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# Hydrothermal fabrication of natural sun light active Dy<sub>2</sub>WO<sub>6</sub> doped ZnO and its enhanced photo-electrocatalytic activity and self-cleaning properties†

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In this article we report the fabrication of 3 wt% Dy<sub>2</sub>WO<sub>6</sub> doped ZnO via a template-free hydrothermal process and its photocatalytic activity against azo dyes Rhodamine-B (Rh-B) and Trypan Blue (TB) in solar light irradiation. The as prepared Dy<sub>2</sub>WO<sub>6</sub> doped ZnO was characterised by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high resolution scanning electron microscopy (HR-SEM) field emission transmission electron microscopy (FE-TEM), X-ray photoelectron spectroscopy (XPS), diffused reflectance (DRS) and photoluminescence (PL) spectroscopy. The results suggested that rare earth tungstate doping, with Dy<sub>2</sub>WO<sub>6</sub>, on ZnO has a great influence on the photocatalytic activity. Dy<sub>2</sub>WO<sub>6</sub>-ZnO possesses high reusability without appreciable loss of catalytic activity up to four runs and exhibits higher electrocatalytic activity than the prepared ZnO for methanol electrooxidation in alkaline medium, revealing its promising potential as the anode catalyst in direct methanol fuel cells. Hydrophobicity of ZnO increases on doping with Dy<sub>2</sub>WO<sub>6</sub>.

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## Introduction

The semiconductor photocatalytic process has been widely applied as an eco-friendly technique for the destruction of organic pollutants in wastewater because of its advantages of photocatalytic activity in both UV and solar light.<sup>1,2</sup> Among various semiconductor nanomaterials, the II-VI semiconductor ZnO possesses a special place due to its several interesting properties and broad applications. The metal oxide, ZnO, a wideband-gap semiconductor with a large exciton binding energy of 60 meV at room temperature, is rationally expected to be a promising candidate for heterogeneous catalysis under solar light and optoelectronics due to its long-term stability and biocompatibility.<sup>3</sup> However, its large band gap energy (3.2 eV), hampers its widespread practical applications. Thus, the photocatalytic activity of ZnO requires to be further improved.

Doping of ZnO nanomaterials significantly increases the surface defects which can presumably shift the absorption towards visible region. The enhancement in optical absorption due to surface defects by doping has been studied by several research groups using different transition metals such as Cd,<sup>4</sup>

Cu,<sup>5</sup> Co,<sup>6</sup> Mn,<sup>7</sup> Sr,<sup>8</sup> Fe,<sup>9</sup> V and W,<sup>10</sup> Mg,<sup>11</sup> Pd<sup>12</sup> etc. and metal oxide such as CdO,<sup>13</sup> WO<sub>3</sub>,<sup>14</sup> Bi<sub>2</sub>O<sub>3</sub>,<sup>15</sup> BiVO<sub>4</sub>.<sup>16</sup> Metal tungstates as ancestors of multicomponent metal oxide compounds, have been well thought-out largely due to their fascinating structures, interesting physico-chemical behavior, as well as their extensive range of applications in various fields specifically in photocatalysis.<sup>17–22</sup> Nowadays research is focussed on doping of ZnO with rare earth metals and their oxides for the enhancement of photocatalytic activity of ZnO.<sup>23–27</sup>

In this connection here we introduced a rare earth metal tungstate, Dy<sub>2</sub>WO<sub>6</sub>, doped ZnO nanoparticles, synthesised by simple hydrothermal method and analysed its photocatalytic activity under natural sun light irradiation in the degradation of two azo dyes (Rhodamine-B and Trypan Blue).

As heterostructured nanocomposites show good hydrophobicity and electrocatalytic activity, these characteristics of Dy<sub>2</sub>WO<sub>6</sub>-ZnO were analysed. We believe that our results can open a new and effective avenue to further improve the solar photocatalytic activity, self cleaning and electrocatalytic applications of rare earth metal tungstate coupled ZnO systems.

## Experimental procedure

### Materials

Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), dysprosium nitrate hexahydrate Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), oxalic acid dihydrate (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), methanol (CH<sub>3</sub>OH) (HPLC grade) were obtained from Himedia chemicals.

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Rhodamine-B (Rh-B, molecular formula  $C_{28}H_{31}ClN_2O_3$  and molecular weight: 479.01), Trypan Blue (TB, molecular formula  $C_{34}H_{28}N_6O_{14}S_4$  and molecular weight: 872.88) from Colour Chem, Pondicherry and ZnO (surface area  $5\text{ m}^2\text{ g}^{-1}$ , particle size  $4.80\text{ }\mu\text{m}$ ) from Merck chemicals were used as received. Deionized distilled water was employed throughout the experiments.

### Preparation of $\text{Dy}_2\text{WO}_6\text{-ZnO}$

1.649 g of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.05 M) was dissolved in 100 mL of deionized water. Under vigorous agitation, 0.243 g of  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution (0.05 M) was added into the  $\text{Na}_2\text{WO}_4$  solution at room temperature. The pH of the solution was adjusted to 10 with NaOH for the complete precipitation of  $\text{Dy}_2\text{WO}_6$ . The  $\text{Dy}_2\text{WO}_6$  suspension was mixed with 100 mL of 0.4 M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (11.90 g) solution and stirred for 30 min. 100 mL of oxalic acid in distilled water (0.6 M) was introduced to the above solution drop wise and stirred for 4 h to ensure complete precipitation of zinc oxalate. The mixed precipitate of zinc oxalate and  $\text{Dy}_2\text{WO}_6$  was treated hydrothermally in a Teflon lined stainless steel autoclave at  $115\text{ }^\circ\text{C}$  for 12 h with the pressure of 18 psi. Hydrothermally treated precipitate was dried in air at  $90\text{ }^\circ\text{C}$  for 12 h and calcined at  $450\text{ }^\circ\text{C}$  for 12 h in a muffle furnace to obtain 3 wt% of  $\text{Dy}_2\text{WO}_6$  in ZnO. In the above procedure, appropriate amounts of  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  were used to get 1 wt% and 5 wt% of  $\text{Dy}_2\text{WO}_6$  in ZnO.

### Catalyst characterization

X-ray diffraction (XRD) patterns were recorded with a Siemens D5005 diffractometer using  $\text{Cu K}\alpha$  ( $k = 0.151418\text{ nm}$ ) radiation. Maximum peak positions were compared with the standard files to identify the crystalline phase. The surface morphology of the  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  was studied by using a field emission scanning electron microscope (FE-SEM) and high resolution scanning electron microscope (HR-SEM) (Model ULTRA-55). EDS analysis was performed on gold coated samples using a FE-SEM (Model ULTRA-55). HR-TEM images were taken from 200 kV ultra high resolution transmission electron microscope (JEOL-2010). X-Ray photoelectron spectra (XPS) of the catalysts were recorded in an ESCA-3 Mark II spectrometer (VG Scientific Ltd, England) using  $\text{Al K}\alpha$  (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C (1s) (285 eV). A Perkin Elmer LS 55 fluorescence spectrometer was employed to record the photoluminescence (PL) spectra at room temperature. Diffuse reflectance spectra were recorded with Shimadzu UV-2450. UV absorbance measurements were taken using Hitachi-U-2001 spectrometer. The water contact angles were measured using a Drop Shape Analyzer (DSA) (Kruuss GmbH, Germany).

