Electrochemical degradation of organic dyes with a porous gold electrode

Jieun Kim, Changjoo Yeom, and Younghun Kim[†]

Department of Chemical Engineering, Kwangwoon University, Wolgye-dong, Nowon-gu, Seoul 01899, Korea

Abstract−Electrochemical degradation of methylene blue (MB) and rhodamine B (RhB) was studied at porous gold (PAu) electrode in presence of KCl as supporting electrolytes. PAu electrode with three-dimensional porous structure was prepared by paper-based method and used as working electrode. Based on the cyclic voltammetric test, the redox potential of of MB and RhB contained in KCl solution was found and the electrochemical degradation was conducted at fixed applied voltage. The direct oxidation of organic dyes involved using PAu and Pt electrodes, while the indirect electrolysis was mediated by active chlorine electro-generated from KCl solution. The results showed that PAu electrode with porous structure has high electrochemical activity with fast kinetics for the destruction of RhB ($0.0448 \ \mathrm{min^{-1}}$) and low energy consumption ($0.315 \ \mathrm{kWh/m^3}$), compared to smooth Au foil and reported others. In addition, the durability test for 10 serial degradation showed that PAu electrode has a good reproducibility and high adaptability for practical application.

Keywords: Paper-based Porous Gold, Electrochemical Degradation, Organic Dye, Rhodamine B

INTRODUCTION

As the textile industry continues to grow, consumption and usage of existing and new organic dyes produce increasing amounts of wastewater. Residual dyestuffs present in small amounts in wastewater are sources of aesthetic pollution and eutrophication of water bodies [1]. To remove dyes from wastewater before it is discharged, several biological, physical and chemical processes are used. Among these, chemical oxidation with ozone, Fenton' reagent and advanced oxidation processes (AOPs) have emerged as potentially powerful methods which are able to transform organic dyes with relatively high molecular weights and aromatic rings into harmless substances [3]. However, chemical treatment may cause secondary pollution due to the addition of potentially hazardous chemical agents such as flocculants and oxidizing agents (H_2O_2, O_3, and $FeSO_4$) [4,5].

For these reasons, electrochemical oxidation has attracted growing interest as an alternative to traditional methods because it is simple, economical, safe and environmentally compatible for treatment of polluted water. This technology does not use harmful chemicals to produce strong oxidants as in traditional AOPs, but rather requires an electrical current to mineralize products [6]. Many studies have demonstrated the complete mineralization of organic dyes, which can be obtained with high efficiency by direct electro-oxidation using SnO_2, PbO_2 [7], TiO_2 [8], carbon fiber [5] and boron-doped diamond (BDD) [2,4]. The hydroxyl radicals electro-generated from water during electrochemical oxidation are responsible for the oxidation of organics until total mineralization [4]. Other than by direct electrolysis, the organic dye can also be

removed electrochemically by indirect electrolysis [2], generating *in situ* chemical reactants such as active chlorine. Chlorides naturally present in solution can anodically produce gaseous chloride, hypochlorous acid or hypochlorite ions [9]. Several researchers reported the possibility of obtaining almost complete mineralization of organic dyes containing model compounds with chlorine-mediated electrolysis [10]. Therefore, during electrochemical oxidation, hydroxyl radicals (OH*) and active chlorine (Cl_2, HOCl, and OCl^-) electro-generated from water or model solutions act as key components to increase mineralization efficiency of organic dyes.

Three-dimensional nano- and/or microporous structures have been of high interest for electrochemical applications, due to porous structure allowing fast transport through the electrolyte/electrode interface as well as rapid electrochemical reaction through many channels and pores [11,12]. Porous structure of the electrode may increase the mineralization efficiency of organic dyes during electrochemical oxidation. Therefore, we report the feasibility of electrochemical degradation of methylene blue (MB) and rhodamine B (RhB) using a porous gold (PAu) electrode. In previous works [13], simple and facile methods for the synthesis of paper-based PAu electrode were reported. PAu electrode exhibited effective nanostructure and was easy to control in the laboratory. Further, a PAu electrode with large surface areas was easily synthesized and shown to possess enhanced electrocatalytic activity for the electro-oxidation of ethanol.

