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Facile one-pot electrosynthesis of high photoreactive hexacoordinated Si with Zr and Zn catalysts

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A facile one-pot electrochemical method was used to synthesize a highly photoreactive hexacoordinated Si with Zr and Zn catalysts, which gave complete photodecolorization of
10 **methylene blue after 1 h of irradiation under visible light.**

Water pollution derived from dye contamination are a problematic issue of great concern to people. Therefore, it is mandatory to treat effluent and ensure it is free of factors toxic, mutagenic and carcinogenic to human and aquatic life, prior to
15 discharge into the receiving water body.[1-2] Pioneers of advanced oxidation processes (AOPs) using semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, CuO, ZrO_2 and CdS as photocatalysts which are important because they can convert a wide range of harmful dyes into non-toxic products, CO_2 and water at ambient
20 temperature.[3] In parallel, mixed metal oxides such as TiO_2-ZrO_2, Ag-ZnO, Fe_2O_3-TiO_2, Sn-ZnO and Ag-TiO_2 also exhibit better performance and enhance the photocatalytic activity.[4-8] Recently, the use of supported metal oxide catalysts such as TiO_2-HZSM5 (TiO_2-Protonated Zeolite Socony Mobil #5), Co-ZSM5 (Co-
25 Zeolite Socony Mobil #5) and CuO-X (CuO-Type X Zeolite) has become more attractive due to their advantage in lesser metal content and higher surface area.[9-11] However, development of supported mixed metal oxide catalysts is still scarce.

We have previously reported a new and simple
30 electrochemical method for preparation of very fine particles of electro-generated zirconia metal (EGZr) with high reactivity and demonstrated its successful use in photodecolorization of methylene blue.[12] EGZnO prepared by a similar procedure was also found to generate an active sites when supported on HY,
35 which enhanced the photodecolorization activity of dyes.[13] Afterwards, a highly photoactive α-Fe_2O_3 supported HY zeolite (Protonated Type Y Zeolite) was also successfully synthesized which efficiently decolorized of various dyes.[3] From these results, it could be seen that nanosized metal oxides, along with
40 the synergistic effect of the metals and support, play important roles in the enhancement of these reactions. Besides, the addition

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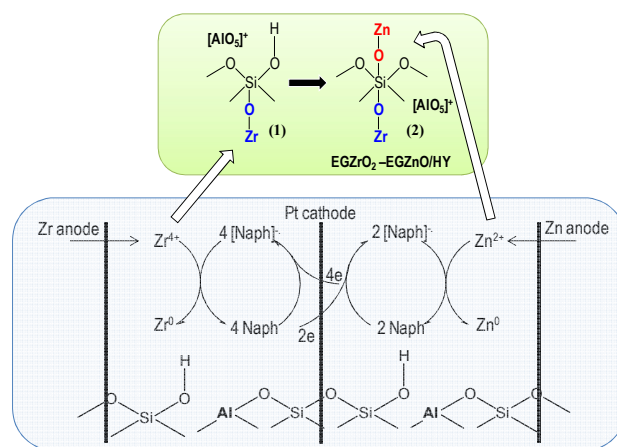
Scheme 1. Proposed mechanism for the formation of hexacoordinated Si with Zr and Zn by *in-situ* electrosynthesis method.

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of a second metal oxide proved to be an effective route to improve and endow extra properties to the photocatalyst, due to alteration and restructuring of the material upon optical and electronic influence.[4] Therefore, herein we report for the first
60 time, a facile and rapid electrosynthesis of $EGZrO_2$ and EGZnO supported by an HY ($EGZrO_2$-EGZnO/HY) catalyst, and its remarkable performance towards photodecolorization of methylene blue (MB). Based on Faraday's law of electrolysis, the electrolysis takes less than four min to yield a ratio of 1 wt %
65 $EGZrO_2$:1 wt % EGZnO to HY. HY zeolite was used in this study due to its larger pore, higher surface area, and can reduce the recombination effects as well as allowing the isomorphous substitution to be occurred in the framework to form an active species.