### Photocatalytic experiment

Photocatalytic experiments were performed under similar conditions on sunny days of April–May 2015 between 11 am and 2 pm. An open borosilicate glass tube of 40 cm height and 20 mm diameter was used as the reaction vessel. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between the dye and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ . Irradiation was carried out in the open air condition. 50 mL of dye

solution with  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed. Heat produced in the experiment was dissipated by natural convection using a cooling fan. After dark adsorption the first sample was taken. At specific time intervals, 2 mL of the sample was withdrawn and centrifuged to separate the catalyst. 1 mL of the centrifugate was diluted to 10 mL and its absorbance was measured at 259 and 236 nm for Rh-B and TB dyes respectively. The absorbance at 259 and 236 nm represents the aromatic content of Rh-B and TB respectively and the decrease indicates the degradation of dye. Solar light intensity was measured for every 30 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set in the position of maximum intensity. The intensity of solar light was measured using LT Lutron LX-10/A Digital Lux meter and the intensity was  $1250 \times 100 \pm 100\text{ lux}$ . The intensity was nearly constant during the experiments.

### Contact angle measurements

Coatings with catalysts and tetra ethoxyorthosilane (TEOS) were successfully fabricated on a glass substrates using spin coating method at room temperature. Catalysts coated substrates were sintered at  $125\text{ }^\circ\text{C}$  for 3 h with heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  in programmed furnace to ensure densification of the gel network. A water droplet of  $4\text{ }\mu\text{L}$  was placed on the coating and its water contact angle was measured. The average of 5 measurements is reported as the water contact angle (WCA) on the substrate.

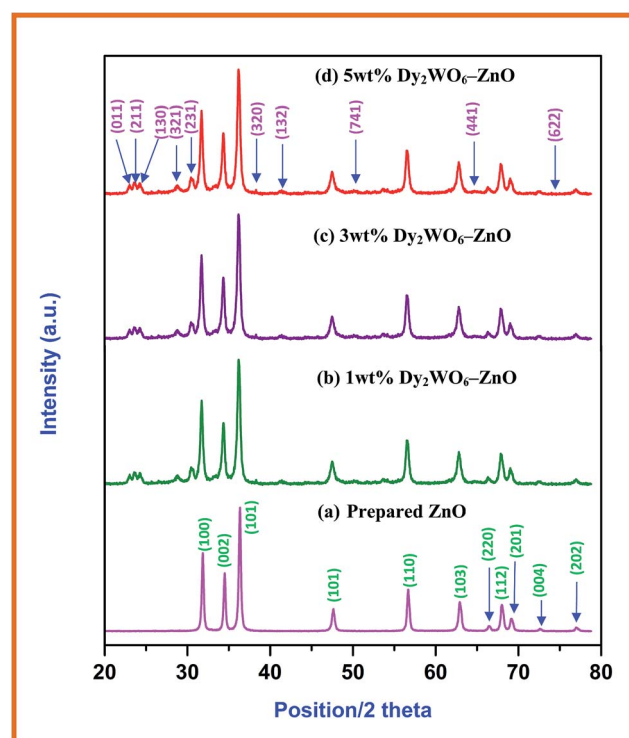


Fig. 1 XRD patterns of (a) prepared ZnO, (b) 1 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ , (c) 3 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  and (d) 5 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ .



## Electrochemical studies

Cyclic voltammetry (CV) was performed with a CHI660 electrochemical workstation (CH Instruments, USA). Cyclic voltammetry has three-electrodes, Ag/AgCl electrode as the reference electrode (saturated KCl reference electrode), a platinum wire as a counter electrode and the modified glassy carbon electrode (GCE) as the working electrode. GCEs were polished before the experiments in sequence with 1, 0.30 and 0.05 micron aluminium/water slurry on micro cloth pads, followed by careful cleaning in 1 : 1  $\text{HNO}_3\text{--H}_2\text{O}$  (v/v), ethanol, and water *via* ultrasonication. The working electrode was prepared by spraying the catalyst dispersed in iso-propyl alcohol. Cyclic voltammograms were obtained between +1.0 and  $-0.1$  V at a scan rate of  $50\text{ mV s}^{-1}$ . All potentials were reported with respect to the reversible hydrogen electrode. The CO stripping voltammetry curves were obtained after adsorption of CO on catalysts at  $-0.2$  V. For methanol electro-oxidation, 0.5 M methanol solution in 0.5 M NaOH solution was used as the electrolyte.

## Results and discussion

Preliminary study on the degradation of Rh-B and TB with 1 wt%, 3 wt% and 5 wt% of  $\text{Dy}_2\text{WO}_6$  in ZnO catalysts was carried out. The percentages of Rh-B degradation with 1, 3 and 5 wt% of  $\text{Dy}_2\text{WO}_6$  in ZnO were found to be 68, 98 and 75 respectively for 75 minutes irradiation. The maximum efficiency (98%) was observed with 3 wt%  $\text{Dy}_2\text{WO}_6$  in ZnO. Similar trend was observed for the degradation TB. Hence this 3 wt%  $\text{Dy}_2\text{WO}_6$  in ZnO was characterized and used for further experiments.

XRD can be used as an effective non destructive tool for qualitative and quantitative analysis of the phase structure. Fig. 1a shows XRD pattern of the prepared ZnO. The diffraction peaks of ZnO at  $31.82^\circ$ ,  $34.55^\circ$ ,  $36.55^\circ$ ,  $47.84^\circ$ ,  $56.75^\circ$ ,  $62.74^\circ$ ,  $66.77^\circ$ ,  $67.85^\circ$ ,  $69.50^\circ$ ,  $72.77^\circ$ , and  $77.32^\circ$  correspond to (100), (002), (101), (101), (110), (103), (220), (112), (201), (004) and (202) planes of wurtzite ZnO (JCPDS card no. 36-1451).<sup>28</sup> The new peaks appeared in the XRD patterns of 1, 3 and 5 wt% of  $\text{Dy}_2\text{WO}_6\text{--ZnO}$