EXPERIMENTAL

1. Preparation of Porous Gold Electrode

PAu electrode was prepared using gold nanoparticles (AuNPs) and syringe-filter paper. AuNPs used in the filtering process were prepared by the reduction of gold ion using citrate as the reductant. The resulting solution had a dark red color and showed ca.
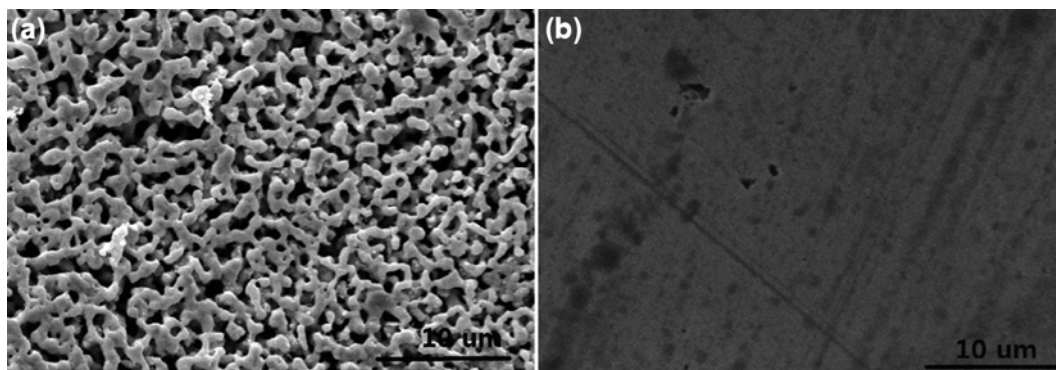
Fig. 1. TEM images of (a) porous gold prepared by paper-based method and (b) gold foil.

20 nm size. The prepared AuNPs were characterized by UV/vis spectroscopy (UV-1800, Shimadzu), and transmission electron microscopy (TEM, JEM1010, JEOL). The syringe filter (Minisart RC15) with 200 nm pore size, prepared from regenerated cellulose, was purchased from Sartorius Stedim Biotech. AuNPs were filtered several times by syringe using a filter. Then, the filter paper was dried overnight in an oven at 60 °C. The dried filter paper was sintered between AuNPs at 450 °C for 90 min to remove cellulose of the filter paper and further sintered between AuNPs at the same temperature. Obtained PAu was attached on the edge of glassy carbon electrode (GCE) using silver glue. Surface morphology of the paper-based PAu was investigated by scanning electron microscopy (SEM, S-4700, Hitachi).

2. Degradation of Organic Dyes

All electrochemical analyses were performed by using a potentiostat (WEIS500, WonA Tech.). Pt wire and Ag/AgCl (saturated KCl) were used as counter and reference electrodes, respectively. PAu was used as the working electrode, and 0.4 M KCl was used as the electrolyte solution. Based on the results of cyclic voltammetry (CV), the applied potential for electrochemical degradation of MB and RhB was determined. The degradation of dyes was carried out in a volume of 40 mL aqueous solution of MB and RhB 5 ppm over 1 hr. The concentration of MB and RhB left in the aqueous solution was determined by UV-vis spectroscopy. To define the enhancement of efficiency of electrochemical degradation by porous structure, smooth gold foil with 0.1 mm thickness (Sigma-Aldrich) was also tested with the same experimental conditions.

