PbO$_2$ decorated ZnO-TiO$_2$ core-shell nanoflower structures by zinc anodising for photo- and anodic degradation of Reactive Black-5 dye

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Received 5 April 2020
Accepted for publication 16 May 2020
Published 10 September 2020

Abstract

This work shows that metallic zinc can be used as a low-cost substrate or electrode for photocatalyst and electrocatalyst use by anodising in mild bicarbonate solution. Electrochemical anodising was used to produce ZnO nanowires by controlling operational conditions and dip-coating the anodised surface with TiO$_2$ to produce a core-shell coating with photocatalytic properties. The PbO$_2$, which is known as good electrocatalyst, was electrodeposited over the ZnO-TiO$_2$ core-shell structure to alter its surface for electrocatalytic degradation of dye. The electrochemical and photocatalytic behaviours of the coatings were analysed for the removal of RB-5 dye as model pollutant. For the ZnO-TiO$_2$ core-shell, the photocatalytic removal mechanism was driven by the heterojunction photocatalytic effect of photocatalytically active anatase TiO$_2$ and wurtzite ZnO. Photocatalysis was switched to electrocatalytic behaviour after incorporation of PbO$_2$. Although the UV light might be blocked by PbO$_2$, the electrochemical degradation was enhanced due to the creation of OH free radicals over the PbO$_2$ particles decorating a ZnO-TiO$_2$ core-shell composite coating.

Keywords: core-shell, PbO$_2$, RB-5 dye, TiO$_2$, ZnO nanowires

1. Introduction

A metallic zinc substrate provides simplicity, reasonable costs, ease of processing and scalability; it can be recycled indefinitely. Here, facile synthesis of widely used catalysts, such as ZnO, TiO$_2$, and PbO$_2$ nanostructures, has been developed on a zinc plate surface for photo and electrocatalysis. ZnO has been shown to offer a flexible coating having significant applications in many scientific areas including photocatalysis [1], photovoltaics [2], water splitting...
and antibacterial surfaces [4]. Its useful characteristics include versatile electron mobility and its bandgap (3.37 eV) absorption in the UV zone [5]. One of the most attractive characteristics is a structural morphology which can range from micron to nanometre sized features, after anodising Zn-based materials.

ZnO nanostructures are often utilised in the form of nanowires. These nanowires can be generated on a different substrate by adopting techniques such as atomic layer deposition [6], chemical vapour deposition [7], and hydrothermal growth [8]. Ordered growth of nanowires produced by these techniques encounters a lower growth rate, which increases reaction time to obtain a required length of the nanowires. Another issue is requirement of high temperature for the development of nanowires, which requires expensive setups and limits the choice of substrate to one that can withstand high temperatures.

Anodising resolved these potential problems and has been employed extensively to grow ZnO nanowires at room temperature. Hu et al have produced ZnO nanowires by anodising Zn foil [9]. Nanodots, nanoflowers, nanostripes and nanowires have all been synthesised by using solutions with strong basic electrolytes, e.g. NaOH or strong acidic solutions [10]. A mild electrolyte, such as sodium bicarbonate used in this work, provides an environmentally friendly anodising process.

ZnO nanoarrays can be improved by controlled synthesis of ZnO-TiO2 core shell structures, which can enhance the photocatalytic properties of the composite [11]. TiO2 contributes to the properties of nanostructures by improving photocatalytic [12], ionic transport [13], and chemical [14] characteristics that yield robust and unusual substitute that contributes towards water splitting [3] and photo-oxidation [15]. Shin et al [16] have utilised chemical vapour deposition to incorporate TiO2 on ZnO creating core-shell structure while a facile dip coating process was used in this work.

The efficiency of PbO2 in anodic oxidation process has been obviously verified by researchers [17–19]. Recent studies have also evidenced that synthesis of more efficient PbO2 electrodes mixed with other catalytic materials such as titanium dioxide nanotubes contributes to improvement in the mineralisation of Reactive Blue 194 [17], Acid Black 194 [18] and Reactive Red 195 [19] dyes with enhanced current efficiencies in electrochemical waste-water treatment. The decoration of electrode with PbO2 can be done by electrodeposition, which is a rapid and controllable process of PbO2 deposition [20].