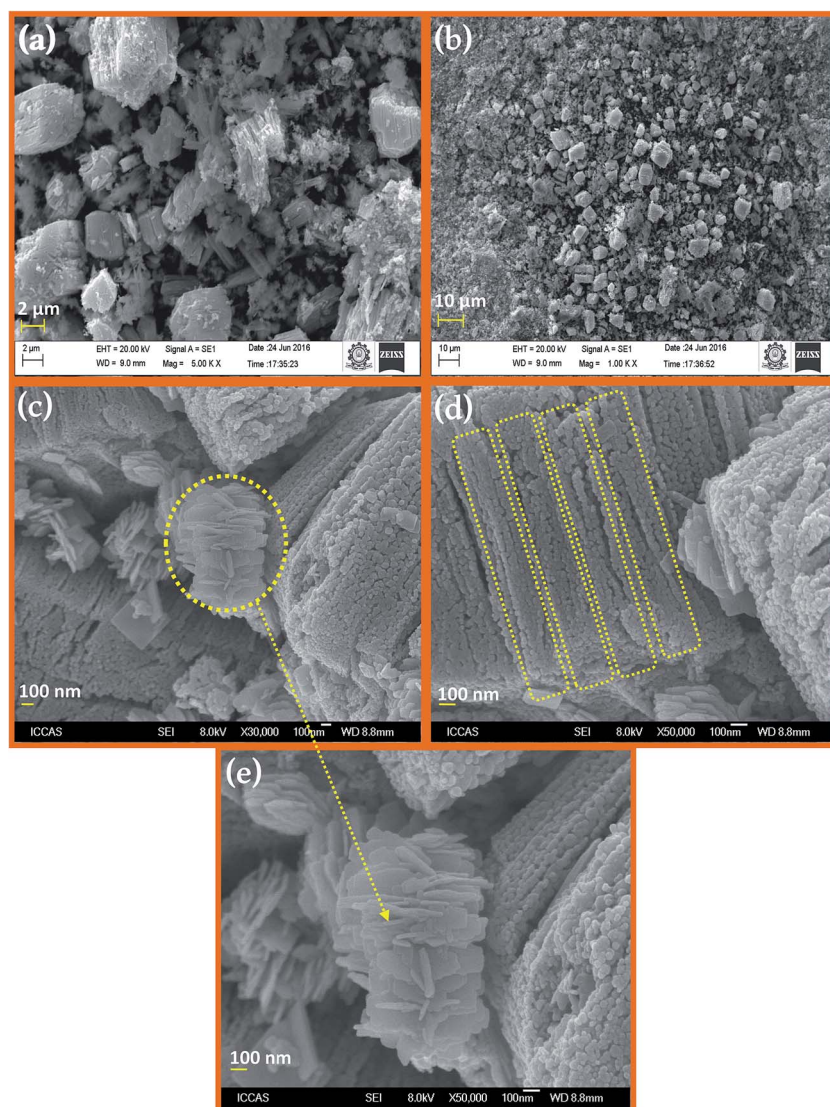


Fig. 2 FESEM and HR-SEM images of  $\text{Dy}_2\text{WO}_6\text{--ZnO}$  (a) FE-SEM image at  $2\text{ }\mu\text{m}$ , (b)  $10\text{ }\mu\text{m}$  and 2 (c–e) HR-SEM images at  $100\text{ nm}$ .





as seen in Fig. 1b–d respectively. The  $2\theta$  values at 22.89, 23.74, 24.21, 28.70, 30.52, 38.26, 41.28, 53.85, 64.73 and 74.17 for the planes (011), (211), (130), (321), (231), (320), (132), (741), (441) and (622) in Fig. 1d (5 wt%  $\text{Dy}_2\text{WO}_6$ -ZnO) are due to the monoclinic body centered structure of  $\text{Dy}_2\text{WO}_6$  which is confirmed by JCPDS card no. 26-0595 and 01-079-1722.<sup>29,30</sup> It should be noted in Fig. 1b–d that  $2\theta$  angles of (100), (002) and (101) planes for pure ZnO were gradually shifted to the lower diffraction values with increasing  $\text{Dy}_2\text{WO}_6$  concentration. This is because of expansion of ZnO lattice caused by the larger radius of  $\text{Dy}^{3+}$  (0.91 Å) than that of  $\text{Zn}^{2+}$  (0.74 Å). The increase in lattice parameter and the shift to lower angle of the XRD peaks with increasing in  $\text{Dy}_2\text{WO}_6$  concentration were expected to have the influence on the lattice deformation and strain resulting from  $\text{Dy}_2\text{WO}_6$  doping.<sup>31,32</sup> The Scherrer formula (eqn (1)) was

used for the calculation of the average crystallite size of  $\text{Dy}_2\text{WO}_6$ -ZnO.

$$\Phi = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $\Phi$  is the crystallite size,  $\lambda$  is the wavelength of X-ray used;  $K$  is the shape factor,  $\beta$  is the full line width at the half-maximum height of the peak, and  $\theta$  is the Bragg angle. Particles sizes were calculated using all the intense peaks. The average crystallite size of  $\text{Dy}_2\text{WO}_6$ -ZnO is found to be 18.5 nm.

Electronic microscopy is a technique widely used in structural and chemical characterizations of materials. It provides information about morphology, grain size, chemical composition, crystallinity, and identification of the phases in the coated materials. Fig. 2 displays typical information about morphological