RESULTS AND DISCUSSION

1. Characterization of PAu Electrode

Since cellulose filters have porous structures with 200 nm pores, small AuNPs can be adsorbed on the surface of cellulose substrate without filling the pore. After injection of AuNPs solutions into a syringe-filter, the color of the filter paper changed from white to dark red, indicating that AuNPs were physically or chemically loaded into the cellulose substrate, which contains many OH moieties. After thermal treatment of the resulting filter with incorporated AuNPs, the cellulose template was removed and AuNPs sintered to form a gold network as free-standing backbone struc-

ture. As shown in Fig. 1(a), the surface morphology of the PAu was a coral-like structure that showed a window pore of 100 nm-400 nm. Conversely, Au foil showed very smooth surface in the TEM image (Fig. 1(b)). As compared with our previous reports [11], this proposed approach for paper-based synthesis of PAu was a very simple and time-saving process.

The supporting electrolyte is an important parameter during the electrochemical degradation of wastewater. The presence of dissolved salts increases the conductivity and decreases the resistance. In addition, Guenfoud et al. [6] reported that the electrolytes containing chloride induce a fast decolorization. Chloride is the most effective conductive electrolyte and is a powerful oxidizing agent of active chlorine generated on electrode, compared to other electrolytes (Na_2SO_4 and $NaNO_3$). Therefore, KCl electrolyte, containing organic dyes was used here.

To check the oxidation/reduction feature of the prepared electrode, the CV data of PAu was measured at 0.4 M KCl with or without MB and RhB. As shown in Fig. 2, CV of electrode showed different features with dependence on the presence of organic dyes. The redox peaks of the PAu immersed in KCl and MB/KCl solutions were found in the range of +0.2 V to −0.2 V and −0.3 V to −0.45 V, respectively. The presence of MB in the KCl solution revealed addi-
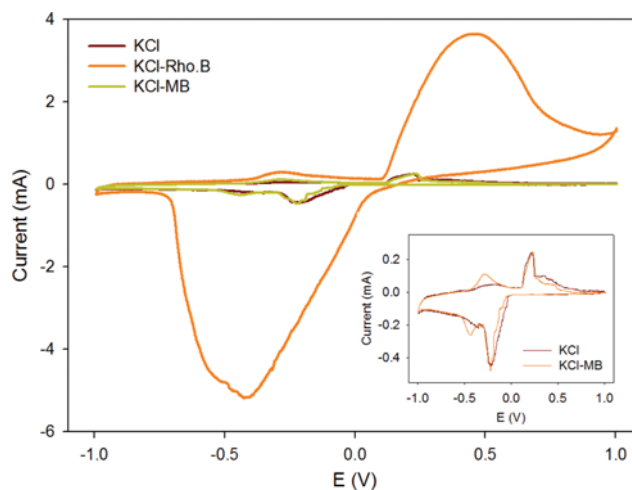

Fig. 2. CV data of PAu electrode in 1 M KCl w/ or w/o MB and RhB at scan rate of 50 mV/s.

tional peaks but a small current loop. The PAu electrode in RhB/KCl solution, on the other hand, showed a significantly large current loop and shift of oxidation/reduction potential, as compared to MB/KCl condition. The oxidation/reduction peaks were found clearly at +0.45 V and −0.45 V, respectively. The current value of PAu in RhB/KCl solutions is ten-times larger than value of PAu in MB/KCl. Notably, the RhB molecule more effectively receives the electrons from the PAu electrode in KCl solution, leading to mineralization of dye.

2. Electrochemical Degradation of MB and RhB

When the electro-degradation of dye was conducted under galvanostatic conditions, the higher current density primarily showed higher kinetics. In this work, the potentiostatic condition was applied to degrade the target dye, demonstrating the applied voltage point to be more significant than the current density. Based on the CV results, the degradation of MB using PAu electrode was conducted at a fixed applied voltage (−0.3 V) over 40 min. As shown in Fig. 3(a), characteristic peaks were found at 600 nm and 665 nm in the UV-vis spectra, but its absorbance slightly decreased over time due to the very low current density at the applied voltage (1.5 mA/cm^2). Applied current density is also an important factor affecting the