The goal of this study is to synthesise ZnO nanowires or nanoflowers by using metallic Zn (99.99%) in sodium bicarbonate solutions. These nanoflower-like nanostructures are used as versatile substrate for electrochemical and photocatalytic degradation of Reactive Black-5 (RB-5) dye by surface alteration. Indeed, robust coatings are required for advanced economic treatment systems and promote the commercial significance of electrode for environmental remediation of organics.

2. Experimental

Reagent grade lead nitrate, sodium bicarbonate, sodium sulphate, ethanol (98%) and acetone were obtained from Fischer Scientific. Titanium (IV) butoxide and Reactive Black-5 (RB-5) dye were acquired from Sigma Aldrich, and boric acid was purchased from Riedel-de Haen. All reagents were used as received.

2.1. Synthesis of ZnO nanowires and nanoflowers by anodising

Planar zinc samples were cleaned by immersion in an ultrasonic bath containing acetone for 5 min at 25 ºC to remove any accumulated dirt and grease. After pre-treatment, the obtained samples were polished by using sand paper and finally washed with ethanol and water to remove any remaining dirt. Anodising was carried out in an undivided, 100 cm3 glass cell. The polished Zn plate was employed as an anode of dimensions 2 cm × 1 cm × 0.20 cm. A Cu wire was attached by means of a stainless-steel alligator clip and connected to a direct current power supply. A graphite plate of dimensions 1.5 cm × 6 cm × 1.2 cm was employed as cathode with an interelectrode gap of 1 cm. The electrolyte was magnetically stirred vigorously at 200 rev min−1 with a 0.06 cm diameter, 0.25 cm long PTFE-coated, cylindrical stirrer (Fischer Scientific) to ensure constant concentration of electrolyte and good mass transport conditions across the electrolyte layer next to the Zn plate. The Zn plates were anodised at various NaHCO3 concentrations from 6.8, 13.6, 30, 50 to 100 mmol dm−3. The electrodes were set 1 cm apart with a cell voltage of 5–10 V for 10 min at 25 ºC. The films were rinsed with deionised water, then thoroughly dried by nitrogen for 5 min.

2.2. Preparation of ZnO-TiO2 core-shell nanostructures by dip coating

A layer of TiO2 was further coated on the as-obtained film of ZnO nanowires to synthesise ZnO-TiO2 core-shell nanostructures. Dip coating was deployed for deposition and titanium (IV) butoxide was used as precursor for the preparation of ZnO-TiO2 core-shell coatings. 300 μl titanium (IV) butoxide was stirred into 10 cm3 of ethanol [21] until the consistent solution appeared. The obtained films of ZnO nanowires were dip coated in the above solution by 10 s immersion. The films were calcined at 400 ºC for 1 h to obtain ZnO-TiO2 core-shell nanowires. To obtain uniform core-shell rods, two cycles of dip coating and calcination were performed.

2.3. Anodic electrodeposition of lead dioxide

Electrodeposition of a ZnO-TiO2 core-shell nanowire substrate was performed in a bath containing 0.1 mol dm−3 boric acid with 0.01 mol dm−3 Pb(NO3)2 at a current density of 5 mA cm−2 and 25 ºC under galvanostatic conditions for 30 min to synthesise PbO2 decorated ZnO-TiO2 core-shell coatings. The ZnO-TiO2 core-shell nanowire covered
substrate, with dimensions of $2 \text{ cm} \times 3 \text{ cm} \times 0.20 \text{ cm}$, was used as an anode. A Cu wire was connected by a stainless steel alligator clip, to a direct current power supply. A graphite plate of dimensions $1.5 \text{ cm} \times 6 \text{ cm} \times 1.2 \text{ cm}$ was employed as cathode and was positioned 1 cm away from the anode. The electrolyte was magnetically stirred at 700 rev min$^{-1}$ with a 0.06 cm diameter, 0.25 cm long PTFE-coated, cylindrical steel stirrer bar to maintain a constant concentration of electrolyte and moderate mass transport conditions across the compact layer of ZnO-TiO$_2$ core-shell nanowires.

