



Affordable dye sensitizer by waste

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Abstract The development of dye sensitizer is growing in line with the increasing demand for renewable energy. A research to obtain a dye sensitizer that is economical, safe, and produces a great value of DSSC efficiency is a challenge unresolved. On the other hand, the efforts for waste reduction are also intensively conducted to create better environment. In this paper, the variation of synthetic dye wastes from batik industries have been successfully applied as dye sensitizer and fabricated on DSSC cells. Congo red (1.0133%) yielded higher efficiency than rhodamine B (0.0126%), methyl orange (0.7560%), and naphthol blue black (0.0083%). The divergence of the efficiency of DSSC is very dependent upon the chromophore group owned by dye. This study has proven that the more chromophore group possessed by dye, the higher the efficiency of DSSC generated. This research concludes that the dye wastes have a bright future to be implemented as dye sensitizer on solar cells.

Keywords Affordable · Batik waste · Dye sensitizer · DSSC · Chromophore

Introduction

Batik industries in Indonesia are great contributors of liquid waste originating from the dyeing process. During the production process, about 10–15% of the dye will be

released into the environment and causing environmental pollution [1]. In addition to substances of high color, batik and textile industry waste contain synthetic ingredients poorly soluble or hard to decompose. Coloring process in batik will produce cloudy and dark liquid waste. Usually the color of liquid waste depends on the dye used [2]. Actually, dye compounds in aquatic environments can decompose naturally by the presence of sunlight. However, the reaction is relatively slow because the intensity of UV light reaching the earth surface is relatively low. In addition, the energy needs of the world prompted many researchers to pursue alternative renewable energy such as DSSC. DSSC is promising renewable energy resource because of zero waste, low cost and eco-friendly [3–5]. DSSC is a solar cell that utilizes a sensitized dye to harvest sunlight [6]. The dye plays important role to harvest solar energy and convert it to electrical energy [7, 8]. The effort to combine the dye wastes as a dye sensitizer on DSSC is a novel solution to overcome the problem of waste and energy at once. In this research, dye wastes from batik home industries in Indonesia (congo red, rhodamine B, methyl orange, naphthol blue black) are applied as dye sensitizer on DSSC. Thin layer titanium dioxide is used as semiconductor and prepared in various synthesis methods. KI₃ is used as electrolyte and graphite as counter electrode. FTO glass is used in the body of DSSC cell.

Experimental

All chemicals were purchased from commercial sources (Sigma Aldrich) except liquid dye wastes which were collected from batik home industries in Indonesia. The dye wastes were rhodamine B, congo red, methyl orange, and naphthol blue black. Materials for preparation of DSSC

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Table 1 The maximum wavelength of dye wastes matched with color theory [12]

| Dye | λ max (nm) | Absorbed color | Complementary color |
|---------------------|--------------------|----------------|---------------------|
| Rhodamine B | 554 | Green | Red |
| Congo red | 498 | Green | Red |
| Methyl orange | 464 | Blue | Orange |
| Naphthol blue black | 619 | Orange | Blue |

were titanium(IV) isopropoxide($\text{Ti}(\text{OC}_3\text{H}_7)_4$) (TTIP), 4-(1,1,3,3-tetramethylbutyl) phenylpolyethylene glycol (Triton X-100), iodine (I_2), potassium iodide (KI), ethanol ($\text{CH}_2\text{CH}_3\text{OH}$), hydrochloric acid (HCl), ether and acetic acid (CH_3COOH). Fluorine doped tin oxide (FTO) (10 Ω , 25 \times 25 \times 3.2 mm) was used as the conductive glass plate and purchased from Latech scientific supply Pte. Ltd Singapore. The top and the left of FTO glass was isolated by adhesive tape about 0.5 cm for the clamp side and to control the thickness of the coating of TiO_2 . Graphite was used as a counter electrode.