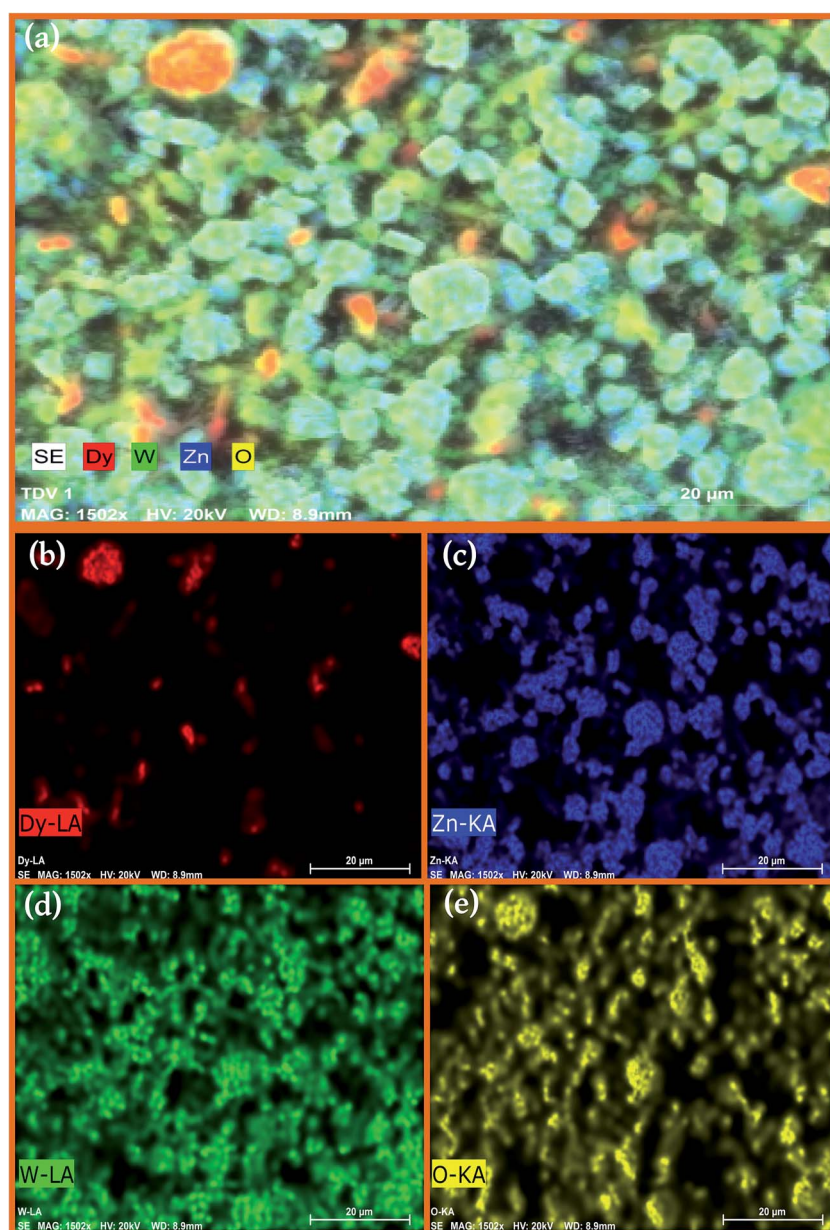


Fig. 3 Elemental colour mapping images of  $\text{Dy}_2\text{WO}_6$ -ZnO (a)  $\text{Dy}_2\text{WO}_6$ -ZnO composition (b) Dy (c) Zn (d) W and (e) O.



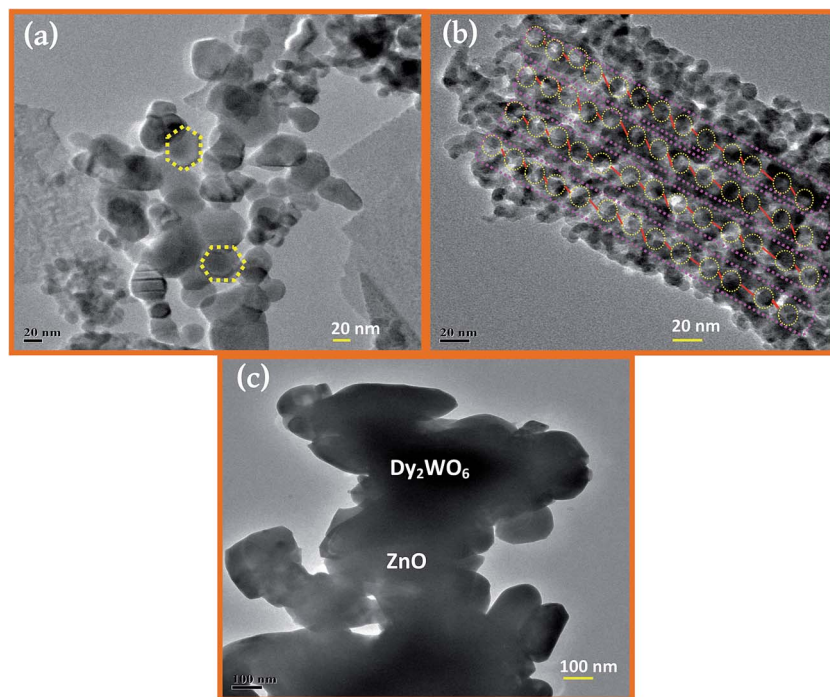


Fig. 4 FE-TEM images of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  (a and b) 20 nm and (c) 100 nm.

features of the  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  through FE-SEM and HR-SEM images. FE-SEM images of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ , shown in Fig. 2a and b, clearly prove that the pure  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  has a highly ordered porous structure in three dimensions over a range of micrometers. The HR-SEM images (Fig. 2c) further confirm the prepared photocatalyst  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  present in the form of combination of nanochain (Fig. 2d) and sandwich-like mesoporous microstructure clustered together (Fig. 2e). The size of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  clusters is around 100 nm. These different morphologies of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  may enhance photoactivity of the catalyst.

Elemental composition of prepared  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  was determined using energy dispersive X-ray (EDX) spectroscopy. FE-SEM elemental colour mapping (Fig. 3a) clearly depicts the distribution of Dy, Zn, W and O on the surface of the catalyst. From Fig. 3a, it is clear that Zn and O are present in higher density and there is a homogenous distribution of Dy, Zn, W and O. Thus elemental mapping reveals that catalyst is composed of Dy, Zn, W and O. Individual element contribution is displayed in Fig. 3b–e for Dy, Zn, W and O respectively. This also indicates the purity of the prepared catalyst  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ . The EDX analysis (Fig. S2†) confirmed the constituents of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  as Dy, Zn, W and O with appropriate ratio.

The FE-TEM images (Fig. 4a–c) reveal that the core and the shell are separated, and there is a strong contrast between the core ( $\text{Dy}_2\text{WO}_6$ -dark) and shell ( $\text{ZnO}$ -bright).<sup>33</sup> As can be seen from Fig. 4a, prepared catalyst has particles with hexagonal structure. Fig. 4b clearly displays a large number of regular-shaped hollow spherical-like particles with a diameter of 20 nm. It further proves that the lattice structure of prepared photocatalyst  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  is highly ordered. The sizes particles are in the range of 15 to 20 nm.

AFM images of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  with  $5\ \mu\text{m} \times 5\ \mu\text{m}$  regions are shown Fig. 5. They clearly indicate the surface roughness and porosity of the catalyst. The observation from AFM analyses confirms that the particles are nanosized. The existence of nanosized particles in the  $\text{Dy}_2\text{WO}_6$  doped ZnO nanomaterial is more clearly reflected in its 2D AFM image (Fig. 5a). The surface roughness of the prepared  $\text{Dy}_2\text{WO}_6$  doped ZnO is also shown in 3D AFM image (Fig. 5b). The average surface roughness was found as 87.4 nm. Higher surface roughness and lower size of the particle imply that the surface is highly porous in nature. The surface porosity and roughness in the photocatalysts permit the adsorption of dye molecules on to the surface, thereby increasing the photodegradation rate.