### 2.4. Characterisation of coated substrate

The samples obtained after anodisation, dip coating and electrodeposition were characterised using field emission-scanning electron microscope (FE-SEM) (JEOL JSM-6500F) to observe its surface morphology. Raman spectra were acquired by Raman spectroscopy (Renishaw, RM) 2000 with a wavelength of 632.8 nm to detect the vibrational mode of TiO$_2$, ZnO, and PbO$_2$ with the duration of exposure of 30 s at 10% laser intensity. Rigaku SmartLab X-ray diffractometer (XRD) was used to identify the phase of TiO$_2$, ZnO, and PbO$_2$ decorated ZnO-TiO$_2$ core-shell coatings considered in the previous section were thoroughly washed with the electrolyte and moderate mass transport conditions across the compact layer of ZnO-TiO$_2$ core-shell nanowires.

### 2.5. Electrocatalytic studies

A computer aided PGSTAT302 N potentiostat/galvanostat from Autolab (EcoChemie, Netherlands) equipped with Nova 1.11 software was used for electrochemical study. The acquired coatings including ZnO-TiO$_2$ core-shell nanowires and PbO$_2$ decorated ZnO-TiO$_2$ core-shell coatings considered in the previous section were thoroughly washed with the ultra-pure water and cleaned. A solution of 100 cm$^{-3}$ containing 20 ppm RB-5 dye in 0.6 mol dm$^{-3}$ of sodium sulphate as background electrolyte was electrolysed at 12 mA cm$^{-2}$, pH 3 and 25 °C. The electrolyte pH was very stable with controlled magnetic stirring throughout the electrochemical experiments. Hg/HgO and Pt mesh were deployed as reference and counter electrodes, respectively. The electrodes were positioned 1 cm from the working electrode.

### 2.6. Photocatalytic experiments

The photocatalytic experiments were performed by evaluating the degradation of 20 ppm RB-5 dye in 100 cm$^{-3}$ solution containing 0.6 mol dm$^{-3}$ of sodium sulphate at pH 3 under UV irradiation. The UV lamp had intensity of 20 mW cm$^{-2}$. The non-calcined and calcined ZnO-TiO$_2$ core-shell nanowires as well as calcined PbO$_2$ decorated ZnO-TiO$_2$ core-shell coatings were immersed in the solution horizontally in which an area of $1.5 \text{ cm} \times 1 \text{ cm}$ was exposed to UV. All solutions were stored in the dark for 90 min before photocatalytic experiments to achieve equilibrium adsorption of RB-5 dye. Hitachi U3010 UV-vis spectroscopy was used to determine the absorbance of the RB-5 in solution at a wavelength of 597 nm. The Beer-Lambert law was used to quantify the concentration of RB-5 in the solutions.

### 3. Results and discussion

#### 3.1. Surface characterisation of Zn flower-like nanowires

To understand the generation and formation of the ZnO nanowires (ZnO NWs), extensive SEM inspections were studied on samples anodised at 5 V and 10 V in several bicarbonate concentrations, producing the results in table 1 (Images 1–7).

For anodising experiments at 10 V in 6.8 mM NaHCO$_3$ for 10 min, inconsistent marks were seen due to the etching of the anode and the mark was shown at higher magnification, in Image 1 of table 1. By changing to a cell voltage of 5 V under the above conditions, few pits with nanower turned longer and expanded uniformly over the whole surface. It was judged from the Image 5b) table 1 that the nanower fibres were about 5 μm. For the 50 mM NaHCO$_3$, the resulting structure was grown radially outwards from the base of Zn plate that resembles flower as well, as revealed in Image 6b) in table 1. The nanower morphology provides high active electrode or photocatalyst area by exhibiting more surface area to be decorated [22, 23]. The length of the NW arrays was up to 100 μm with a diameter varying from 30 to 70 nm. At a concentration of 100 mM NaHCO$_3$, the Zn plate was dissolved during the anodising (see Image 7 in table 1).
Table 1. Morphological evolution of anodised Zn plate at different conditions for finding the optimum conditions for Zn flower-like nanowires: Image 1 a) 10 V and 6.8 mM, 2 a) 5 V and 6.8 mM, 3 a) 10 V and 13.6 mM, 4 a) 5 V and 13.6 mM, 5 a) 5 V and 30 mM Image, 6 a) 5 V and 50 mM, 7a) 5 V and 100 mM meanwhile images 1–7 b) were morphologies represented in images 1–7 a) at higher magnification.

