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Altered properties of TiO_2 for photocatalytic oxidative desulphurisation

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Abstract

Photocatalytic oxidative desulphurisation has become a promising technique as a result of its high capability, mild reaction conditions, economical, and low energy usage. In the present study, copper oxide doped on titanium dioxide (CuO/TiO_2) was prepared by facile electrolysis method. The presence of mesoporous materials with high surface area was confirmed by nitrogen (N_2) adsorption-desorption analysis where the band gap energies were determined by ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS). The photoactivity testing on desulphurisation of 100 mg L^{-1} dibenzothiophene (DBT) revealed the highest extraction (7.5 x 10^{-3} mM min^{-1}) and photooxidation rates (1.8 x 10^{-3} mM min^{-1}), which were acquired by 0.8 g L^{-1} $Cu_{0.1}T_{0.9}$ after 2 h under visible irradiation. This is attributed by the well dispersion of CuO on TiO_2, suitable band gap energy, and better charge carrier separation by the synergistic interaction of both materials.

Keywords: photocatalytic oxidative desulphurisation; copper oxide; titanium dioxide; facile electrolysis; synergistic interaction.

1.0 INTRODUCTION

Environmental pollution is one of the life-threatening issues faced by the modern society nowadays [1]. The emission of exhaust gas and sulphate particulate matter by the burning of sulphur compounds in fuels has led to global warming, air pollution, and acid rain, which seriously impacted the environment and human health [2]. Photocatalytic desulphurisation as an economical and green technology has become a recent focus as one of the most promising ways to solve these problems [3]. Titanium dioxide (TiO_2) is considered as a prevalent candidate for these purposes with the advantage of high photocatalytic ability, chemical stability, non-toxicity, and low cost [4,5]. However, its practical applications have been hindered by the fast photogenerated electron-hole pair recombination and poor utilisation of solar energy [6,7].

In order to solve these deficiencies, various approaches have been developed including the doping of various metals such as silver (Ag), platinum (Pt), palladium (Pd), iron (Fe), and copper (Cu) to enhance charge carrier separation and simultaneously alter band gap energies [8,9]. Copper oxide (CuO) is an idyllic candidate to be coupled with TiO2 due to its suitable band gap, inexpensive, less toxicity, and plenteous source [9].

Plentiful nanometal oxides of nickel oxide (NiO) doped on mesostructured silica nanoparticles (MSN), Fe, Co and Ni supported on Al_2O_4, CuO doped on carbon nanotubes (CNT), and TiO_2 supported on fibrous SiO_2–ZSM-5 have been successfully synthesised by electrolysis [10–14]. These materials show outstanding performances in the photodegradation of organic contaminants and dyes, catalytic CO_2 reforming of CH_4, and adsorption of heavy metals. Electrolysis method is not only capable to reduce the agglomeration of dopants by forming uniform and nano-sized particles, but also capable of providing a stronger dopant-support interaction [10]. Inspired by the above-mentioned factors, the objectives of this study are to synthesise CuO/TiO_2 and examine its performance in photocatalytic oxidative desulphurisation.

2.0 METHODOLOGY

2.1 Materials

All chemicals were used and prepared based on the previous study [15].

2.2 Synthesis of Catalyst

TiO2 was produced via sol-gel method by mixing an appropriate amount of ethanol, distilled water, and TBOT under constant stirring for 30 min, aged for 24 h, and oven-dried for overnight to form TiO_2 powder. Electrolysis was used to prepare CuO/TiO_2 composite using TiO_2 powder as a support according to an earlier study [16] and the ratios of Cu/TiO_2 were varied with 0.1/0.9 and 0.2/0.8, which were designated as $Cu_{0.1}T_{0.9}$ and $Cu_{0.2}T_{0.8}$, respectively.

2.3 Characterisation of Catalyst

N_2 physisorption to study the textural properties of the catalysts was performed by using a Beckman Coulter SA3100 instrument. The observed isotherms were utilised to calculate surface area using Brunauer-Emmett-Teller (BET) method. The ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were acquired by a PIKE Technologies DiffusIR accessory to determine the band gap according to Kubelka-Munk equation.