70 In this work, a new structure was ascertained during the preparation of $EGZrO_2$-EGZnO/HY (Scheme 1), on the basis of restructuring of the aluminosilicate HY framework to form a novel hexacoordinated Si with Zr and Zn, as shown by the ^{29}Si and ^{27}Al MAS NMR, FTIR, and XPS results. A 10 mL *N,N*-
75 dimethylformamide (DMF) solution containing 0.1 M tetraethyl-ammonium perchlorate was electrolyzed in the presence of a 1.5 g HY zeolite and 6 mmol naphthalene as a mediator in a normal one-compartment cell fitted with a Pt plate cathode (2 × 2 cm^2)

and a Zr plate anode (2×2 cm^2), then switched to a Zn plate anode (2×2 cm^2), at a constant current density of 120 mA/cm^2 under a nitrogen atmosphere at 273 K.[3] Dealumination of HY occurred to form a non-framework Al, $(AlO_5)^+$, which provide the oxygen source, in combination with the oxygen from the framework, to allow the insertion of Zr ions resulting from the anodic dissolution to form **(1)**.[12,14] Similar phenomenon also occurred for Zn ions, which finally gave **(2)** (EGZrO$_2$-EGZnO/HY). In parallel, electron transfer from naphthalene radical anions at the cathode also occurred to form EGZr^0 and EGZn^0 metal, which then were oxidized to EGZrO$_2$ and EGZnO during the calcination.[12,15] After electrolysis, the mixture was impregnated and oven dried overnight at 378 K, and calcined at 823 K for 3 h to yield a white powder, EGZrO$_2$-EGZnO/HY **(2)** catalyst, which was then ready for characterization.

^{29}Si MAS NMR chemical shifts were used to define the Si environments and provide information regarding the coordination of Si. As illustrated in Fig. 1a, the intensity of the sharp peak observed for bare HY at −107 ppm was shifted to a higher ppm for EGZrO$_2$-EGZnO/HY. A doublet peak at −120 to −140 ppm suggests the presence of hexacoordinated Si environment characteristics, as reported in literature.[16–18] ^{27}Al MAS NMR was employed to distinguish the Al in framework sites or from extra framework sites (non-framework). Fig. 1b indicates that the peak corresponding to the tetrahedral Al framework in HY was eliminated when EGZrO$_2$-EGZnO was added and a new peak appeared at 29 ppm. According to Klinowski, this peak corresponds to the presence of penta-coordinated aluminium (non-frameworks) in the aluminosilicate.[19]

To clarify the substitution between Zr and/or Zn into the HY framework, the amount of unbounded Zr and Zn in the framework was studied. The corresponding catalyst was stirred in DMF solution for 30 min and then filtered before being subjecting to ICP-MS analysis. It was found that 1.54×10^{18} and 1.20×10^{19} of Zr and Zn atoms were detected in the filtrate solution, respectively, referring to unbounded EGZrO$_2$ (1.6 %) and EGZnO (8.7 %). Therefore, 98.4 % and 91.3 % of total Zr and Zn ions in EGZrO$_2$-EGZnO/HY catalyst, respectively, appeared to be bonded to the Si in the HY framework to form a hexacoordinated structure of Si with Zr and Zn. All of the calculations were based on the ratio of elements in HY of $(Al_7Si_{17}O_{48}).32(H_2O)$.

Fig. 1c shows the FTIR spectra of the as-prepared catalysts, which demonstrate a broad band at 3465 cm^{-1} due to the H$_2$O molecules adsorbed on the catalyst surface, and 1638 cm^{-1}, attributed to the vibrational distortion of O–H groups on the catalyst surface. The weak bands between 800 and 370 cm^{-1}, which correspond to the Si–O–Si flexural vibration, decreased in intensity with the EGZrO$_2$-EGZnO loading, this may be due to the superposition of Si–O and M–O bonds (M=Zr, Zn).[20] An obvious band was observed at 1027 cm^{-1}, corresponding to the vibration of the Si–O–Zr bonds, verifying that Zr was inserted into the zeolite framework (Fig. 1d).[21] The formation of Si–O–Zn bonds was confirmed by the existence of the corresponding peak at 902 cm^{-1}.[22]