Preparation of semiconductor

In this study, synthesis of semiconductor (titanium dioxide) was done by two techniques. First, thin film of titanium dioxide was prepared using surfactants triton X-100 by sol-gel method. Second, thin film of titanium dioxide was prepared without surfactants triton X-100 by sol-gel method. First technique, 5 mL of triton X-100 was added into acetic acid and transferred into a 225 mL ethanol while being stirred for 3 min. Then 15 mL TTIP was added to 1 mL of concentrated hydrochloric acid in the solution. The mixture was stirred for 2 h to form a sol [9]. In the second technique, 15 mL TTIP in 1 mL of concentrated hydrochloric acid in the solution was stirred for 2 h to form a sol.

Preparation of working electrode

First, the FTO glasses were washed with deionized water and then dried at 80 $^\circ\text{C}$ for 10 min. The conductive side of the FTO glass was covered on two edges with adhesive tape to control the thickness of TiO_2 film. Subsequently, the FTO glass was coated with TiO_2 sol 3 times. Then each FTO glass was dried at 80 $^\circ\text{C}$ for 10 min. In the last coating, FTO glasses were calcined at 450 $^\circ\text{C}$ for 2 h and then cooling down in ambient temperature [10]. The electrode was immersed in the each solution of dye (0.1 mmol L^{-1}) for 24 h at room temperature and then dried [11]. The dyes were congo red, rhodamine B, methyl orange and naphthol blue black.

Preparation of counter electrode

The counter electrode was prepared by coating the conductive side of FTO glass with carbon from a graphite pencil until evenly distributed. Then, FTO glasses were heated at 450 $^\circ\text{C}$ for 30 min and then washed and dried. Graphite was chosen as a counter electrode because less costly and easily prepared.

Fabrication of DSSC cells

Before the working electrode and counter electrode were assembled, the electrolyte solution was prepared by dissolving the iodine (I_2) into potassium iodide (KI) solution until formed KI_3 . The DSSC cells were assembled by sandwiched working electrode and counter electrodes, respectively, and then sealed with crocodile clips.

Characterizations

The maximum wavelength of each synthetic dye was measured using UV-VIS Shimadzu 1800. The functional groups and infrared spectra were recorded using Jasco FTIR 5300. The electrical conductivity of dye was analyzed using

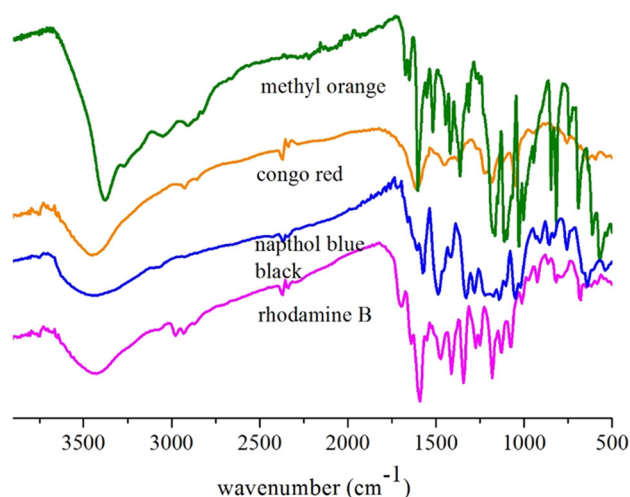
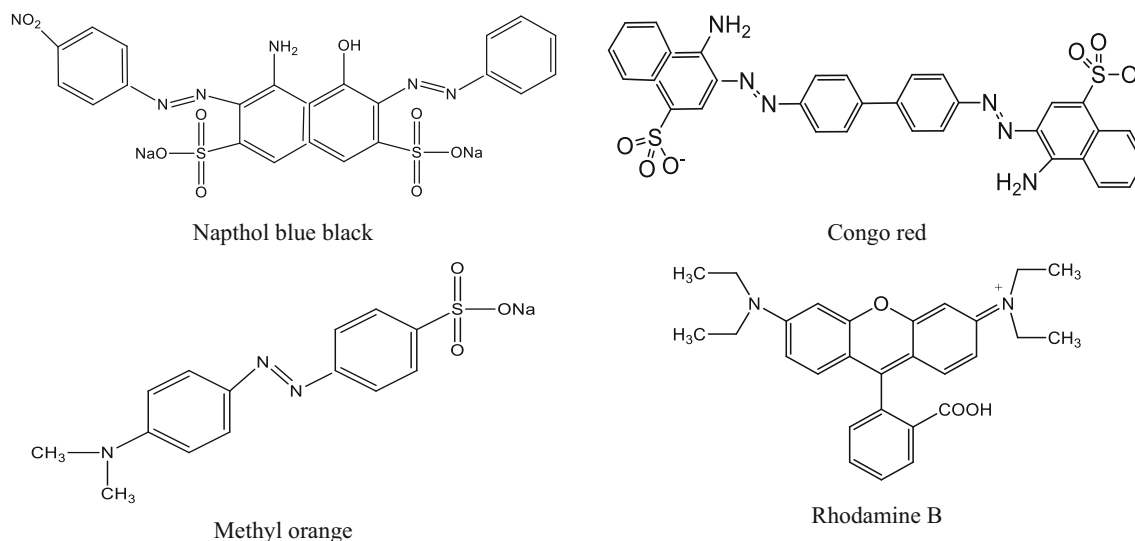
**Fig. 1** FTIR spectra of dye wastes

