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## 1 Introduction

Widespread discharge of wastewaters from the textile industries, which contain large amounts of dyes has become a great concern to the delicate environment and ecosystem due to their non-biodegradability, toxicity, and potential carcinogenicity. The need to meet stringent international regulations and standards for wastewater discharge has motivated the development of efficient, non-toxic and low-cost photocatalytic materials for cleaning up the pollutants in wastewater effluent. In recent years, the use of semiconductor metal oxides for photocatalytic degradation of pollutants has attracted immense attention. Although TiO2 is universally known as the most important photocatalyst, ZnO is also a good alternative photocatalyst candidate. ZnO is a II-IV semiconductor with a bandgap energy (3.2 eV) similar to that of TiO<sub>2</sub>, and it is suitable for photocatalytic purposes due to its non-toxicity, thermal and chemical stability as well as low cost. Besides attracting intensive research efforts in applications such as memory, transistors, light emission, gas sensing, anti-reflection, UV photodetection and water splitting,1-4 ZnO has also been widely studied for photodegradation of pollutants5 due to its efficacy in degrading various pollutants owing to its high catalytic activity, photosensitivity, ease of preparation, etc. However, ZnO is a direct bandgap semiconductor which exhibits rapid recombination of the photoinduced electrons and holes, thus limiting its photocatalytic efficiency. Hence, various methods have been devised to improve the photocatalytic properties of ZnO.

# Metal nanoparticle-loaded hierarchically assembled ZnO nanoflakes for enhanced photocatalytic performance†

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We have demonstrated an environmentally friendly and template-free aqueous synthesis of hierarchically assembled 3D ZnO nanoflakes. The ZnO nanoflakes self-assembled to expose highly interconnected networks of well-defined catalytic active {0001} facets. Well dispersed Pt, Ag and Au metal nanoparticles were loaded to form hybrid ZnO nanoflakes for enhanced photocatalytic activity. The enhanced photocatalytic activity may be attributed to the synergetic effects of well-structured ZnO crystal facets, high metal nanoparticles dispersity, enhanced light absorption and charge-transfer kinetics which leads to high photocatalytic degradation.

One of the methods to improve photocatalytic properties is devoted to the controlled synthesis of the ZnO material in terms of size and morphological structure. Structures that are small yet stable against agglomeration and at the same time possess porous and high surface area structure are highly sought. In consideration of photocatalytic reactions which take place mainly on the surface of the catalyst, a nanoscale ZnO material is believed to exhibit better performance than its bulk counterpart due to its higher surface-to-volume ratio. Moreover, if the photocatalyst used is of nanoscale dimension, the probability of photogenerated electron-hole pair recombination will drastically reduce owing to their fast arrival at the surface of the reaction sites. In terms of morphological structure, the use of 3D hierarchically assembled nanoflakes or nanoplatelets structures is likely to improve structural-mechanical stability and dispersity in comparison to 1D vertically aligned nanowires and 0D nanoparticles structures which are more susceptible to surface tension of water pollutants which will result in severe agglomeration. Other advantages include high surface area for effective loading and interfacing of metal co-catalysts with wellexposed crystal facets.

Another method to improve the photocatalytic properties has been devoted to the development of hybrid nanostructures made up of semiconductor-metal nanoparticles and semiconductor-graphene nanocomposites. It is reported that hybrid ZnO and TiO<sub>2</sub> nanostructures decorated with noble metal nanoparticles (*e.g.* Au, Ag, Pt) and graphene have shown improved photocatalytic efficiency.<sup>6-13</sup> In these heterostructured systems, metal nanoparticles act as electron scavenging centers to allow effective electron and hole pair separation, leading to improved photocatalytic activity. Similarly, graphene acts as an excellent electron-transport material, so that the hybridization of metal oxide with graphene hinders the recombination of charge carriers which enhances the photocatalytic performance.

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Here we have demonstrated the development of scalable 3D hierarchically assembled ZnO nanoflakes *via* a facile and template-free aqueous solution route. Subsequently aqueous photoreduction and deposition precipitation methods are employed to functionalize 3D ZnO nanoflakes with Pt, Ag and Au metal nanoparticles to form hybrid functional materials for photocatalytic studies. Such hybrid structures are important for the exploration of nanosized and well-dispersed metal nanoparticles on ZnO nanostructures for photocatalytic applications. The enhanced photocatalytic activity may be attributed to the synergetic effect of well-structured crystal facets, high metal nanoparticles dispersity, enhanced light absorption and charge-transfer kinetics which render high photocatalytic degradation.

