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

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

Water pollution derived from dye contamination is 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 discharge into the receiving water body.^{1,2} Pioneers of advanced oxidation processes (AOPs) used semiconductors such as TiO₂, ZnO, WO₃, Fe₂O₃, CuO, ZrO₂ and CdS as photocatalysts which are important because they can convert a wide range of harmful dyes into non-toxic products, CO₂ and water at ambient temperature.³ In parallel, mixed metal oxides such as TiO₂-ZrO₂, Ag-ZnO, Fe₂O₃-TiO₂, Sn-ZnO and Ag-TiO₂ also exhibit better performance and enhance the photocatalytic activity.⁴⁻⁸ Recently, the use of supported metal oxide catalysts such as TiO₂-HZSM5 (TiO₂-Protonated Zeolite Socony Mobil #5), Co-ZSM5 (Co-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 electrochemical method for preparation of very fine particles of electrogenerated 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, which enhanced the photodecolorization activity of dyes.¹³

Afterwards, a highly photoactive α -Fe₂O₃ 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 the synergistic effect of the metals and support, play important roles in the enhancement of these reactions. Besides, the addition 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 time, a facile and rapid electrosynthesis of EGZrO₂ and EGZnO supported by an HY (EGZrO₂-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% EGZrO₂ : 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.

In this work, a new structure was ascertained during the preparation of EGZrO₂-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 ²⁹Si and ²⁷Al MAS NMR, FTIR, and XPS results. A 10 mL *N,N*-dimethylformamide (DMF) solution containing 0.1 M tetraethylammonium 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 cm²) and a Zr plate anode (2 × 2 cm²), then switched to a Zn plate anode (2 × 2 cm²), 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, (AlO₅)⁺, 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) (EGZrO₂-EGZnO/HY). In parallel, electron transfer from naphthalene radical

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