electrolyte kinetics, and the high current density related to the water discharge region (where the mediated oxidation of organics with OH* becomes predominant) is required for the electrochemical degradation of organic dyes [2-8]. Namely, herein, the current value in CV data is too low to induce the mineralization via electrochemical method. However, when the recording of CV was performed between −1.0 V and 1.0 V, the peak currents gradually decreased and clear decolorization of MB solution was noticeable by the naked eye. As shown in Fig. 3(b), the main peak at 665 nm gradually decreased with increasing cycle numbers. This feature could be found in other reports [14]. After cycling 20 times, the absorbance peak reached the minimum value and corresponded to the complete decolorization of MB. There is no new absorption band in UV-vis spectra after 20 cycles. The decolorization resulted from the degradation of MB molecules. Therefore, the degradation of MB at fixed applied voltage with low current density was not suitable compared to the voltammetric scanning method.
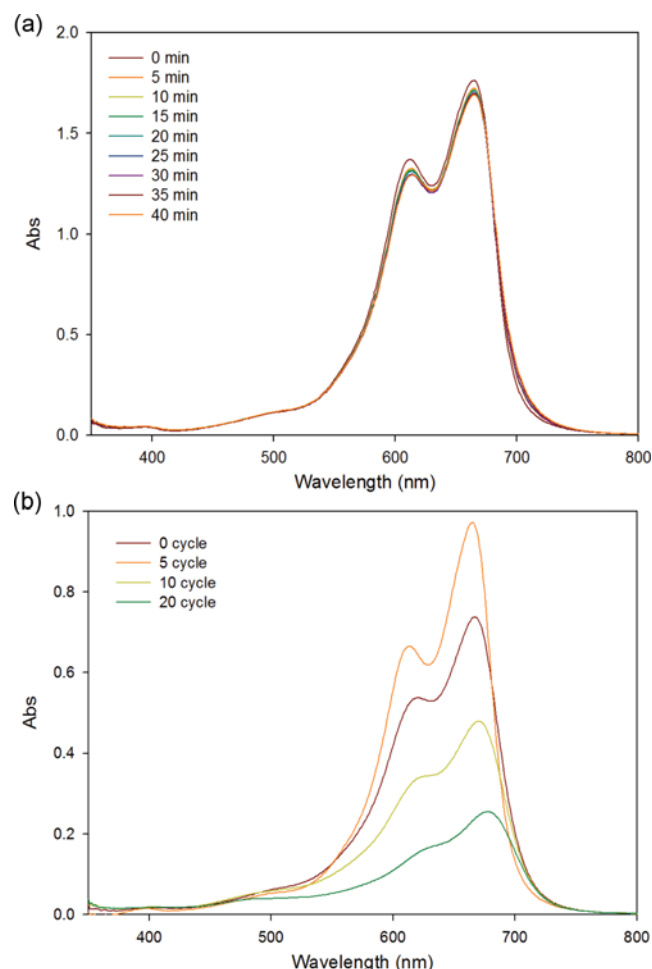