XPS is a selective and sensitive surface characterization technique to determine the chemical compositions of materials, and it is also effective in investigating the characteristics (valence) of the constituent atoms (ions) by monitoring their binding energies. Fig. 6a reveals the survey spectrum of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  photocatalyst and it mainly consists of dysprosium (Dy), zinc (Zn), oxygen (O), tungsten (W) along with weak carbon (C) peak and no peaks of other elements are observed. Fig. 6b shows the XPS binding energy peak at 158.37 eV for Dy 4d<sub>5/2</sub>. This indicates dysprosium (Dy) ion is present in +3 oxidation state.<sup>30</sup> XPS spectra of Zn 2p is shown in Fig. 6c and the peak positions of Zn 2p<sub>1/2</sub> and Zn 2p<sub>3/2</sub> orbitals locate at 1044.74 and 1022.41 eV respectively.<sup>34</sup> From these peaks, we can conclude that Zn is in the oxidation state of Zn<sup>2+</sup>. From the Fig. 6d we can observe that one set of lines for W (4f<sub>7/2</sub>) and W (4f<sub>5/2</sub>) at binding energies of 31.15 and 38.74 eV, respectively. The peak energies are consistent with W<sup>6+</sup> standard peaks.<sup>35</sup> Binding energy peak of O 1s is asymmetric and can be fitted to two symmetrical peaks (locating at 528.86 and





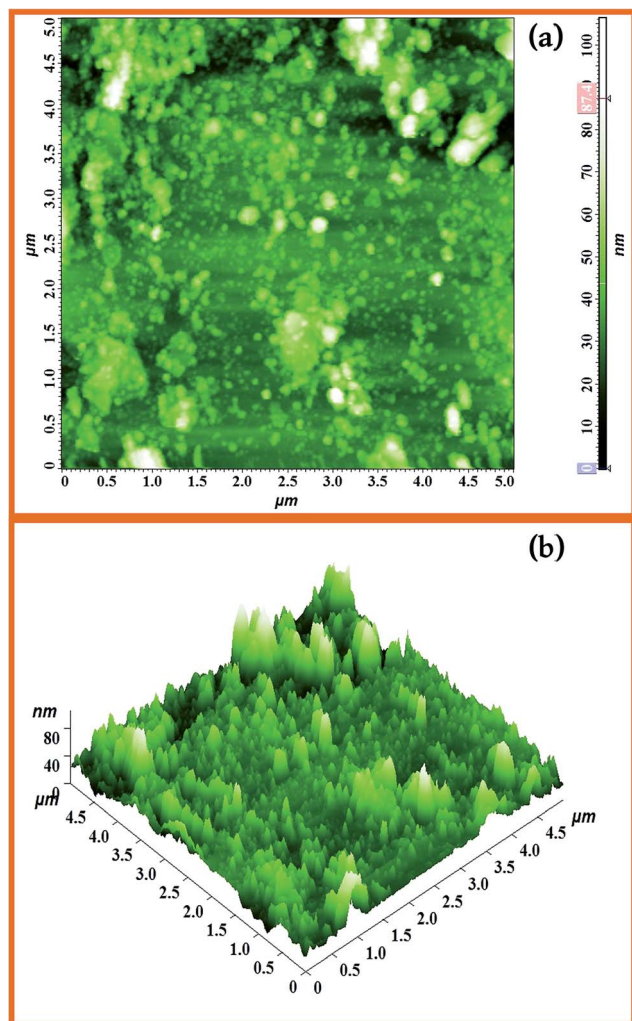


Fig. 5 AFM images of the surface morphology of 5  $\mu\text{m} \times 5 \mu\text{m}$  region of the  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  (a) 2D image and (b) 3D image of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ .

531.2 eV), for two different kinds of O species in the sample (Fig. 6e). These two peaks should be associated with the lattice oxygen (OL) of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  and chemisorbed oxygen (OH) caused by the surface hydroxyl groups.<sup>36</sup>

To find out the optical characteristics, UV-Vis diffuse reflectance and photoluminescence spectra for the ZnO and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  catalysts were recorded. Fig. S3† shows the DRS spectrum of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ . Any impurity in the semiconductor oxide can form intermittent band energy levels and this leads to the decrease of bandgap energy, which increases the UV-visible absorption. The prepared ZnO presents a sharp absorption edge at 380 nm. From the Fig. S3,† prepared photocatalyst shows an increased absorption over the undoped ZnO material both in the visible and the ultraviolet regions. Hence the band gap energy is reduced relative to prepared ZnO and it serves as a support to resist the recombination process together with the f orbitals of dysprosium tungstate, which traps the electrons excited during the photodegradation process. These would facilitate the reaction of the separated hole with the water molecules to produce OH free radicals, thus enhancing the

efficiency of the photodegradation of the organic dye molecule by the prepared photocatalyst. UV-Vis spectra in the diffuse reflectance mode ( $R$ ) were transformed to the Kubelka-Munk function  $F(R)$  to separate the extent of light absorption from scattering. The band gap energy was obtained from the plot of the modified Kubelka-Munk function  $(F(R)E)^{1/2}$  versus the energy of the absorbed light  $E$  (eqn (2))

$$F(R)E^{1/2} = \left[ \frac{(1-R)^2}{2R} \times hv \right]^{1/2} \quad (2)$$

Photocatalysts generate electrons and holes after being activated by light, and recombination of some electrons and holes can release energy in the form of fluorescence emission. Lower fluorescence emission intensity implies lower electron-hole recombination rate. The fluorescence emission is mostly from the recombination of the photogenerated electron-hole pairs, and a strong correlation between PL intensity and photocatalytic activity has been previously reported.<sup>37</sup> Fig. 7 presents the photoluminescence spectra of the prepared ZnO (a), and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  (b). The excitation wavelength is 380 nm and two emission bands occur at 419 and 489 nm. It can be seen that the positions of the peaks are similar, while PL intensities are different. The PL intensity of prepared ZnO at 419 nm, which is due to electron-hole recombination, is higher than  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ . The electron capture by the loaded  $\text{Dy}_2\text{WO}_6$  will decrease the electron-hole recombination and cause a decrease in emission intensity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  as reported for  $\text{Pr}_6\text{O}_{11}\text{-ZnO}$ .<sup>23</sup> Higher photocatalytic activity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  reveals that the decrease in emission intensity is due to suppression of electron-hole recombination by the loaded  $\text{Dy}_2\text{WO}_6$ .<sup>15,38</sup> Reduction in electron-hole recombination leads to the increased availability of electrons and holes for the production of radicals for degradation.

