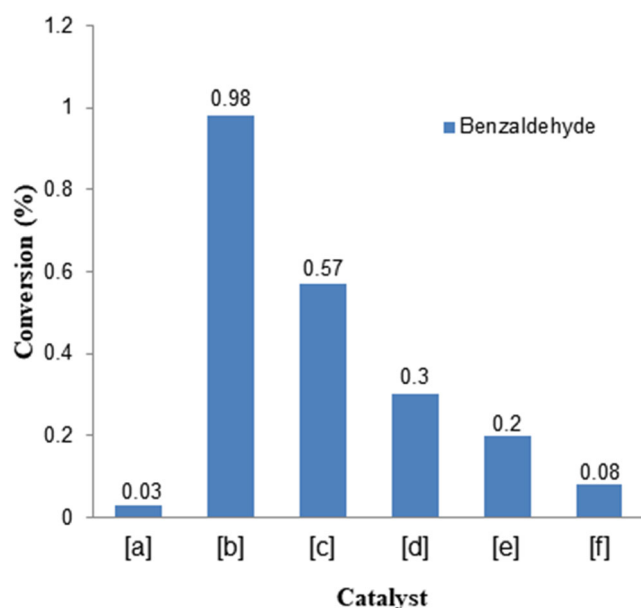


FIGURE 9 Oxidation of styrene by hydrogen peroxide using octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) series as catalyst at room temperature for 24 hr in static condition by induced electrical current. (a) OTS/12XRGO/CT, (b) OTS/20%PPy/12XRGO/CT, (c) OTS/40%PPy/9XRGO/CT, (d) OTS/60%PPy/6XRGO/CT, (e) OTS/80%PPy/3XRGO/CT, and (f) OTS/100%PPy/CT

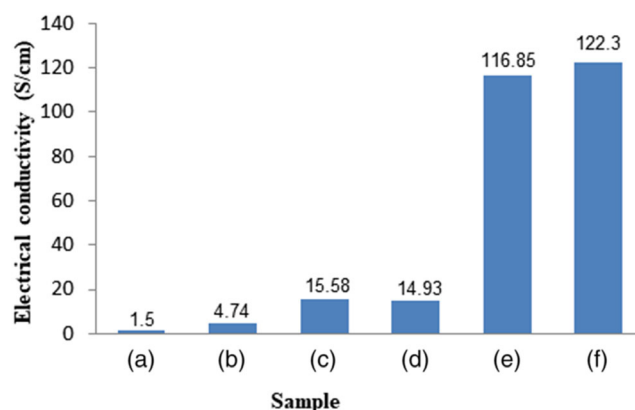


FIGURE 10 The electrical conductivity of octadecyltrichlorosilane/polypyrrole/reduced graphene oxide/cotton (OTS/PPy/RGO/CT) series by using Van der Pauw techniques. (a) OTS/12XRGO/CT, (b) OTS/20%PPy/12XRGO/CT, (c) OTS/40%PPy/9XRGO/CT, (d) OTS/60%PPy/6XRGO/CT, (e) OTS/80%PPy/3XRGO/CT, and (f) OTS/100%PPy/CT

amount of RGO in the presence of current showed a trace activity. One expected that electrical current may have helped in increasing the adsorption rate of H_2O_2 on the surface of layered catalyst.

However, these results (Figure 10) still could not prove that styrene oxidation using OTS/PPy/RGO/CT series as PBC was affected by electrical current. The products obtained were in trace amounts. Therefore, more study is still needed to explore the effects of electrical current on the catalytic activity and selectivity. On the other hand, the measured magnetic that has produced from the applied current (0.50 mA) through samples was limited to less than 0.5 mT. Meanwhile, it seemed that the small quantity of magnetic field was not enough to cause a significant enhancement in catalytic activity by improving the adsorption process. In conclusion, decreasing the resistance of the cotton textile fibres still remained a challenge in this research. Therefore, more efforts for future work is required to improve the electrical properties of the fibres.

4 | CONCLUSION

We investigated the catalytic activity of OTS/PPy/RGO/CT in stirring and static condition by aim of electrical current. Results demonstrated that styrene oxidation using OTS/PPy/RGO/CT series as a PBC was not affected by electrical current. In the case of catalytic performance of OTS/PPy/RGO/CT as heterogeneous catalyst, the best catalyst activity was reported, it was related to OTS/RGO/CT sample when reduced graphene oxide-coated textile catalyst was used in the styrene oxidation reaction in stirring condition, the high catalyst activity



was achieved up to 21%, and the selectivity towards styrene oxide dramatically increased up to 80%. Another fact about the selectivity of styrene oxidation towards oxidized product has been found. In this regard, in the presence of cellulose fibres, the selectivity was towards styrene oxide. In contrast, in GO, RGO, and PPy catalysts or when the cellulose fibres were blocked by PPy, the selectivity was towards benzaldehyde. Therefore, it would be expected from these results that when the cellulose fibres were covered by polypyrrole or without the presence of cellulose fibres, the catalyst favoured the carbon-carbon bond cleavage. Conversely, by the introduction of the cellulose fibres in catalyst series, the conversion led to styrene oxide as the main product.

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