## 2 Experimental details

#### Synthesis of mesoporous 3D ZnO nanoflakes

The ZnO nanoflakes were synthesized using 0.07 g of Pluronic F123, 3.31 g of zinc nitrate hexahydrate  $(Zn(NO_3)_2 \cdot 6H_2O)$  and 2.68 g of urea were added to 25 mL DI water. The mixed solution was placed in an oven at 80 °C for 24 h. The collected precipitate was then washed and dried overnight. Subsequently, the precipitate was calcined at 450 °C for 30 min to obtain mesoporous 3D ZnO nanoflakes.

#### Metal loading of mesoporous 3D ZnO nanoflakes

10% metal loadings on 3D ZnO nanoflakes were carried out. 5 mL of 0.0102 M hydrogen hexachloroplatinate(IV) hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) and 5 mL of 0.0185 M silver nitrate (AgNO<sub>3</sub>) were added to the 100 mg ZnO nanoflakes for Pt and Ag respectively. The two suspensions in 10 mL methanol were then irradiated with a Xe arc lamp (300 W) for 3 h with constant magnetic stirring. The loaded powder was washed and dried overnight. 5.08 mL of 0.01 M gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) in 10 mL of DI water solution was tuned to a pH of 8–9 with the addition of sodium hydroxide (NaOH). The solution was stirred in 80 °C water bath for 2 h before being washed, dried and calcined at 300 °C for 30 min.

#### Material characterisation

Scanning electron microscopy (SEM, JEOL FEG JSM 7001F) operated at 15 kV was used to characterize the morphology of the synthesized nanostructures. The elements present in the nanostructures were analyzed using energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments). The crystalline structures of the ZnO nanoflakes and metal nanoparticles were analyzed using transmission electron microscopy (TEM, Philips FEG CM300) operated at 200 kV and X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu K $\alpha$  radiation at  $\lambda = 1.541$  Å). Brunauer–Emmett–Teller (BET) measurements were conducted using a Quantachrome Nova 1200 with N<sub>2</sub> as the adsorbate at liquid nitrogen temperature. Absorption spectra of the samples were measured with a UV-VIS-NIR spectrophotometer (UV-Vis, Shimadzu UV-3600). X-Ray photoelectron spectroscopy (XPS) was employed to

study the elemental composition of the pristine ZnO nanoflakes and ZnO nanoflakes loaded with Au, Pt and Ag.

#### Photocatalytic testing

25 mg of prepared photocatalyst was added to 25 mL of 0.03 mM methyl orange (MO) aqueous solution in a cylindrical quartz tube with a sealed bottom. The suspension was irradiated with a Xe arc lamp (300 W) with constant magnetic stirring to ensure a higher level of homogeneity of photocatalyst presence in the suspension. 1.5 mL of sample was drawn every 30 min with a syringe. The concentration of MO was determined using a UV-VIS-NIR spectrophotometer (UV-Vis, Shimadzu UV-3600) and the maximal absorbance peak value (at 462.5 nm) was noted to plot the amount of MO degraded and thus, determine the photo-activity of the catalysts. The residual dye content was calculated as  $C/C_0$ , where C and  $C_0$  are the concentrations of the tested and the original control solution (just after dark stirring), respectively.

# 3 Results and discussion

A high yield of white precipitate (ZnO nanoflakes) can be collected from the solution. Fig. 1a and b shows the SEM images of pristine ZnO nanoflakes which are homogeneously deposited in the growth solution. The precipitate is made up of nanoflakes which are self-assembled into a hierarchical flower-like microstructure with an average diameter of  $\sim 10 \ \mu$ m. The ZnO nanoflakes exhibit fairly regular sheets that are of a few micrometers in diameter and 20-30 nm in thickness. Fig. 1c shows that the nanoflakes are spaced out fairly evenly with no stacking observed. The nanoflakes are intersected at various angles to form "petals" of a flower-like microstructure. The magnified SEM image Fig. 1d shows an individual nanoflake with plenty of voids forming interconnected network of pores. Such a porous network structure can potentially increase the accessible surface area for enhanced reactant diffusivity which are highly favourable for catalytic applications. It is observed that the ZnO



Fig. 1 SEM images of pristine ZnO nanoflakes which are self-assembled into a hierarchical flower-like microstructure with an interconnected network of pores.

nanoflakes loaded with metal nanoparticles appeared similar to pristine ones either due to the metal nanoparticles deposits being too small or similar in size in comparison to the ZnO porous network structure as such they cannot be resolved or differentiated by SEM respectively.