### Photocatalytic activity of $\text{Dy}_2\text{WO}_6$ doped ZnO

Photocatalytic degradation of Rh-B under different conditions with increasing irradiation times is displayed in Fig. 8. Dye is resistant to self photolysis and for the same experiment with  $\text{Dy}_2\text{WO}_6$  in the dark, a decrease (8%) in dye concentration was observed due to the adsorption of dye on the catalyst. Rh-B undergoes 98% degradation in the presence of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  under natural sunlight in 75 min. But, prepared ZnO,  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-P25}$ , and undoped  $\text{Dy}_2\text{WO}_6$  shows 72%, 57%, 68% and 64% degradations, respectively in 75 min. These results show that prepared 3 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  nanomaterial is most efficient for degradation of Rh-B dye than other photocatalysts (Fig. 8). 3 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  shows higher activity (98%) than other 5 wt%  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  (80%). It is obvious that the higher photocatalytic activity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  is due to the support of  $\text{Dy}_2\text{WO}_6$ . To test the effectiveness of the catalyst on the degradations of other azo dyes, we had carried out the experiments on the degradation of TB under the same conditions. Fig. S4† shows the comparative studies of degradations of Rh-B and TB using  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  at different irradiation times. Rh-B and TB undergo 98% and 94% degradation respectively in 75 min, revealing that this catalyst is efficient in the degradation of azo dyes.



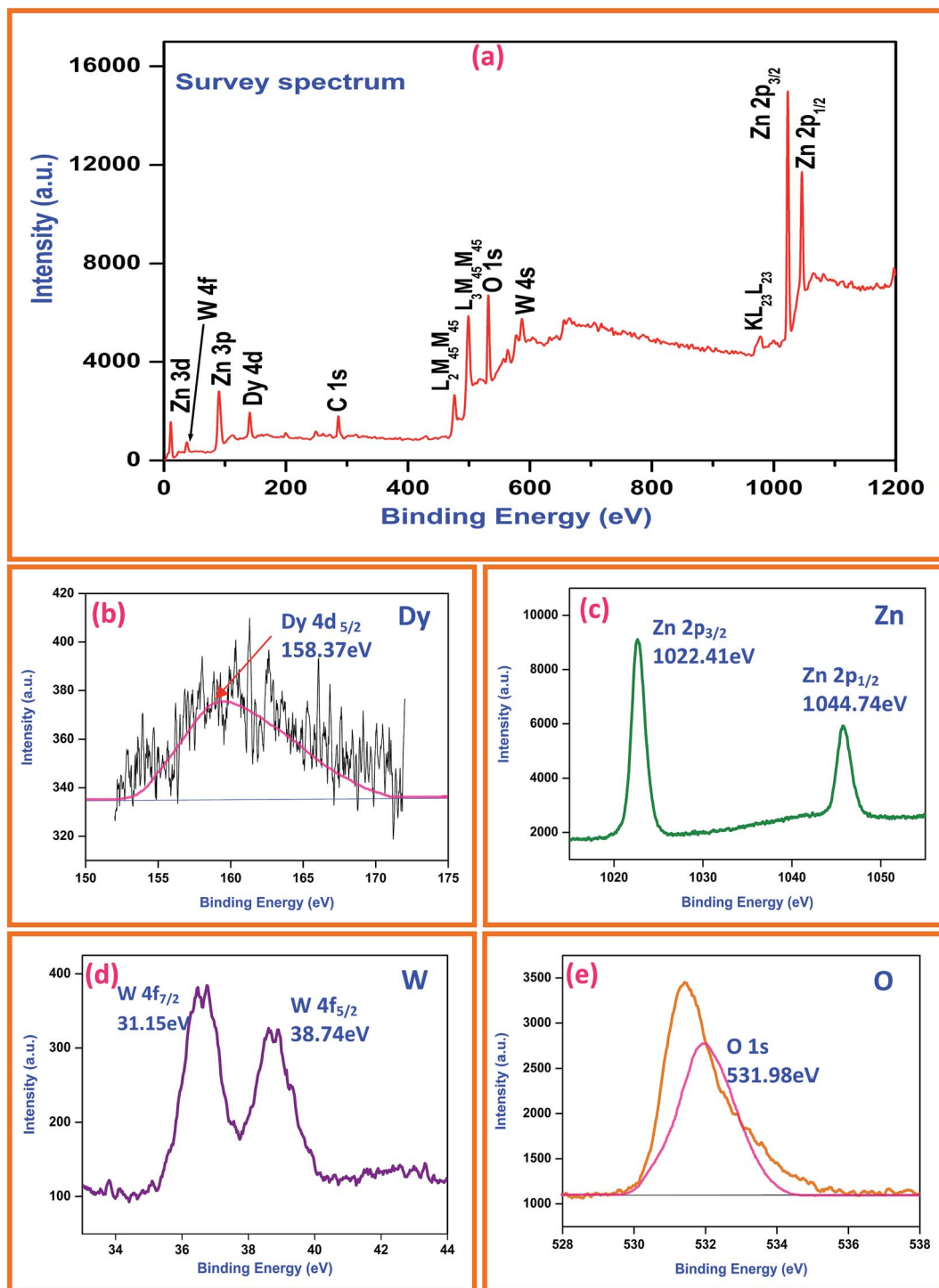


Fig. 6 XPS analysis of Dy<sub>2</sub>WO<sub>6</sub>-ZnO (a) survey spectrum, (b) Dy 4d, (c) Zn 2p, (d) W 4f and (e) O 1s.

The solution pH plays a crucial role in the photocatalytic degradation. The effect of pH on the photodegradation of Rh-B was studied in the pH range 3–11 and the results are shown in Fig. S5.† The degradation efficiency is high at pH 7 and it decreases when the pH is above or below 7. Low removal efficiency at acidic pH range may be due to the dissolution of ZnO in Dy<sub>2</sub>WO<sub>6</sub>-ZnO. It shows prepared catalyst is more advantageous

than undoped ZnO in the degradation of Rh-B because it has maximum efficiency at the neutral pH 7.

The reusability of Dy<sub>2</sub>WO<sub>6</sub>-ZnO was tested for the degradation of Rh-B dye under the same reaction environment. After complete degradation, the catalyst was separated and washed with deionized water. The recovered catalyst was dried in hot air oven at 100 °C for 3 h and used for a second run. Fig. S6† shows



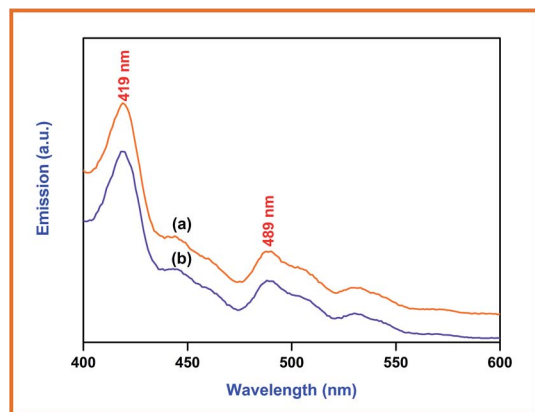


Fig. 7 Photoluminescence spectrum of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  (a) prepared ZnO and (b)  $\text{Dy}_2\text{WO}_6$  doped ZnO.

the result of Rh-B degradation for four successive runs.  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  gives enhanced activity in Rh-B dye degradation percentages as 98.0, 97.4, 96.0 and 96.0 for 75 min in the first, second, third and fourth run respectively. There is no significant change in the degradation efficiency of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  after second run.