| Concentration of NaHCO₃ | Cell volt. | FE-SEM image |
|-------------------------|------------|--------------|
| 6.8 mM                  | 10 V       | ![Image](image1.png) |
| 6.8 mM                  | 5 V        | ![Image](image2.png) |
| 13.6 mM                 | 10 V       | ![Image](image3.png) |
| 13.6 mM                 | 5 V        | ![Image](image4.png) |
| 30 mM                   | 5 V        | ![Image](image5.png) |
mechanism, anodising was initiated by the following electrochemical reactions.

Oxidation of zinc species at the anode:

1. \[ \text{Zn} + \text{H}_2\text{O} \rightarrow [\text{Zn(OH)}_2]^{2+} + 2e^- \]
2. \[ [\text{Zn(OH)}_2]^{2+} \rightarrow [\text{Zn(OH)}(\text{OH}_2)]^{+} + \text{H}^+ \]
3. \[ [\text{Zn(OH)}(\text{OH}_2)]^{+} + \text{HCO}_3^- \rightarrow [\text{Zn(OH)}(\text{HCO}_3)(\text{OH}_2)]^{+} + \text{H}_2\text{O} \]

Proton reduction at the cathode:

4. \[ x[\text{Zn(OH)}_2(\text{OH}_2)]_x + y[\text{Zn(OH)}(\text{HCO}_3)(\text{OH}_2)]_y \rightarrow [\text{Zn}(x+y)(\text{OH})_2](\text{CO}_3)_y + 4(x+y)\text{H}_2\text{O} \]

The rapid condensation of the complex was proceeded by an olation mechanism, while diffusion of the metal oxides may often limit the condensation during anodising. In this case, due to electrolyte stirring, anodising was not controlled by mass transport in the electrolyte and NWs eventually grew. The bicarbonate ions present in the electrolyte would further speed up reaction (3) by substitution of water molecules. Reactions (4) and (5) further accelerated rapid growth of the NW array by zinc anodising.

3.2. ZnO-TiO₂ core-shell surface characterisation

The ZnO-TiO₂ core-shell coating was successfully synthesised via a dip coating method by coating TiO₂ film over the previously obtained ZnO NWs. The FE-SEM images showed uniform deposition, as seen in figure 1(a) and closer look in figure 1(b) indicated a consistent morphology of the developed TiO₂ coating over the ZnO nanowires. The inset showed a high-resolution image, which exhibited clear and smooth interior morphology of the TiO₂ shell layer, deposited over the ZnO nanowire core after two cycles of dip coating and calcination at 400 °C. The TiO₂ was confirmed to the surface of ZnO nanowires in which the presence of anatase TiO₂ after calcination was proven by Raman spectroscopy in figure 2(a). The distinct peaks were seen at 47 cm⁻¹, 167 cm⁻¹, 319 cm⁻¹, 427 cm⁻¹ which corresponded to anatase phase of TiO₂ and peak at 717 cm⁻¹ related to the wurtzite phase of ZnO, as seen in figure 2(a), indicating that heat treatment converted the substrate to the anatase and wurtzite phases. No peak was shown in the Raman spectra of non-calcined samples, indicating the formation of amorphous phases of zinc and titanium salt before calcination. The XRD characterisation exhibited the (101), (200), (213) facets of anatase TiO₂ at around 25°, 47°, 63° while (101) and (110) facets of wurtzite ZnO at 36° and 57° as shown in figure 2(b), the result is in accordance with another ZnO-TiO₂ study [26].