Table 2 The functional groups of dye wastes and the wavenumber

| Methyl orange | | Congo red | | Naphthol blue black | | Rhodamine | |
|-------------------------------|---------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|-------------------|--------------------------------|
| Functional groups | Wave number (cm ⁻¹) | Functional groups | Wavenumber (cm ⁻¹) | Functional groups | Wavenumber (cm ⁻¹) | Functional groups | Wavenumber (cm ⁻¹) |
| C=C aromatic | 1604.77 [13] | C=C aromatic | 1612 [14] | C=C aromatic | 1573.91 [15] | C=C aromatic | 1589.34 [13] |
| RSO ₃ ⁻ | 1118.71 [13] | RSO ₃ ⁻ | 1149.28 [14] | RSO ₃ ⁻ | 1141.86 [16] | C-H aromatic | 925.83 [13] |
| N=N | 1365.60 [13] | N=N | 1458.15 [14] | N=N | 1419.61 [17] | Cl- | 794.67 [18] |
| | | NH ₂ | 3448.72 [14] | NH ₂ | 3749.62 [17] | C=N | 1342.46 [13] |
| | | C-S | 594.08 [14] | NO ₂ | 1489.05 [17] | -CH ₃ | 1411.89 [13] |
| | | | | O-H | 3441.01 [19] | C=O | 1697.36 [13] |
| | | | | | | O-H | 3425.58 [13] |

**Fig. 2** Structure of dye wastes**Table 3** Theoretical calculation of the amount of chromophore

| Compound | Chromophore | | | | Total |
|---------------------|-------------|-----|-----|---------|-------|
| | C=O | N=N | S=O | Benzene | |
| Methyl orange | 0 | 1 | 2 | 2 | 5 |
| Congo red | 0 | 2 | 4 | 6 | 12 |
| Naphthol blue black | 0 | 2 | 4 | 4 | 10 |
| Rhodamine | 1 | 0 | 0 | 3 | 4 |

EUTECH conductometer. The crystallinity and phase analysis of two kinds of thin film titanium dioxide was characterized using X'pert PRO Diffractometer. Photovoltaic performance of DSSC cells for each dye sensitizer was measured by measuring current density–voltage curves under solar irradiation in real condition (outdoor) as long as 5 days. The voltage and current density of the cell were measured with multimeter Dekko using potentiometer circuit while intensity of light was measured with Light Meter Krisbow KW06-288.