XPS analyses were performed to determine the chemical states of Zr and Zn in the catalyst (Figs. 1e and 1f). A doublet peak with binding energies of 183.1 eV (Zr$_{3d5/2}$) and 185.2 eV (Zr$_{3d3/2}$) was

observed, which exactly matches the chemical oxidation state of Zr^{4+} ions.[23] The Zn$_{2p3/2}$ peak at 1022.4 eV corresponded to the characteristic peak of Zn^{2+}.[24] However, the observed value for the EGZrO$_2$-EGZnO/HY sample was slightly shifted to higher binding energies, compared to those reported value of pure ZrO$_2$ (182.2 eV) and (184.5 eV) and ZnO (1021.2 eV), suggesting an interaction between the EGZrO$_2$-EGZnO and HY.[25]
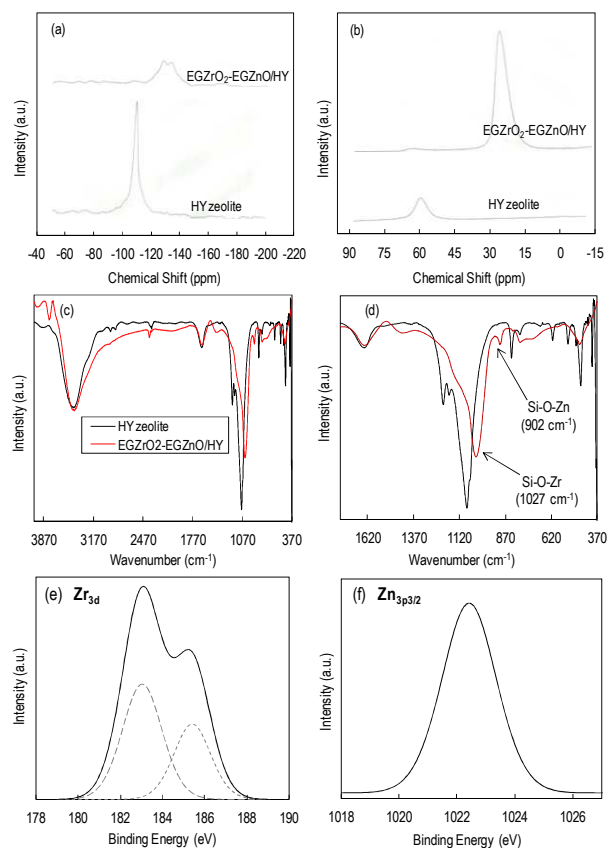

Fig. 1 MAS NMR spectra of (a) ^{29}Si (b) ^{27}Al of bare HY and EGZrO$_2$-EGZnO/HY; FTIR spectra of catalysts at region (c) 4000−370cm^{-1} (d) 1770−370cm^{-1}; XPS spectra of (e) Zr$_{3d}$ and (f) Zn$_{2p3/2}$ for EGZrO$_2$-EGZnO/HY catalyst.

The XRD pattern of the prepared EGZrO$_2$-EGZnO/HY catalysts was compared with EGZrO$_2$, EGZnO, EGZrO$_2$-EGZnO, and bare HY. Fig. S1a (ESI†) shows almost all peaks corresponding to EGZrO$_2$ and EGZnO were detected in EGZrO$_2$-EGZnO, indicating that the as-prepared catalysts were well mixed. A series of peaks were observed for EGZrO$_2$ and EGZnO, which are consistent with the tetragonal and monoclinic phase of ZrO$_2$ (JCPDS 01–072–2743), and the hexagonal wurtzite structure of ZnO (JCPDS 01–071–6424), respectively, with no other diffraction peaks being detected, indicating the purity of the as-prepared catalysts.[26,27] Fig. S1b (ESI†) shows the enlargement of a selected area XRD pattern from 26º to 86º for EGZrO$_2$-EGZnO/HY and bare HY. There are several peaks detected corresponding to ZrO$_2$ and ZnO, verifying the presence of EGZrO$_2$ and EGZnO metal on the HY framework.