3.3. PbO₂ deposition over the ZnO-TiO₂ core shell characterisation

The images of the structural characteristics of the PbO₂ decorated ZnO-TiO₂ core-shell coatings, analysed by FE-SEM, were shown in figures 3(a) and (b). During the following electrodeposition of PbO₂, the Pb²⁺ ions in the boric acid solution transformed into solid lead dioxide, adapting the generation mechanism of PbO₂ [27]. Comparing figures 3(a) and 1(a), considerable variation was seen, due to the deposition of agglomerates of PbO₂ on the surface of ZnO-TiO₂ core-shell coating.

| Concentration of NaHCO₃ | Cell volt. | FE-SEM image |
|-------------------------|-----------|--------------|
| 50 mM                   | 5 V       | a            |
| 100 mM                  | 5 V       | b            |
Figure 1. FE-SEM images of (a) dip coating and calcination (400 °C) of anodised zinc plate at optimum conditions (5 V and 30 mM NaHCO₃ at 10 min anodising time); (b) magnified image of (a) with inset showing up the ZnO-TiO₂ core-shell.

Figure 2. (a) Raman spectra of (1) non-calcined and (2) PbO₂ decorated ZnO-TiO₂ core-shell coatings calcined at 400 °C; (b) XRD spectra of calcined PbO₂ decorated ZnO-TiO₂ core-shell. A = anatase TiO₂, W = wurtzite ZnO.

Figure 3. FE-SEM images of (a) electrodeposition of PbO₂ using ZnO-TiO₂ core-shell and (b) magnified image of (a) with inset showing up the PbO₂ decorated ZnO-TiO₂ core-shell coating.
On increasing the magnification of the same image of the confined region, PbO2 particles were deposited over the ZnO-TiO2 core shell, as shown in figure 3(b). The PbO2 particles were dispersed over the core shell and were attached on the surfaces of nanowires by electrodeposition. Each nanoflower-like ZnO-TiO2 core shell covered with PbO2 was expected to be electrochemically active by nature and can be used to degrade Reactive Black-5 dye. The peaks of PbO2 were shown in figures 2(a) and 2(b) by Raman spectroscopy and XRD in agreement with another PbO2 study [28].

3.4. Electrochemical measurements of coatings

It is well known that the oxygen evolution reaction (OER) at the anode is the result of intermediate reactions taking place producing hydroxyl radicals. The first common reaction is the water discharge which produces $\cdot$OH radical as indicated in equation (7).

$$\text{M} + \text{H}_2\text{O} \rightarrow \text{M(\text{OH})} + \text{H}^+ + e^-.$$ (7)

The subsequent reactions depend upon the interaction between $\cdot$OH radical and electrode surface. The interaction capacity of $\cdot$OH radical is based on the nature of the electrode substrate. Therefore, two prominent classes of the electrode material can be divided as non-active and active electrodes [29]. Active electrodes have been classified to have a strong relationship with hydroxyl radical and the oxygen evolution reaction takes place by the formation of relevant oxides during the electrochemical process [30]. In non-active electrodes, however, the hydroxyl radical weakly adsorbed over the substrate which in turn initiated the oxidation of the electroactive species leading to oxygen evolution reaction. For example, Pt is said to be an active anode as it has strong interaction with hydroxyl radical and tends to attract hydroxyl radicals. Adsorption enthalpies in case of PbO2 are lower towards hydroxyl radicals, so PbO2 surfaces weakly attract $\cdot$OH radicals.