Results and discussion

This research successfully developed a novel dye sensitizer from dye wastes. Liquid dye wastes used are rhodamine B, congo red, methyl orange and naphthol blue black obtained from batik industries. At batik home industries, dyeing process is generally done manually by immersion of fabric into the dye in large vat. Each vat containing a particular dye. Liquid dye wastes in the study came from the vat dye

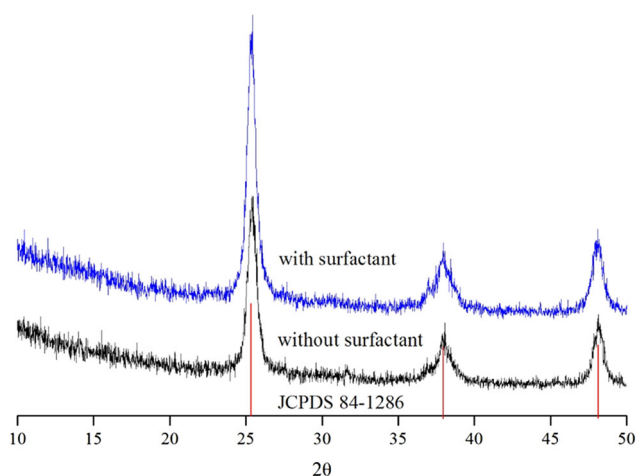


Fig. 3 XRD pattern of thin layer titanium dioxide as semiconductor on DSSC

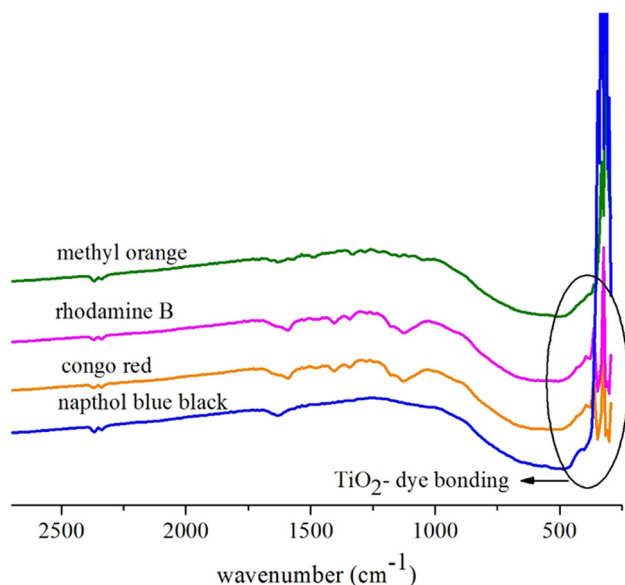


Fig. 4 FTIR spectra of the interaction bonding of TiO_2 -dye wastes

that can be ascertained dye waste is not mixed with each other.

Characteristic of dye wastes

Characterizations of dyes have been done to determine the characteristics of each dye that support their dye sensitizer performance. The result of measurement spectrophotometer UV–VIS is shown in Table 1. All of dyes show the maximum wavelength in the 400–600 nm range as the absorbed color is blue–orange. This result indicates that each dye can absorb the visible light from solar light. These properties are very advantageous because the visible

energy range is so wide that allows many levels of energy to be absorbed by the dyes [11].

Figure 1 shows the fourier transform infrared spectra of rhodamine B, congo red, methyl orange and naphthol blue black. The spectra have been recorded using Jasco FTIR 5300 in the wave number range $500\text{--}4000\text{ cm}^{-1}$. Each dye has specific functional group and is tabulated in Table 2.

Table 2 shows that each dye has chromophore group in their structure which is able to support their performance as dye sensitizer on DSSC. Chromophore is the part of molecule that is sensitive to light [20, 21]. The chromophore owned by dye will increase the dye's ability for capturing the photon from sunlight so the amount of photon used to generate a cycle of electrons in DSSC cells will increase. This process will generate a continuous electrical current. The number of chromophore groups highly influences the ability of dye on capturing photon of solar light. The more of chromophore groups the more photons absorbed. Thus, the current produced will be higher. Description of the structure and the amount of dye chromophore are presented in Fig. 2 and Table 3.