EDX spectra as shown in Fig. 2a show that the Zn  $L\alpha_{1,2}$  peaks at 1.01 keV,  $K\alpha_1$  peaks at 8.63 keV and  $K\beta_1$  peaks at 9.57 keV are uniform among all the metal-loaded ZnO nanoflakes. This proves that the metal-loading process does not affect the ZnO structures or properties. Au  $M\alpha_1$  peak at 2.12 keV, Ag  $L\alpha_1$  peak at 2.98 keV and  $L\beta_1$  peak at 3.15 keV and Pt  $M\alpha_1$  peak at 2.05 keV were consistently observed in Au-loaded, Ag-loaded and Ptloaded ZnO nanoflakes respectively. Fig. 2b also shows the elemental mapping of Au-loaded ZnO nanoflakes. Uniform loading is observed from the yellow dots that represent Au. Similar elemental mappings were observed for Ag and Pt metal nanoparticles loaded ZnO nanoflakes as well without presence of any other impurities.

TEM micrographs in Fig. 3a–c clearly show that the ZnO nanoflakes possess irregular mesopores. The average pores sizes are of tens of nanometers with a wide size distribution from 10–80 nm. The high-resolution TEM micrograph in Fig. 3d shows that the ZnO nanoflakes are single crystalline and possess a wurtzite structure with a lattice spacing of 2.6 Å. This indicates that the ZnO nanoflakes grow predominantly perpendicular to the [0001] zone axis (Fig. 3d, left inset). The growth along the  $\langle 0001 \rangle$  direction or along the *c*-axis is suppressed which resulted in a lateral growth to largely expose the  $\{0001\}$  facet (Fig. 3d, left inset). This is in contrast to 1D ZnO



Fig. 2 (a) EDX spectra of Au, Ag and Pt-loaded ZnO nanoflakes. (b) EDX elemental mapping of Au-loaded ZnO nanoflakes.



Fig. 3 (a–c) Low and (d) high resolution TEM images of ZnO nanoflakes. (d) Insets show schematic of 2D nanoflake and 1D nanowire/nanorod with {0001} facets.

nanostructure, where the preferred growth is along the  $\langle 0001 \rangle$  direction which means that only the tip of the nanowire/nanorod exposes the  $\{0001\}$  crystal facet (Fig. 3d, right inset). Photocatalytic activity is strongly dependent on specific crystal planes. It has been reported that well-defined ZnO nanodisks with predominant (0001) crystal planes show enhanced catalytic activity.<sup>14</sup> In our work, it is apparent that the architectural structures of the 3D nanoflakes have extensively exposed active (0001) facets beneficial for enhanced photocatalytic applications.

Deposition of metal nanoparticles on ZnO nanoflakes was devised to overcome the limitations of high recombination rate of photogenerated electrons and holes which will lead to reduced photocatalytic activity. Fig. 4a and b shows the ZnO nanoflakes that are deposited with Au nanoparticles where the darker contrast spherical particles of diameter ca. 3 nm are ascribed to Au nanoparticles. It can be observed that the Au nanoparticles are highly and uniformly dispersed on ZnO nanoflakes with a tight distribution of 2-4 nm in diameter. Fig. 4c and d shows the ZnO nanoflakes that are loaded with Pt nanoparticles by the photodeposition method. The Pt nanoparticles are observed to be smaller in diameter of ca. 2 nm with a tight diameter distribution of 1-3 nm. The Pt nanoparticles are also well-dispersed and uniformly deposited on the ZnO nanoflakes. Fig. 4e and f show typical TEM images of the ZnO nanoflakes after photodeposition of Ag nanoparticles. The Ag nanoparticles were considerably bigger than Au and Pt nanoparticles as the nearly spherical Ag nanoparticles were observed with sizes varying from 20-80 nm. The EDX has identified the nanoparticles with darker contrasts as the Ag nanoparticles, whereas the lighter-contrast ones are attributed to the ZnO porous nanoflakes. The Fig. 4f inset shows a high resolution



Fig. 4 TEM images of (a and b) Au (c and d) Pt and (e and f) Ag nanoparticles loaded ZnO nanoflakes respectively. (f) Inset shows high resolution image of Ag nanoparticle.

image of Ag nanoparticle with interplanar fringe of 0.245 nm corresponding to the d spacing of the fcc Ag (111) crystal plane.