The polarisation curves of the ZnO-TiO2 core-shell coating and PbO2 decorated ZnO-TiO2 core-shell coating obtained in 1.0 M Na2SO4 at a scan rate of 10 mV s$^{-1}$ were different from each other and indicated the potential in which oxygen evolution takes place depending on the electrocatalyst. The potential in which oxygen evolution began increased from 0.25 V to 1.7 V versus Hg/HgO (NaCl sat.) ZnO-TiO2 core-shell coating and PbO2 decorated ZnO-TiO2 core-shell coating respectively. ZnO-TiO2 core-shell coating showed slightly lower oxygen evolution potential starting at 0.25 V rising slightly to 0.6 V (curve 1) where oxygen evolution reaction exhibited. Oxygen evolution reaction kept increasing at 0.6 V for ZnO-TiO2 electrode, increased the current slightly (> 5 mA cm$^{-2}$) (curve 1) and oxygen evolution reaction was more apparent. This lower potential indicated that ZnO-TiO2 core-shell coating could be a good electrocatalyst for the oxygen evolution reaction (OER), while PbO2 decorated ZnO-TiO2 core-shell coating had high oxygen evolution potential (>1.2 V) as seen in curve 2, hence it was a poor electrocatalyst for the OER [30]. OER initiated at more positive potential when PbO2 decorated ZnO-TiO2 core-shell coating was used. In this case, the oxygen evolution initiated at 1.3 V and rose up to 1.7 V (curve 2), with the increment of current density (> 15 mA cm$^{-2}$) (figure 4) which evidenced oxygen evolution reaction at higher potential, this behaviour exhibited that oxygen evolution seemed unfavourable for PbO2 decorated ZnO-TiO2 core-shell coating and this electrode tends to possess electrocatalytic nature for electrochemical removal of organic species in solution due to smaller adsorption of oxidising species ($\cdot$OH) radicals over the anode surface. In this context, an organic compound (RB-5 dye) was chosen as model pollutant to examine the electrochemical behaviour of the anode materials.

3.5. Electrochemical discoloration of RB-5 dye

Anodic oxidation studies were conducted in order to evaluate discoloration of model pollutant in RB-5 dye by using ZnO-TiO2 core-shell coating and PbO2 decorated ZnO-TiO2 core-shell coating as an anode by applying current density of 12 mA cm$^{-2}$, 100 cm$^{-3}$ of electrolyte comprised of 20 mg dm$^{-3}$ of RB-5 dye and 0.6 mol dm$^{-3}$ of Na2SO4 at pH 3 was employed for electrolysis experiments with working electrode (ZnO-TiO2 core-shell coating and PbO2 decorated ZnO-TiO2 core-shell coating), counter electrode (platinum) and reference electrode (Hg/HgO in 1 mol dm$^{-3}$ NaOH sat.). The absorbance values were decreased at a reasonable rate, without the appearance of new bands, indicating that dye oxidation involved formation of simple organics [31].

The oxidation of RB-5 dye involves removal of the chromophore (azo) group ($-\text{N} = \text{N}-$) which imparts colour to RB-5 dye. The displacement of chromophore group ($-\text{N} = \text{N}-$) of complex RB-5 dye may produce aromatic and aliphatic intermediates, which ultimately transform to smaller molecules [32]. The normalised concentration with respect to the time for anodic oxidation electrolysis of dye using ZnO-TiO2 core-shell coating and PbO2 decorated ZnO-TiO2 core-shell coating as an anode is shown in figure 5. First order
3.6. Photocatalytic degradation of RB-5 dye

The Raman spectroscopy and XRD studies revealed anatase phase for TiO₂ and wurtzite ZnO phase (see figure 2), the active nature of anatase and wurtzite ZnO phases was discovered by photocatalytic studies of ZnO-TiO₂ core-shell nanowires and PbO₂ decorated ZnO-TiO₂ core-shell coatings regarding discoloration of solution containing RB-5 dye as pollutant in Na₂SO₄ at pH 3. The coating displayed obvious photocatalytic behaviour for the degradation of RB-5 dye. This photocatalytic behaviour of the coatings relates to the features such as protonation of anatase TiO₂ under acidic conditions [33], the origination of holes and electrons over the anatase TiO₂ under illuminated UV-irradiation [34, 35].