Fig. 3. UV-vis spectra of electrochemical degradation of MB using PAu electrode in 4 M KCl at (a) fixed applied voltage and (b) voltammetric scan number.
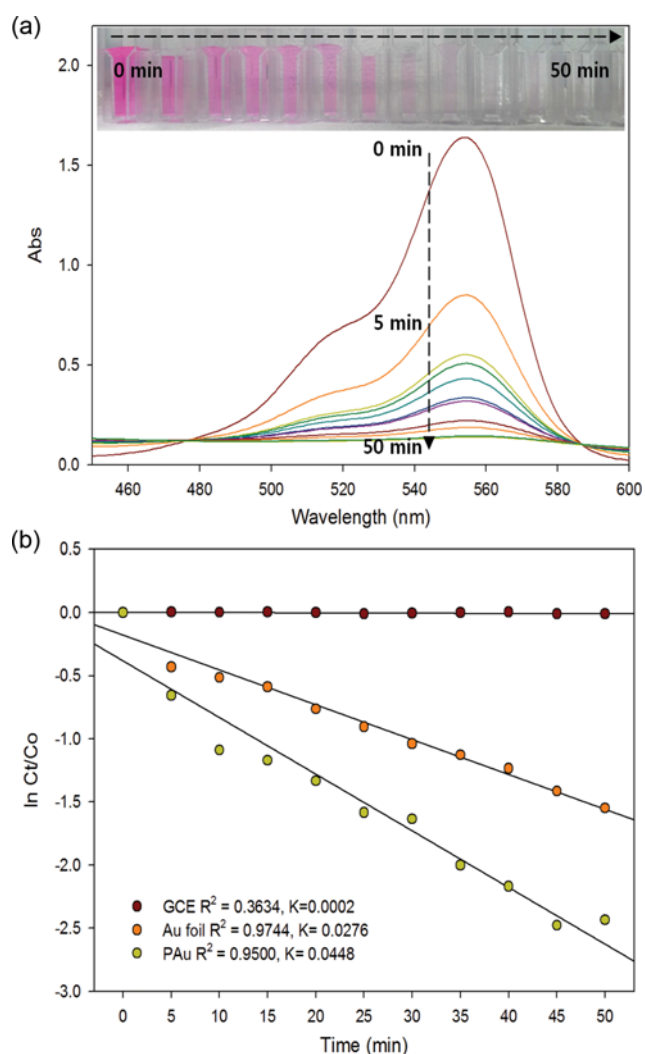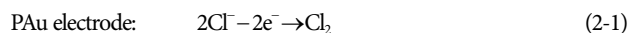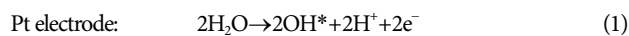

Fig. 4. (a) UV-vis spectra of electrochemical degradation of RhB using PAu electrode in 4 M KCl at fixed applied voltage. (b) Kinetic data of RhB degradation using GCE, Au foil, and PAu electrodes. Inset in (a) is color change of RhB solution by electrochemical degradation.

Unlike MB dye, RhB solution containing KCl was easily and rapidly degraded by electrochemical oxidation. The electrochemical degradation was conducted at −0.45 V with 28 mA/cm^2 (reduction voltage) and the decolorization was measured over time, as shown in inset figure of Fig. 4(a). Within 50 min, 5 ppm of RhB was completely decolorized without any additional new peaks (Fig. 4(a)). When the PAu electrode was applied at +0.45 V (Pauling electronegativity oxidation voltage), there is no color change with applied time. Since Pauling electronegativity (2.54) of the Au electrode is higher than of the Pt electrode (2.28), Pt functions as the anode electrode. A proposed mechanism of electrochemical degradation in the presence of KCl is given below:

Pt electrode: $2H_2O \rightarrow 2OH^* + 2H^+ + 2e^-$ (1)

PAu electrode: $2Cl^- - 2e^- \rightarrow Cl_2$ (2-1)

                              $Cl_2 + H_2O - 2H^+ \rightarrow Cl^- + OCl^-$ (2-1)

The above mechanism represents the combination between direct (OH*) and indirect (OCl$^-$) electrooxidation of pollutant. According to reactions (1) and (2), H$_2$O and Cl$^-$ were adsorbed to the Pt and the PAu electrodes, resulting in the formation of super-oxidative hydroxyl radical (OH*) and hypochlorite ions (OCl$^-$). In addition, it is also possible for hypochlorite (HClO$^-$) and chlorate (ClO$_3^-$) ions to be reduced at the surface of the PAu cathode to generate chloride radicals [14]. While hydroxyl radicals electrogenerated on the Pt electrode by oxidation are used for destruction of dye molecule, hypochlorite ions generated on the PAu electrode via reduction are used as strong oxidizing agent to degrade organic molecules. The electrochemical degradation of RhB proceeds via series of parallel and consecutive reactions is accomplished simultaneously by the redox processes [16].