 $N_2$  adsorption-desorption isotherms were measured using BET to give further insight into the surface area and pore size distribution of the pristine ZnO nanoflakes. The sample exhibited a type IV isotherm of a type H3 hysteresis loop, which signifies the presence of a mesoporous structure (Fig. 5a). The surface area was determined to be 31.049 m<sup>2</sup> g<sup>-1</sup>, comparatively higher than that of commercial ZnO powders *ca.* 4–5 m<sup>2</sup> g<sup>-1,15</sup> The specific surface area is similar to the reported multilayered



**Fig. 5** (a) BET adsorption/desorption isotherms and (b) BJH pore size distribution of ZnO nanoflakes.

ZnO nanosheets with hierarchically porous structures.<sup>15</sup> However, the obtained surface area is expected to be relatively lower than a thick ZnO mesoporous film where pores are embedded in the matrix which is unlike pores/voids formed on thin 2D nanoflakes.<sup>16</sup> The BJH pore size distribution curve (Fig. 5b) reveals that the ZnO nanoflakes possess an average pore size of 14.1 nm and pore volume of 0.16 cm<sup>3</sup> g<sup>-1</sup>.

The crystal phases of the metal loaded ZnO nanoflakes are characterized by XRD. As shown in Fig. 6a, the XRD pattern shows peaks at 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 66.4, 68.0, and 69.1° indexed to (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes of the wurtzite ZnO, respectively. For the Au loaded ZnO nanoflakes, the diffraction peaks at 38.3° and 44.5° are assigned to the (111) and (200) planes of facecentered cubic (fcc) Au (JCPDS 01-1172). A broad diffraction peak at  $2\theta$  about 39.8° can be observed, indicating the presence of metallic Pt (JCPDS no. 65-2868). The Ag loaded ZnO nanoflakes diffraction pattern exhibits three additional peaks at 38.1, 44.3 and 64.4° which can be indexed to the (111), (200) and (220) planes of Ag, revealing that fcc structure (JCPDS file no. 65-2871). In general, no characteristic peaks for other impurities other than the loaded metal nanoparticles were observed, which indicated that the final products are of high purity.

The UV-Vis absorption spectra of the ZnO nanoflakes before and after surface modification by metal nanoparticles are shown in Fig. 6b. All the samples exhibited an absorption edge at 370 nm due to the bandgap of ZnO nanoflakes. The pristine ZnO nanoflakes showed the lowest absorbance while the ZnO nanoflakes decorated with metal nanoparticles exhibited enhanced absorption intensity, with the ZnO nanoflakes decorated with Au nanoparticles exhibiting the highest absorbance among the samples. A peak at 540 nm was also observed in the absorbance spectrum of the Au loaded ZnO nanoflakes sample, and it is attributed to the surface plasmon resonance of the Au nanoparticles.<sup>17</sup> It is noted that this peak has shifted to a longer

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**Fig. 6** (a) XRD and (b) UV-Vis spectra of pristine and metal nanoparticles loaded ZnO nanoflakes.

wavelength due to electron deficiency in the Au nanoparticles, which is caused by the transfer of electrons from Au to ZnO nanoflake.<sup>17</sup>