Characteristic of thin layer TiO_2 as semiconductor on DSSC

Figure 3 shows the result of semiconductor characterization using XRD X'pert PRO Diffractometer. In this work, preparation of thin film titanium dioxide was varied by adding surfactants and without surfactants. The result shows that the patterns of thin film titanium dioxide by adding and without surfactants is similar and refers to the structure of TiO_2 anatase according the database JCPDS 84-1286. If we see the intensity, thin film with surfactants is different from that without surfactants. It means that surfactants that added contributed to form structure in film layer titanium dioxide [22, 23].

In DSSC, dye sensitizer was attached to the semiconductor. Therefore, the interaction of TiO_2 and dye was characterized using FTIR to determine the bonding of TiO_2 and dye. Figure 4 shows that the interaction of TiO_2 and dye was chemical interaction of Ti and O from dye formed Ti–O bonding at $400\text{--}500\text{ cm}^{-1}$ [18]. This interaction highly supports the flow of electron transfer from dye to the semiconductor [7, 8].

Photovoltaic performance

The performance of dye wastes as dye sensitizer is shown in Fig. 5 and Table 4. The current density–voltage (J–V) curve of dye wastes are shown in Fig. 5. Table 4 shows that congo red yielded the highest efficiency (1.9%) among

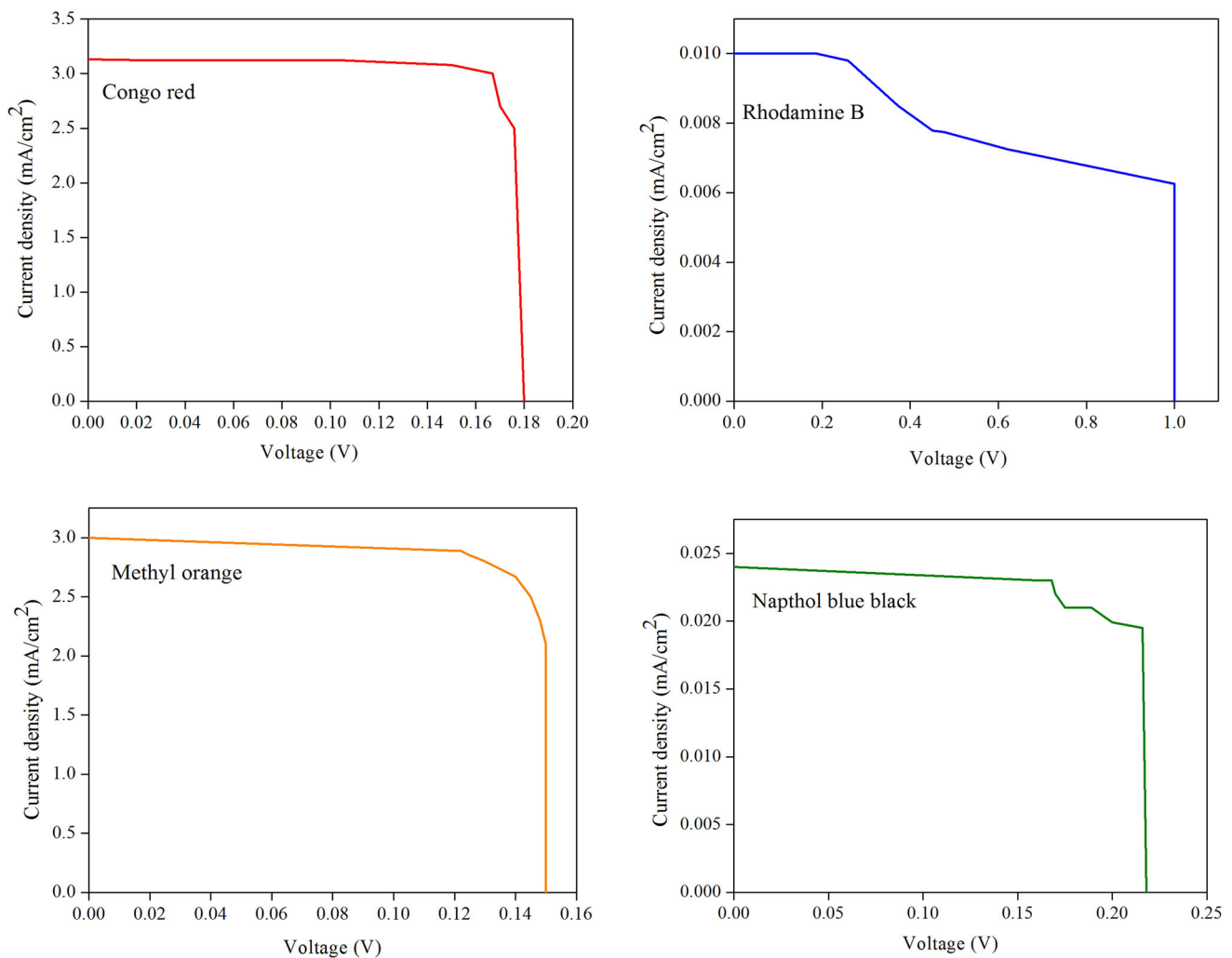


Fig. 5 J-V characteristic curve of dye wastes on DSSC

Table 4 The photovoltaic parameters of the DSSC cells

| Dye | J_{Sc} (mAcm ⁻²) | V_{oc} (V) | J_{max} (mAcm ⁻²) | V_{max} (V) | P Lux (W m ⁻²) | FF | η (%) |
|---------------------|--------------------------------|--------------|---------------------------------|---------------|----------------------------|--------|------------|
| Congo red | 3.130 | 0.18 | 3 | 0.167 | 49.44 | 0.8892 | 1.0133 |
| Rhodamine B | 0.010 | 1 | 0.00625 | 1 | 49.44 | 0.6250 | 0.0126 |