To define the decolorization kinetic of RhB, a pseudo-first order kinetic model was employed. As shown in Fig. 4(b), the rate constant (k) of electro-degradation using PAu electrode is two times larger than that of Au foil (0.0276 min^{-1}). In the literature, the rate constant for electro-degradation of MB using a Pt electrode [14], malachite green using a BDD electrode [6], and methyl orange using a TiO$_2$ nanotube array [8] showed constants of 0.0075 min^{-1}, 0.028 min^{-1}, and 0.00003 min^{-1}, respectively. Bare GCE does not show any color change during reaction, indicating the surface morphology of electrode may be influencing the electrochemical activity during electro-degradation of RhB. Therefore, the CV test was conducted in an acidic solution (0.5 M H$_2$SO$_4$) to calculate the roughness factor (RF) of the PAu and Au foil electrodes. The electrochemically active area was calculated from the H$_{UPD}$ method with assumption of the charge densities for H$_{UPD}$ as 0.210 mC/cm^2 [17]. The RF was calculated by dividing the electrochemical active area by the geometry area (0.20 cm^2). The RF of PAu electrode and Au foil were ca. 14 and 147, respectively. In the previous report, the specific surface of PAu area was measured as 4.31 m^2/g [13]. Therefore, the increased surface roughness and large surface area of PAu electrode with three-dimensional (3D) porous structure may be helpful in enhancing the electrochemical activity, compared to two-dimensional smooth Au foil.

During electrochemical degradation process, the major operating cost is associated with the electrical energy consumption (E).
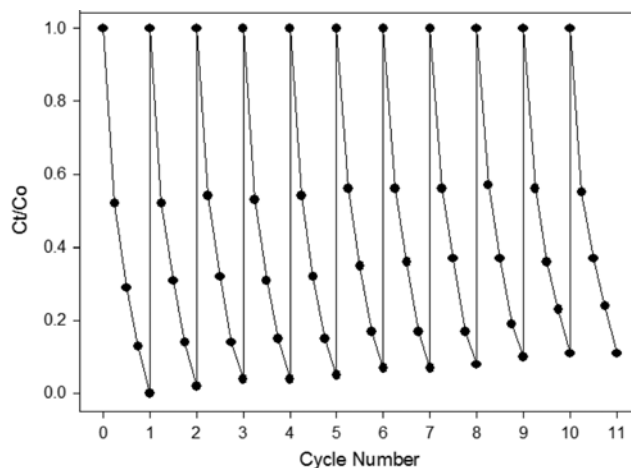

Fig. 5. Reproducibility test of PAu electrode for electrochemical degradation of RhB over 60 min.

The E (kWh/m^3) required to decompose 5 ppm RhB solutions at −0.45 V (28 mA/cm^2) can be calculated using a simple energy consumption relation [18]. The minimum electrical energy consumption was calculated to be 0.315 kWh/m^3 for this system. In a report of electrodegradation of organic dye by aromatic ring from a graphite electrode, the minimum E reached 0.886 kWh/m^3 [18], which is ca. 2.8 times larger than our case. In addition, ca. 160 kWh/m^3 is required to degrade methyl orange using a Ti electrode [7]. Therefore, PAu electrode system appears to be more adaptable in a real field test due to very low energy consumption.

The durability or lifetime of the PAu electrode used in the degradation process of organic dye is very important for the practical application. The PAu electrode was tested for the degradation of RhB in aqueous solution in a series of ten identically repeated tests. The performance of the PAu electrode showed good reproducibility and retained the degradation rate and efficiency of almost 95% during the ten repetition experiments for electrochemical degradation of RhB over 60 min (Fig. 5).