From the XPS spectra in Fig. 7, the chemical compositions of the Au loaded ZnO nanoflakes sample were analyzed. In Fig. 7a, the Zn 2p<sub>3/2</sub> peak obtained is located at 1021.7 eV, which corresponds to Zn bonded to O in ZnO. The O 1s spectrum obtained in Fig. 7b is asymmetric, suggesting the presence of more than one oxygen species. Deconvolution of the O 1s peak revealed two peaks centered at 530.2 eV and 531.9 eV. The peak at 530.2 eV can be attributed to the O(-2) in ZnO, while the peak at 531.9 eV is ascribed to the chemisorbed oxygen caused by the surface hydroxyl groups, which corresponds to the O-H bonds.18 The Au 4f peaks are presented in Fig. 7c and the Au  $4f_{7/2}$  and Au  $4f_{5/2}$  peaks are clearly seen at 83.1 eV and 86.9 eV. These binding energy positions correspond to those of metallic Au but they are much lower than that found in bulk metallic Au (84.0 eV and 87.67 eV). This negative shift could be due to the larger electronegativity of Au compared to Zn, hence causing a charge transfer from ZnO nanoflakes to the Au nanoparticles.<sup>19</sup> Another possible reason for the shift could be due to the spherical shape of the Au nanoparticles. It was reported that the more spherical the nanoparticles, the lower the binding energy.20 This is due to the initial state effects, where the spherical nanoparticles have less coordinated surface atoms, thus reducing their binding energies relative to nanoparticles with large faces. Besides the two Au 4f peaks, a weak shoulder peak was also observed at 88.9 eV due to the Zn 3p<sub>3/2</sub> peak



**Fig. 7** XPS spectra of (a) Zn 2p (b) O 1s and (c) Au 4f of ZnO nanoflakes loaded with Au nanoparticles.

from ZnO. The other shoulder peak at 91.5 eV is attributed to Zn  $3p_{1/2}$ .

The photocatalytic performance was evaluated by photodegradation of the organic dye MO, a typical pollutant in textile industry, which has a severe impact on the environment. Fig. 8a-d shows a series of absorption spectra of the aqueous solution of MO with 25 mg of ZnO nanoflakes and Au, Pt and Ag loaded ZnO nanoflakes powder as photocatalyst and exposure to ultraviolet light for different durations. The characteristic absorption of MO at about 462.5 nm decreases gradually over time for all the four samples, and finally almost disappears within 60-180 min by using ZnO nanoflakes with and without metal nanoparticles loading as photocatalysts. It can be clearly seen that pristine ZnO nanoflakes display a slower photocatalytic activity than that of metal loaded ZnO nanoflakes. It is noted that in the absence of photoirradiation and photocatalyst, the concentration of MO has no obvious change for a long time. The results show that both light and photocatalyst are required for the MO dye degradation whilst metal loaded ZnO nanoflakes show enhanced photocatalytic activity. Amongst the metal loaded ZnO nanoflake samples, the Au nanoparticle-loaded ZnO nanoflakes sample shows the fastest photodegradation

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Fig. 8 (a–d) Absorption spectra of the aqueous solution of MO with ZnO nanoflakes and Au, Pt and Ag loaded ZnO nanoflakes photocatalysts exposed to ultraviolet light for different durations respectively.

characteristics. In the case of ZnO–Au nanoflakes it can be seen that the characteristic absorption of MO decreases rapidly with exposure time, and completely disappears after 60 min. A complete photo-assisted decomposition of MO was evident as no MO absorption peak was seen after an hour.

Degradation kinetics of the MO molecules were monitored by the change in their concentration, which was approximately calculated according to the absorbance peak. Fig. 9a shows the comparison of the time profiles of the decrease in MO concentration in the absence and in the presence of different photocatalysts. A control experiment was carried out where it shows that the photodegradation is not apparent without the use of photocatalyst. The photocatalytic abilities of conventional ZnO nanostructures such as commercial ZnO nanoparticles (Sigma Aldrich, product number: 544906) and ZnO nanorods synthesized in our lab were also measured and compared with the ZnO nanoflakes. SEM images (Fig. S1<sup>†</sup>) and synthesis procedure of the ZnO nanorods are provided in the ESI.† The ZnO nanoparticles and nanorods were not able to fully degrade the MO molecules after 180 min of UV irradiation as shown in Fig. 9a. In contrast, pristine ZnO nanoflakes show appreciable photocatalytic activity under UV irradiation and was able to fully degrade the MO dye after 180 min. The reason for this enhancement in performance is due to the higher surface area of the ZnO nanoflakes. On the other hand, ZnO nanoflakes with loaded metal nanoparticles show significant enhancement in MO degradation. The degradation of MO dye is approximately 58, 68, 76 and 100% for ZnO-pristine, ZnO-Pt, ZnO-Ag and ZnO-Au respectively after photo-irradiation for 60 min (Fig. 9a).