The morphological properties of the EGZrO$_2$-ZnO/HY catalysts were examined by HR-TEM, and the images are

presented in Figs. S2a–2d (ESI†). The inset images show the fast Fourier transform patterns (FFT) and magnification of the selected area in the FFT patterns showed the atomic arrangement in the crystal, and allowed the estimation of the interplanar distance. The value of the interplanar distance (*d*–spacing) of the lattice fringes estimated from this image was consistent with the value of lattice spacing of $EGZrO_2$ and EGZnO obtained from the XRD analysis, which is tabulated in Table S1 (ESI†). Based on this result, as well as in agreement with the FTIR study, it was confirmed that $EGZrO_2$ and EGZnO were bounded in the HY support.

The topological properties of the solid powder form $EGZrO_2$–EGZnO/HY catalysts were studied by FE–SEM and the results are shown in Figs. S3a–3b (ESI†). The micrographs show the presence of small crystallites like uniformly distributed along some intergrowth. The fine particles of zirconia and zinc oxide may be well dispersed but their presence did not result in significant contrast at magnification up to 60 000×. Smooth surface with multi–dimensional of $EGZrO_2$–EGZnO/HY catalyst was observed that could provide better contact angle area to light penetration, thereby improving the utilization rate of photodecolorization of MB.[12]

In addition, the optical properties of the respective catalysts were studied by UV-vis diffuse reflectance spectroscopy (UV-vis/DRS). $EGZrO_2$ exhibited a blue shift region whereas EGZnO was in a red shift region, signifying that the photoreaction was suitable to be conducted under UV light and visible light regions, respectively. However, the combination of mixed oxide, $EGZrO_2$–EGZnO, enhanced the optical properties to appear in the visible light region. As revealed by this study, this modification makes the mixed metal oxide most preferable and practical for use in the visible light region. The band gap energies of $EGZrO_2$, EGZnO, $EGZrO_2$–EGZnO, and $EGZrO_2$–EGZnO/HY were determined using the Kubelka–Munk (K–M) spectrum by plotting $f_{K-M} = (hc/\lambda)^2$ as a function of hv (Fig. S4, ESI†), the results of which are tabulated in Table S2 (ESI†). The band gap value of $EGZrO_2$ and EGZnO were similar and agreed with those reported in previous study.[12,13] The advantage of using this electrochemical system can be observed when the system reduces the band gap energy of $EGZrO_2$–EGZnO/HY to 1.82 eV.

The photocatalytic activity of $EGZrO_2$-EGZnO/HY was tested for the ability to decolorize MB and compared with $EGZrO_2$/HY, EGZnO/HY and bare HY (Fig. 2a). A 0.12 g sample of the catalyst was dispersed in 200 mL of 10 mg L^{-1} MB aqueous solution. The adsorption-desorption equilibrium was achieved under dark conditions after 1 h, and the mixture was irradiated at room temperature for 6 h with constant stirring under a fluorescent lamp (Philips TLD 36W/865; 15000 h; 6500 K; 420–520 nm emission). At specific time intervals, 2.5 mL of the sample solution was withdrawn and centrifuged prior to measurements of the residual MB concentration by a UV–vis spectrophotometer at adsorption band 664 nm. The result shows complete decolorization of MB when using the $EGZrO_2$-EGZnO/HY catalyst within 1.5 h of contact time (Fig. 2a), indicating the high photoactivity of hexacoordinated Si with Zr and Zn catalyst under visible light conditions, compared to other catalysts. Fig. 2b shows that the percentage of chemical oxygen demand (COD) increased rapidly during the first 1 h of reaction,