| Methyl orange | 3 | 0.15 | 2.67 | 0.14 | 49.44 | 0.8306 | 0.7560 |
| Naphthol blue black | 0.024 | 0.218 | 0.019 | 0.216 | 49.44 | 0.7844 | 0.0083 |

Area of DSSC cells: 4 cm²

dyes because congo red has the highest number of chromophore group, i.e., benzene rings, azo (N=N), and sulfoxide (S=O). This result indicates that congo red has the best ability in capturing photon from solar energy because of the supporting of their chromophore group. The highest efficiency means that the most photon of solar energy can be absorbed by dye sensitizer [10, 20, 21].

Table 4 shows that dye wastes generate diverse efficiency of DSSC value; the efficiency of DSSC reached is 1.0133%. This value is considerably higher than those of the

DSSC sensitized by other synthetic dyes or natural dyes. Synthetic dyes from hydrazonoyl and their derivatives reported obtain the efficiency of DSSC of 0.00009–0.003% [24]. Natural dyes from five plants *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander* and *Spathodea campanulata* obtained the highest efficiency of DSSC reached 0.610% from *Amaranthus caudatus* [25]. Natural dyes from beet, red cabbage, strawberry, spinach, mallow, and henna extract obtained the highest efficiency of 0.229% [26]. Chlorophyll and xanthophyll from

Cladophora sp. reported obtained the highest efficiency of 0.08% [27]. This result indicates that dye waste was potentially applied as dye sensitizer on DSSC.

Conclusion

In this work, DSSC were assembled using four dye wastes from batik industries in Indonesia as dye sensitizer. Congo red has been proven to yield the highest efficiency among the dye wastes, i.e., 1.0133%. This is because congo red has the most of chromophore group than the other dyes. This study proves that the chromophore group greatly contributes to improving the efficiency of DSSC.

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