Fig. 9b shows the pseudo-first order kinetics of the MO degradation of the various photocatalysts. The efficiency of MO

photodegradation by the photocatalyst was determined quantitatively using the pseudo-first order model<sup>21</sup> as follow;

$$\ln(C_0/C_t) = kt \tag{1}$$

where  $C_0$  and  $C_t$  are the concentrations of dye at time 0 and t respectively and k is the pseudo-first order rate constant.

The pseudo-first order rate constants k of the various photocatalysts are shown in Table 1. The results clearly demonstrate that the Au loaded ZnO nanoflakes with its high Au nanoparticles dispersion and highest UV-Vis absorption prove to have the fastest photodegradation rate among all the samples tested. Evidently, MO is decomposed thoroughly within 60 min with the presence of the ZnO–Au photocatalyst as shown in the digital photographs of time evolution photodegradation study (Fig. 9c).

The ZnO nanoflakes when irradiated with UV light of energy higher than the bandgap (3.37 eV), generate electrons in the conduction band and holes in the valence band. The photoinduced electrons in the conduction band will be transferred to the metal nanoparticles acting as electron sink, which impede electron-hole pairs recombination. The semiconductor ZnO and metal (i.e. Ag, Au, Pt and Pd) composite have been reported to enhance photocatalytic activity by trapping the photoinduced charge carriers, thereby improving the charge transfer processes.22 When metal nanoparticles are deposited on ZnO nanoflakes, they will induce bending of the energy band of the semiconductor at the interface. In this case, since the work functions of the noble metals are higher than that of the n-type ZnO nanoflakes, upward bending of the energy band occurs, resulting in the formation of a Schottky barrier which facilitates electron capture.23 The degree of surface band bending



**Fig. 9** (a) Degradation kinetics (b) pseudo-first order kinetics and (c) digital photographs of time evolution MO photodegradation study in the absence and presence of various photocatalysts.

Table 1	Pseudo-first	order rat	e constants <i>k</i>	of the	various	photocatalysts
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Photocatalysts	Kinetic constants, $k (\min^{-1})$	Correlation coefficient, $R^2$
ZnO + Au	0.0517	0.9285
ZnO + Ag	0.0348	0.8782
ZnO + Pt	0.0281	0.9365
Pristine ZnO	0.0183	0.9747
Commercial ZnO	0.0177	0.9138
ZnO nanorods	0.0138	0.9673

indicates the amount of electrons being transferred to the metal nanoparticles. Therefore, a greater amount of band bending indicates a larger number of electrons transferred to the metal nanoparticles, resulting in lesser recombination and higher photocatalytic activity. Pt has the highest work function of 5.65 eV,<sup>24</sup> followed by Au which is 5.31–5.47 eV <sup>25</sup> and Ag has the lowest value of 4.52–4.74 eV.<sup>25</sup> In this case, Pt should show the highest photocatalytic activity while Ag should show the lowest

photocatalytic activity. However, based on our results, Au loaded ZnO nanoflakes shows the highest photocatalytic activity while Pt and Ag exhibited the same performance. The reason is because there are more Pt nanoparticles than Au nanoparticles deposited on the ZnO nanoflakes, resulting in a shadowing effect which deteriorates the photocatalytic activity.<sup>26</sup> Moreover, the high photon absorbance with superior interfacial charge transfer at Au–ZnO interface, and the long-lived charge separated states promotes generation of photoreactive oxidative species, *i.e.*  $O_2^-$  and OH,<sup>27,28</sup> enabling the highest photocatalytic activity of the Au loaded ZnO nanoflakes composites as compared to other ZnO nanoflakes hybrid samples.

#### 4 Conclusion

We have synthesized hierarchically assembled 3D ZnO nanoflakes based on an environmentally friendly and template-free aqueous synthesis route. HRTEM reveals that the ZnO nanoflakes were self-assembled to expose well-defined catalytic active {0001} facets. In addition, the loading of the metal nanoparticles were observed to be well-dispersed to form hybrid ZnO nanoflakes. The hybrid ZnO nanoflakes show appreciable photocatalytic activity under UV irradiation and was able to fully degrade the MO dye in 60 min. In contrast, conventional ZnO nanostructures such as ZnO nanoparticles and nanorods were not able to fully degrade the MO molecules after 180 min of UV irradiation. The enhanced photocatalytic activity may be attributed to the synergetic effects of well-structured ZnO crystal facets, high metal nanoparticles dispersity, enhanced light absorption and charge-transfer kinetics which render high photocatalytic degradation.

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