2.4 Photooxidative Desulphurisation Reaction

The performance of the composites was tested on photooxidative desulphurisation of dibenzothiophene (DBT) as described in the previous report [9,16]. 100 mg L-1 of DBT in iso-octane was mixed with acetonitrile before the addition of catalyst and stirred in the dark for 1 h. Then, the mixed solution was irradiated with visible light and samples were taken every 10 min.

3.0 RESULTS AND DISCUSSION

3.1 Textural Properties

N_2 physisorption isotherms were employed to evaluate the surface area and pore dispersion of the composites. In Figure 1A, a distinctive isotherm type IV with a hysteresis loop H3 was detected for all catalysts, verifying the characteristic adsorption profile for mesoporous materials [17,18]. Besides, a noticeable two-step capillary condensation was perceived at P/Po = 0.3 and 0.9, which was attributed to intra- and interparticle pores, accordingly. The addition of 0.1 Cu onto TiO_2 support reduced the surface area from 402 to 136.4 $m^2\ g^{-1}$, probably due to the partial pore blockage by the existence of a new metal species on the support surface [10]. This is proven by the reduction in the intra- and interparticle pores of TiO_2 support, as can be seen by the decrease of the dotted reference line (Figure 1A) and pore size distribution as shown in Figure 1B. Nevertheless, further loading of Cu onto TiO_2 to the ratio 0.2/0.8 significantly increased the surface area to 152.4 $m^2\ g^{-1}$, which might be caused by the formation of new pores containing agglomerated Cu particles on the TiO_2 surface [11].

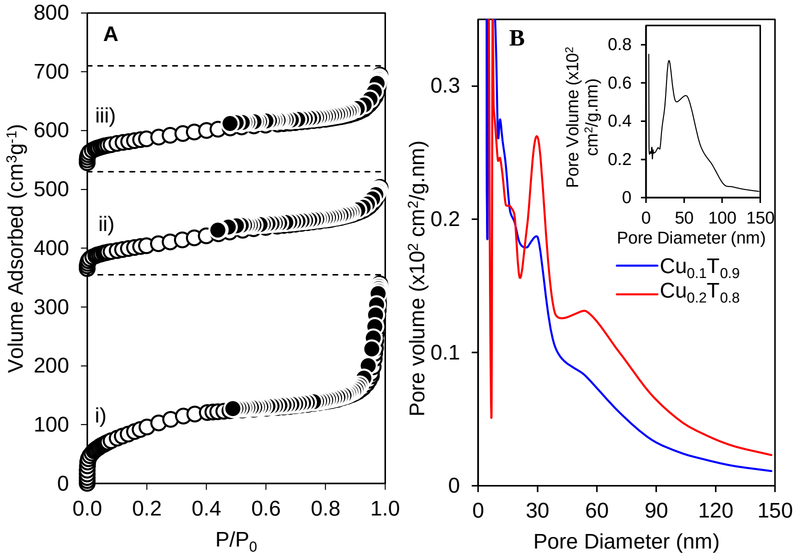

Figure 1. (A) Nitrogen physisorption isotherms of i) TiO_2, ii) $Cu_{0.1}T_{0.9}$, and iii) $Cu_{0.2}T_{0.8}$ and (B) pore distribution of composites and TiO_2 (inset figure).

3.2 Optical Studies

Figures 2A displays the UV-Vis spectra of TiO_2, $Cu_{0.1}T_{0.9}$, and $Cu_{0.2}T_{0.8}$. Pure TiO_2 has a significant absorption edge located at 380 nm, demonstrating that it is simply an ultraviolet-driven catalyst. The absorption edge of the composite is substantially extended with the incorporation of Cu species, indicating a probable interaction between Cu dopant and TiO_2 support [19]. As can be seen from Figure 2B, the TiO_2 possesses the highest band gap (E_g) of 3.50 eV, in which a considerably decreased of E_g was observed after addition of Cu. It should be noted that the improved absorption edge and narrowed E_g of the CuO/TiO_2 composite may lead to a better charge carrier separation and high harvesting rate of solar light, which subsequently resulted in enhanced performance [20].