### Mechanism for dye degradation

The dysprosium is a rare earth metal belongs to lanthanide group and the element possessing f shells and they are capable of trapping the electrons generated due to presence of f-f transition at visible light by the photocatalyst.<sup>39</sup> The transitions of 4f electrons of lanthanides lead to the implementation of the optical adsorption of catalysts and support the separation of photogenerated electron-hole pairs. In the case of dysprosium dopant, it can exist as  $\text{Dy}^{3+}$  and  $\text{Dy}^{4+}$ . Thus,  $\text{Dy}^{3+}$  may give an electron to  $\text{O}_2$  adsorbed on the surface of  $\text{Dy}_2\text{WO}_6$ -doped ZnO to form  $\text{O}_2^-$  by transforming into  $\text{Dy}^{4+}$ , favouring a charged migration to  $\text{O}_2$  and an enhancement of the photoreaction rate

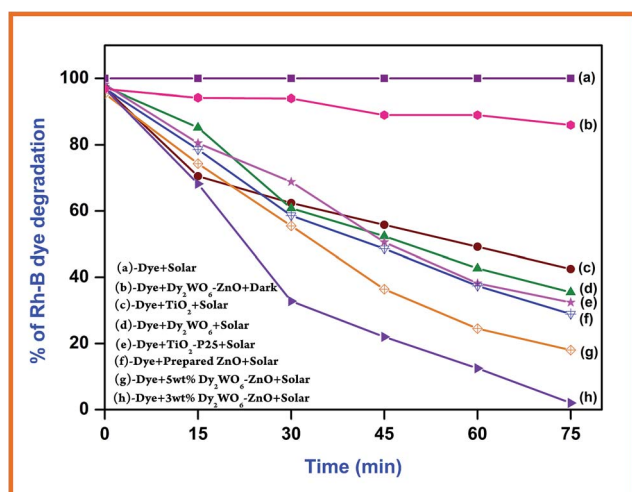
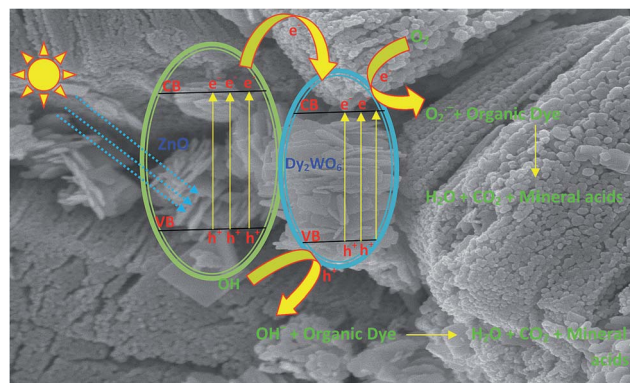


Fig. 8 Primary analysis: Rh-B dye concentration =  $3 \times 10^{-4}$  M, catalyst suspended =  $3 \text{ g L}^{-1}$ , pH = 7, airflow rate =  $8.1 \text{ mL s}^{-1}$  and irradiation time 75 min,  $I_{\text{solar}} = 1250 \times 100 \text{ lux} \pm 100$ .



Scheme 1 Degradation mechanism.

in comparison with that of pure ZnO.<sup>27</sup> The mechanism of electron capture and transfer is displayed in Scheme 1. The decreased PL intensity in  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ , reveals that the recombination of electron is suppressed by  $\text{Dy}_2\text{WO}_6$  particles, indicating that an appropriate amount of  $\text{Dy}_2\text{WO}_6$  could significantly reduce the irradiative recombination rate of photogenerated electrons and holes in ZnO. The band gap energy obtained by Kubelka-Munk function is comparatively lower than pure undoped ZnO. AFM studies also prove that the surface of the synthesized photocatalyst is very rough and porous in nature and this may assist the absorption of organic molecules on the surface of the catalyst.

### Electrochemical methanol oxidation

The electronic structure of the electrode greatly influences its electrocatalytic activity. It has been proved that the electro-oxidation of methanol is a surface-sensitive reaction. Pt and Ag/AgCl electrodes are normally used as the counter and reference electrodes, respectively. Fig. 9a and b shows the cyclic voltammograms (CVs) of glassy carbon electrode coated with prepared ZnO and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ , taken in  $\text{N}_2$  saturated 0.5 M NaOH solution at a scan rate of  $50 \text{ mV s}^{-1}$ . Typical potential regions for hydrogen adsorption/desorption and the formation/reduction of surfaces of metal oxide or metal- $\text{OH}_{\text{ads}}$  of ZnO, and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  are clearly seen in Fig. 9a and b.

Anodic and cathodic reactions of methanol fuel cell are given below. Water is consumed at the anode and generated at the cathode. Electrons pass through externally from anode to cathode, producing the current.

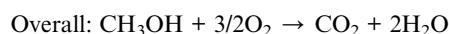
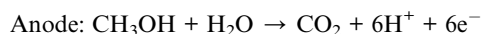


Fig. 9a shows the typical cyclic voltammograms of prepared ZnO for methanol electrochemical oxidation up to 20 segments. The current cathodic oxidation peak at  $-0.27 \text{ V}$  (vs. Ag/AgCl) in the forward scan and the reduction peak appearing at  $-0.037 \text{ V}$  correspond to the methanol oxidation and removal of the CO