this may be due to the degradation of MB into two different compounds of hydroxylated and amine substituent products, and then gradually increased until the reaction was completed, to form the final products of CO_2 and H_2O.[11,28] Total organic carbon ratio (TOC/TOC_0) shows a significant decrease, which may be attributed to the fact that structured dye molecules were fragmented and converted into small organic molecules, thus, enhancing the mineralization during the irradiation process.[29] Cycling runs for the MB decolorization were also performed to evaluate the $EGZrO_2$-EGZnO/HY photocatalytic activity (Fig. S5, ESI†). A high MB decolorization (>90 %) could be maintained after five cycling runs and there was no obvious catalyst deactivation.
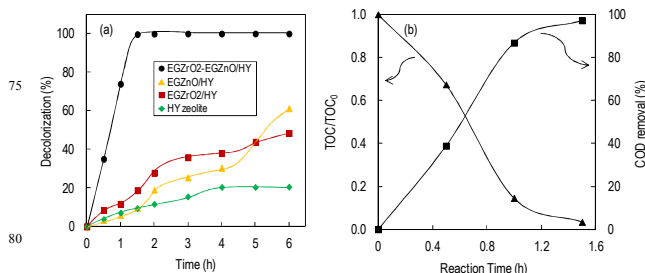

Fig. 2 (a) Photocatalytic decolorization of MB using different type of catalysts; (b) The graph of COD removal and TOC reduction levels after 1.5 h of reaction using $EGZrO_2$-EGZnO/HY [C_{MB} = 10 mg L^{-1}, W = 0.60 g L^{-1}, t = 1.5 h, 303 K].

Conclusions

In conclusion, we have introduced a new synthesis method of high photoactive hexacoordinated Si with Zr and Zn catalyst for efficient degradation of MB. The excellent photoresponse of $EGZrO_2$-EGZnO/HY under visible light conditions was also advantageous. Significantly, the simple operation, short reaction time, high decolorization percentage of MB, and above all, the unique structure of $EGZrO_2$-EGZnO/HY may make this synthesis method an obvious choice for preparation of various catalysts for a variety applications.

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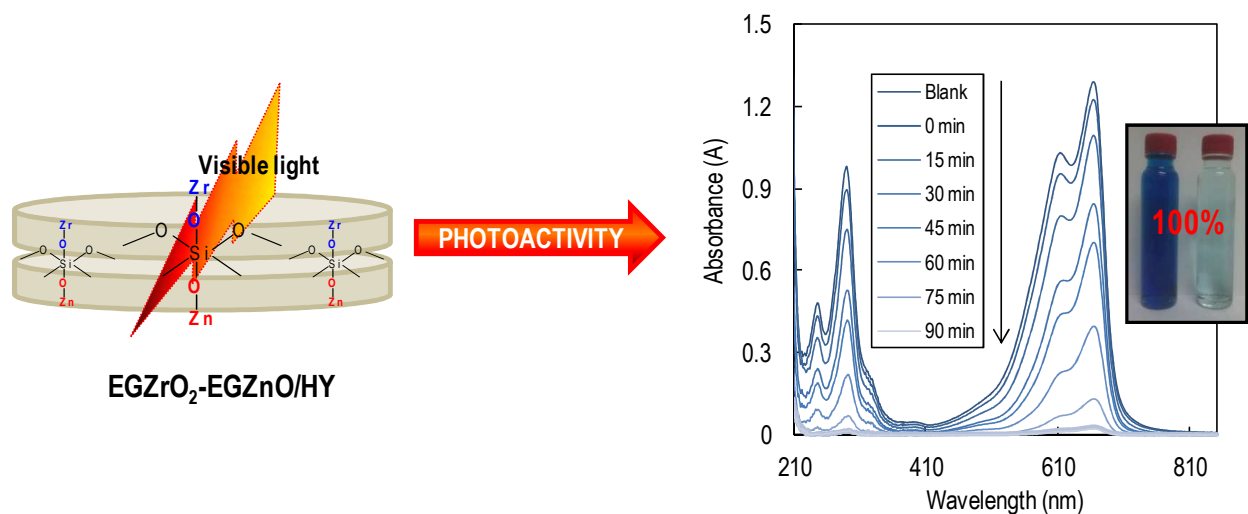
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Facile one-pot electrosynthesis of high photoreactive hexacoordinated Si with Zr and Zn catalyst.

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The one-pot electrochemical synthesis of $EGZrO_2$-EGZnO/HY generates a six-coordination number of Si with Zr and Zn, which enhanced the photodecolorization of methylene blue.