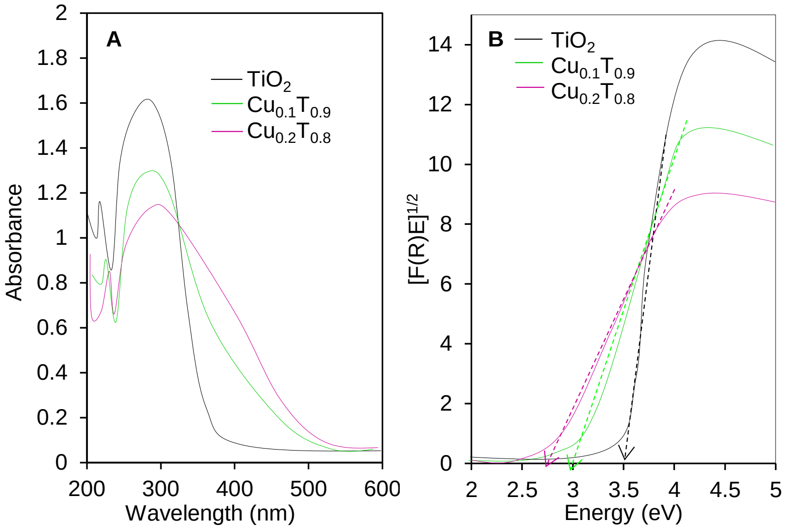

Figure 2 (A) UV-Vis spectra and (B) band gap energy of the composites

3.3 Photocatalytic Oxidative Desulphurisation Performance

Figure 3 shows the desulphurisation rates of the catalysts under visible light irradiation. For comparison, photolysis reaction was also conducted to examine the role of the catalyst. As predicted, the photolysis proceeded at very low extraction and photooxidation rates, verifying the crucial role of the catalyst in the reaction [9]. The extraction and photooxidation rates of CuO/TiO_2 are higher than TiO_2, possibly due to its wider visible light response and reduced charge carrier recombination by the inclusion of Cu [7]. The highest extraction and photooxidation rates were achieved using $Cu_{0.1}T_{0.9}$ catalyst, which then showed a decreasing trend when more Cu was added to TiO_2. Even though the band gap of $Cu_{0.2}T_{0.8}$ is narrower, its lower reaction rate might be attributed by the agglomeration of Cu particles on TiO_2 support as suggested by the N_2 physisorption analysis.

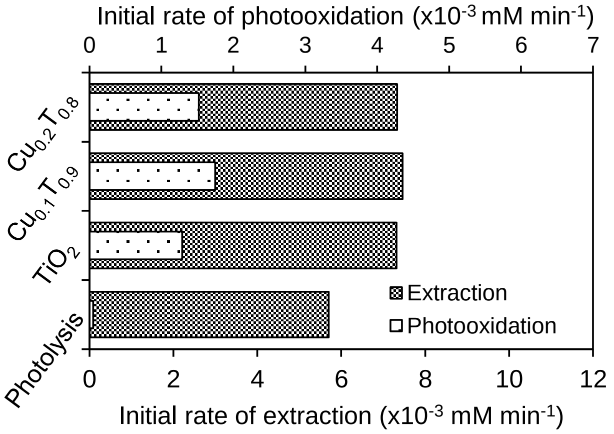

Figure 3 Photocatalytic oxidative desulphurisation performance of the catalysts.

4.0 CONCLUSION

In this study, CuO/TiO_2 was prepared by facile electrolysis method. The catalysts were examined by N_2 physisorption and UV-Vis DRS. The N_2 physisorption analysis shows that all catalysts have an isotherm type IV with a hysteresis loop H3, confirming the presence of mesoporosity. The decrease in intra/interparticle pores of TiO_2 support, as well as the reduced pore volume, indicated successful incorporation of Cu on TiO_2. Based on UV-Vis DRS analysis, the absorption edge of TiO_2 shifted to a higher wavelength by the addition of Cu, suggesting a probable $CuO-TiO_2$ interaction. The photocatalytic oxidative desulphurisation was evaluated on 100 mg L^{-1} of DBT using 0.8 g L^{-1} catalyst. The highest extraction (7.5 x 10^{-3} mM min^{-1}) and photooxidation (1.8 x 10^{-3} mM min^{-1}) rates acquired by $Cu_{0.1}T_{0.9}$ catalyst could be influenced by well dispersion of CuO on TiO_2, suitable band gap energy, and better charge carrier separation.

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