The anatase TiO₂ acts as a positively charged species under acidic pH, in turn it tends to attract the negatively charged RB-5 dye, following degradation of RB 5 dye, formation of hole-electron pairs, resulting in high photocatalytic performance [36]. Under UV-light illumination, heterostructures of ZnO-TiO₂ created efficient separation and suppressed recombination of photogenerated electron-hole pairs, resulting in high photocatalytic activity. Although both of the bandgaps of wurtzite ZnO and anatase TiO₂ were similar (≈3.2 eV), the positions of conduction and valence bands of ZnO and TiO₂ were different, where the conduction and valence bands for ZnO were −0.32 eV and 2.88 eV versus normal hydrogen electrode (NHE) while those for TiO₂ were −0.30 eV and 2.94 eV versus NHE [38]. Hence, the photo-excitied holes in valence band migrated from TiO₂ to ZnO inducing photo-oxidation of RB-5 dye while the photo-excited electrons transferred from ZnO to TiO₂ exhibiting photo-reduction of oxygen. Heterogenous catalyst is known as an effective approach to improve catalytic properties [39, 40].

However, for PbO₂ decorated ZnO-TiO₂ (30 min PbO₂ deposition), PbO₂ blocked the UV light at the top surface of conduction band of TiO₂ and ZnO. As the PbO₂ particles were not uniformly deposited, UV light excited the hole pair of valence band related to the anatase TiO₂ and wurtzite ZnO phase. The formation of the electron-hole pair induced breakdown of RB-5 dye molecules upon photoexcitation. The photocatalytic degradation is represented in figure 6, the time dependent concentration of Reactive Black-5 dye after 25 min of photocatalytic degradation by ZnO-TiO₂ core-shell nanowires and PbO₂ decorated ZnO-TiO₂ core-shell coatings is shown.

The rate constant (k) for photochemical degradation of non-calcined and calcined ZnO-TiO₂ core-shell, and calcined PbO₂ decorated ZnO-TiO₂ was 0.0033, 0.0159, and 0.1458. The calcination exhibited anatase TiO₂ and wurtzite ZnO which improved the photocatalytic activity when irradiated to UV light in figure 2. In the case of calcined ZnO-TiO₂ core-shell nanowires, the Reactive Black-5 was removed in 25 min. In non-calcined ZnO-TiO₂ core-shell, titanium (IV) butoxide was washed away in the solution leaving amorphous zinc bicarbonate which yielded a very low catalytic activity. In PbO₂ decorated ZnO-TiO₂, a part of UV light was blocked by PbO₂ hampering the catalytic activity of anatase TiO₂ and wurtzite ZnO. For future work, modification of metallic zinc can be further explored using emerging bismuth-based
materials, transition metal carbides and nitrides (MXenes) [41, 42].

4. Conclusions

Successful results have been obtained for the growth of ZnO nanowires over Zn plate surface by effective anodising in a bicarbonate electrolyte. The best conditions for ZnO nanowire growth have been identified by examining the operational parameters of cell voltage and electrolyte concentration. ZnO-TiO2 core-shell nanowires were produced by dip coating and then used as photocatalyst for the environmental remediation of organic dye. Electrodeposition method was utilised to deposit PbO2 creating first time PbO2 decorated ZnO-TiO2 core-shell coating which was used for electrochemical oxidation of the dye. Raman and XRD studies showed the presence of anatase phase and wurtzite phase over the PbO2 decorated ZnO-TiO2 core-shell coating. Electrochemical oxidation and photocatalytic degradation of RB-5 dye were found to be favourable by using PbO2 decorated ZnO-TiO2 core-shell coating and ZnO-TiO2 core-shell nanowires coating, respectively. This study will open an important area to the researchers in developing versatile nanowire catalyst over an inexpensive zinc substrate, for applications in wastewater treatment.

Acknowledgments

S. Z. J. Zaidi is grateful to the Faculty of Engineering and the Environment at the University of Southampton for the Rayleigh studentship, and to the Bestway Foundation, Charity No. 297178, UK as well as the European Commission Project H2020 CO2EXIDE, for the financial support.

Conflict of interest

The authors declare that they have no conflict of interest.

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