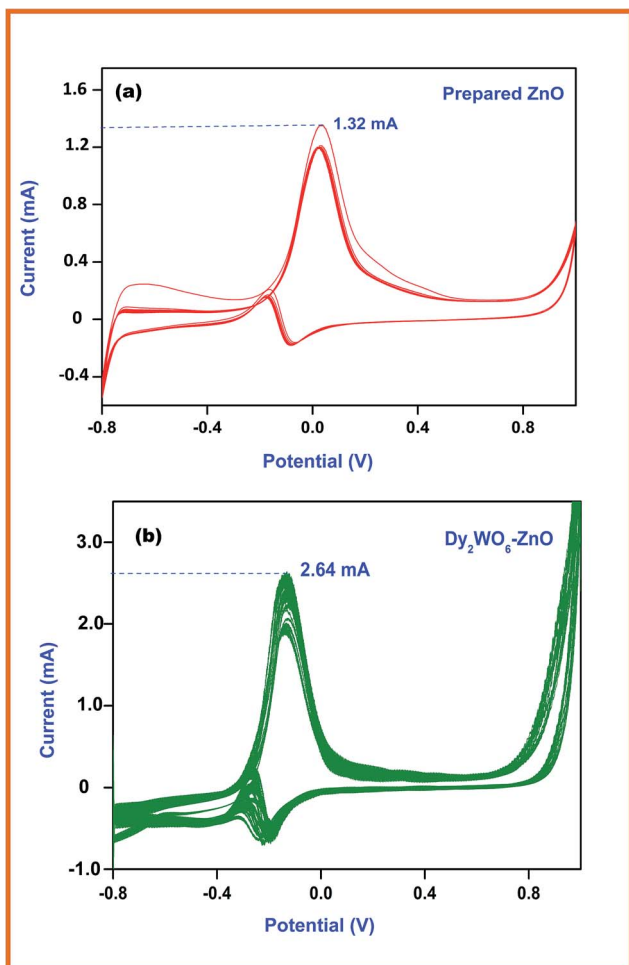


Fig. 9 Cyclic voltammogram of (a) prepared ZnO (b) and  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  in  $\text{N}_2$  and saturated 0.5 M NaOH + 0.5 M  $\text{CH}_3\text{OH}$  solution at a scan rate of  $50 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$ .

species adsorbed on the catalyst surface respectively. Therefore, the peak potential and current density of the forward anodic oxidation peak can be used to evaluate the catalytic activity of the electrocatalyst. Fig. 9b depicts cyclic voltammogram of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ , and it clearly explains the effect of  $\text{Dy}_2\text{WO}_6$  on ZnO in methanol oxidation. The sharp anodic peak at  $-0.13 \text{ V}$  due to oxidation of methanol and the current efficiency reached around  $2.64 \text{ mA}$ , which is two times higher than prepared ZnO ( $1.32 \text{ mA}$ ). This enhanced electrochemical activity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  reveals that the catalyst will be useful in fuel cell application.

The electrochemical stability of the catalysts for methanol electro-oxidation was investigated by chronoamperometric experiments at  $-0.1 \text{ V}$  in 0.5 M NaOH + 0.5 M  $\text{CH}_3\text{OH}$  solution and the curves are shown in Fig. S7a–c.† All these catalysts initially show a rapid decrease in current for the oxidation of methanol, and then a relatively steady current is achieved. The rapid current decay is due to the poisoning of intermediate and various poisoning species formed during methanol oxidation reaction in alkaline medium.<sup>40,41</sup> It is clear from the Fig. S7a† that the current decay for the reaction on the  $\text{Dy}_2\text{WO}_6\text{-ZnO}$

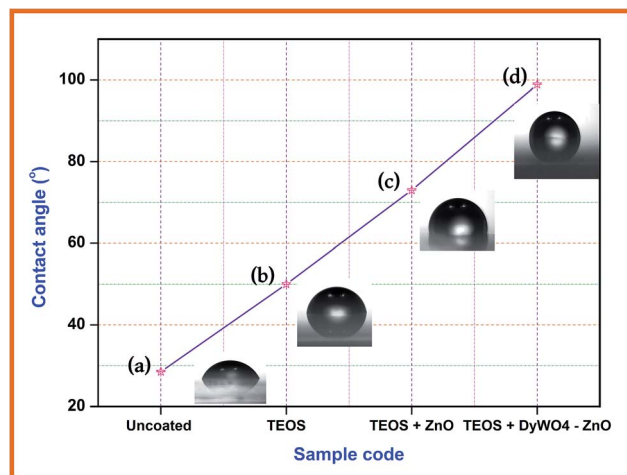


Fig. 10 Water contact angle measurements (a) uncoated glass slide, (b) TEOS coated glass slide, (c) TEOS + ZnO coated glass slide and (d) TEOS +  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  coated glass slide.

nanomaterial is significantly less ( $4.8 \text{ mA}$  to  $2.64 \text{ mA}$ ) than that on the prepared ZnO (Fig. S7c,†  $4.8 \text{ mA}$  to  $1.5 \text{ mA}$ ) and  $\text{Dy}_2\text{WO}_6$  (Fig. S7b,†  $4.8 \text{ mA}$  to  $2.1 \text{ mA}$ ) and the steady current is reached at  $2.64 \text{ mA}$  for  $\text{Dy}_2\text{WO}_6\text{-ZnO}$ . This indicates that  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  attained stability earlier than other catalysts and the improvement in the electrochemical constancy for methanol electro-oxidation in alkaline medium.

### Contact angle measurements

Surface non-wettability or the hydrophobicity of the catalyst is exposed by water contact angle. If a surface has a contact angle with water that is greater than  $90^\circ$ , then the surface is classed as hydrophobic and if the contact angle is less than  $90^\circ$ , the surface is hydrophilic. Water contact angles were determined using glass slides coated with TEOS, TEOS + ZnO and TEOS +  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  to investigate the hydrophobicity of the catalysts. Fig. 10 shows the images of water drops on coated and uncoated glass slides. Water contact angle (WCA) of  $28.5^\circ$  on uncoated glass slide shows the hydrophilicity and this WCA increases gradually on glass slides coated with TEOS ( $50.2^\circ$ ), TEOS + ZnO ( $73.6^\circ$ ) and TEOS +  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  ( $98.9^\circ$ ). Surface coated with TEOS +  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  has more hydrophobic character. In TEOS, the O–Si–O groups are modified by  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  to make the surface rougher, stable and non-wettable. Hence the contact angle increases above  $90^\circ$  exhibiting the hydrophobicity of the catalyst. This surface non-wettability leads to a self cleaning property of the catalyst.

## Conclusion

In conclusion, a new sunlight active  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  photocatalyst was synthesized by a simple hydrothermal-thermal decomposition method and characterized by the various analytical techniques. The XRD pattern confirms that ZnO has wurtzite structure with good crystallinity and  $\text{Dy}_2\text{WO}_6$  has body-centered monoclinic structure with crystallite size of  $18.5 \text{ nm}$ . The HRSEM images of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  indicate a sandwich-like



microstructure loosely clustered together, and the average size of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  particles is about 100 nm. FETEM further proves the morphology of prepared  $\text{Dy}_2\text{WO}_6$  doped ZnO as hexagonal and regular sphere shaped particles. Elemental colour mapping studies reveal the homogeneous distribution of Dy, Zn, W and O in the catalyst.  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  shows enhanced activity in the degradation of azo dyes Rh-B and TB compared to the prepared ZnO,  $\text{Dy}_2\text{WO}_6$ ,  $\text{TiO}_2$ , and  $\text{TiO}_2\text{-P25}$ . This catalyst was found to be stable and reusable. Electrocatalytic activity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  exhibited enhanced current production by electrochemical methanol oxidation under room temperature. Hydrophobicity of  $\text{Dy}_2\text{WO}_6\text{-ZnO}$  makes it useful for industrial self-cleaning material.

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