CONCLUSIONS

Effective destruction of an RhB solution was achieved by electrochemical degradation with a PAu electrode. The RhB degradation was fitted to pseudo-first-order kinetics with the rate constant of 0.0448 min^{-1}, and decolorization reached 100% within 50 min. Conversely, MB degradation was only achieved by 20 times CV scanning method with a fixed applied voltage. The rate constant of the electro-degradation of RhB using a PAu electrode is two-times larger than Au foil or Pt electrode. The increased surface roughness of the three-dimensional PAu electrode may be helpful in enhancing the electrochemical activity. In addition, as compared to several reports, PAu electrode system showed very small electrical energy consumption. In a serial electro-degradation test, the degradation rate and efficiency was maintained at almost 95% during 10 times repetition experiment. Therefore, the PAu electrode system has good adaptability to practical applications due to very low energy consumption and high durability.

ACKNOWLEDGEMENTS

REFERENCES

1. V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak and S. Agarwal, *RSC Adv.*, **2**, 6380 (2012).
2. M. Panizza, A. Barbucci, R. Ricotti and G. Cerisola, *Sep. Sci. Technol.*, **54**, 382 (2007).
3. V. K. Gupta, R. Jain, A. Mittal, T. A. Saleh, A. Nayak, S. Agarwal and S. Sikarwar, *Mater. Sci. Eng. C*, **32**, 12 (2012).
4. F. Sopaj, M. A. Rodrigo, N. Oturan, F. I. Podvorica and J. Pinson, *Chem. Eng. J.*, **262**, 286 (2015).
5. G. Xia, Y. Lu, X. Gao, C. Gao and H. Xu, *CLEAN-soil Air Water*, **43**, 229 (2015).
6. F. Guenfoud, M. Mokhtari and H. Akrout, *Diam. Relat. Mater.*, **46**, 8 (2014).
7. X. Li, X. Li, W. Yang, X. Chen, W. Li, B. Luo and K. Wang, *Electrochim. Acta*, **146**, 15 (2014).
8. Z. Zhang, Y. Yuan, G. Shi, Y. Fang, L. Liang, H. Ding and L. Jin, *Environ. Sci. Technol.*, **41**, 6259 (2007).
9. S. Singh, V. C. Srivastava and I. D. Mall, *J. Phys. Chem. C*, **117**, 15229 (2013).
10. F. Bonfatti, A. DeBattisti, S. Ferro, G. Lodi and S. Osti, *Electrochim. Acta*, **46**, 305 (2000).
11. J. Kim, S. Y. Oh, J. Y. Park and Y. Kim, *Korean J. Chem. Eng.*, **33**, 344 (2016).
12. V. Malgras, Q. Ji, Y. Kamachi, T. Mori, F. K. Shieh, K. C. W. Wu, K. Ariga and Y. Yamauchi, *Bull. Chem. Soc. Jpn.*, **88**, 1171 (2015).
13. S. Y. Oh, J. Kim and Y. Kim, *Mater. Lett.*, **154**, 60 (2015).
14. M. A. Hasnat, J. A. Safwan, M. S. Islam, Z. Rahman, M. R. Karim, T. J. Pirzada, A. J. Samed and M. M. Rahman, *J. Ind. Eng. Chem.*, **21**, 787 (2015).
15. E. Pajootan, M. Arami and M. Rahimdokht, *Ind. Eng. Chem. Res.*, **53**, 16261 (2014).
16. Y. Yang, H. Zhang, S. Lee, D. Kim, W. Hwang and Z. L. Wang, *Nano Lett.*, **13**, 803 (2013).
17. M. Shao, J. H. Odell, S. I. Choi and Y. Xia, *Electrochem. Commun.*, **31**, 46 (2013).
18. R. Kariyajjanavar, N. Jogttappa and Y. A. Nayaka, *J. Hazad. Mater.*, **190**, 952 (2011).