Synthesis and characterisation of copper vanadate quantum dots / nanostructured zinc oxide

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Abstract. 0D/3D heterojunction photocatalyst, specifically copper vanadate (CuVA) quantum dots (0D) / nanostructured zinc oxide (ZnO) (3D), has been prepared using in-situ reaction method. pH of 8 yielded the optimum nanostructure for the hydrothermal synthesis of ZnO nanorods. Characterisation of heterojunction photocatalysts obtained using Fourier transform infrared (FTIR) spectrometer, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis indicates that this method is effective for incorporating quantum dots (QDs) onto ZnO. FTIR at wavenumber 3537, 1360 and 734 cm⁻¹ showed a decreasing transmission peak as the amount of CuVA increases with respect to ZnO. EDX had showed an increasing trend in copper and vanadium elemental percentage in CuVA-ZnO as the targeted CuVA loading increases. 30 wt% CuVA QDs loaded onto ZnO was found to be the optimal mass loading to degrade sulfadiazine (SDZ), at 17.01% with initial concentration of 10 mgL⁻¹. This work is expected to provide a suitable alternative as a photocatalyst to degrade pollutants, with antibiotics being the focus of this work.

1. Introduction
Quantum dots (QDs) have been studied heavily due to their unique properties of small size (<10 nm) which leads to large surface area, higher electron transfer rate and tuneable optical absorptivity [1-3]. Despite these advantages, QDs are very vulnerable to self-aggregation and high recombination rate of electron-hole pairs [4-6]. To overcome these issues, heterojunction may be employed by loading QDs onto another semiconductor-based material such as titanium dioxide (TiO₂) and zinc oxide (ZnO). The interaction between these semiconductor materials can make QDs more dispersive and stable [7], while suppressing the recombination of electron-hole pairs by interfacial charge separation in the composites [8].

In semiconductor photocatalyst, there exists an energy gap that the electron is needed to overcome to escape from the valence band to conduction band, such gap is called band gap. ZnO has a wide band gap of 3.3 eV [9] while copper vanadate (CuVA) has a narrower band gap at 1.83 eV [10]. Individually, ZnO and CuVA separately are not an efficient photocatalyst due to high recombination rate of electron-hole pairs.
The objective of this work is to synthesise and identify the performance of 0D/3D heterojunction photocatalyst through the incorporation of CuVA QDs (0D) onto nanostructured ZnO (3D). By incorporating both semiconductors together, a heterojunction photocatalyst is formed that in theory will improving the photocatalytic performance. Heterojunction photocatalyst is promising as the conduction band of semiconductor A will “catch” the excited electron from semiconductor B, thus decrease the recombination rate [11]. As control, the individual semiconductor will undergo the same photocatalytic degradation procedures. To the best of our knowledge, this work is the first to identify the performance of such photocatalyst towards degrading antibiotics, particularly sulfadiazine.

2. Methodology

2.1. Materials

All chemicals were used as received with no further purification, including zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, ≥ 98.0%, Sigma-Aldrich), hexamethylenetetramine (HMTA, ≥ 99.0%, Sigma-Aldrich), copper (II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, ≥ 99.0%, R&M Chemicals), ammonium metavanadate (NH$_4$VO$_3$, ≥ 99.0%, Sigma-Aldrich), 2-propanol (C$_3$H$_6$O, ≥ 99.5%, Sigma-Aldrich), sodium hydroxide (NaOH, ≥ 98.0%, Sigma-Aldrich), ammonium hydroxide (NH$_2$OH, 28.0 – 30.0%, Sigma-Aldrich) and sulfadiazine (C$_{10}$H$_{10}$N$_2$O$_5$S, 99%, Alfa Aesar).

2.2. Synthesis of zinc oxide

Zinc Oxide (ZnO) precursors were synthesised through hydrothermal method [12]. It involved mixing 1.25 mmol of Zn(CH$_3$COO)$_2$·2H$_2$O and 0.375 mmol of HMTA in 100 mL of distilled water under stirring for 30 min. The mixture was raised to pH 8 using 0.1 M sodium hydroxide solution. The solution was transferred into a Teflon liner stainless-steel autoclave (100 mL) and heated at 110 °C in oven for 15 h. The white precipitate formed were separated by centrifugation at 10000 RCF and washed with distilled water and 2-propanol to remove any residue precursor. The cleaned white precipitates were then dried at 60 °C overnight. After drying, the precipitate was annealed at 400 °C for 2 h, forming nanostructured ZnO.

2.3. Synthesis of copper vanadate / zinc oxide composites

The composites of CuVA QDs and ZnO were synthesised by using in-situ reaction method [13]. The overall yield of pristine CuVA QDs during preliminary studies were found to be 50%. Using this as basis, the ZnO loading is adjusted to the yield on top of 10 wt% dosage calculation. The ZnO was dispersed into 50 mL of 5 mmol/L Cu(NO$_3$)$_2$·3H$_2$O solution and stirred until homogeneous. 50 mL of 5 mmol/L NH$_4$VO$_3$ solution were added dropwise into the mixture. As shown in figure 1, the solution slowly turned yellow indicating formation of CuVA QDs. The pH was maintained at 7 using 0.1 M ammonium hydroxide solution throughout the synthesis. After adding all NH$_4$VO$_3$, the mixture was ultrasonicated for 40 min to allow the vanadate to crystallise. The obtained precipitates were washed similarly to the washing steps involved in ZnO synthesis. The obtained sample were named 10 wt% CuVA-ZnO.

These procedures were repeated for different weight percentage of CuVA, namely 30 wt%, and 50 wt%. The sample were denoted as x wt% CuVA-ZnO with x being the weight percentage of copper vanadate in the sample. As comparison, pristine CuVA QDs was also synthesised with the above method in the absence of ZnO.
Figure 1. Copper (II) nitrate solutions at (a) beginning of adding NH₄VO₃ and (b) end of adding NH₄VO₃.

2.4. Characterisation
Fourier transform infrared (FTIR) spectra were collected on a Nicolet iS10 FTIR Spectrometer to identify the interaction between CuVA and ZnO. Morphology and elemental distribution of samples were performed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. It was carried out on Hitachi S-3400N variable pressure SEM at 15 kV and 20 kV acceleration voltage, respectively.

2.5. Photocatalytic degradation performance
Sulfadiazine (SDZ) was selected to investigate the photocatalytic performance of prepared catalyst in an aqueous solution under visible light irradiation [14]. The visible light source is a 13 W LED bulb (Philips Standard LED Bulb 13 W E27 6500K). The distance between the bulb and top liquid surface of solution was 10 cm. For each test, 100 mg of catalyst was dispersed in 100 mL solution of 10 mgL⁻¹ SDZ. Prior to introducing the catalyst, a first 4 mL aliquot was collected and denoted as time, T = -960 min. To ensure adsorption-desorption equilibrium, the mixture was stirred overnight in the dark prior to the light irradiation for 16 hrs. During light irradiation process, 4 mL of the aqueous solution was collected every 20 min for 2 h and filtered using a 0.22 μm syringe filter to separate the photocatalysts. The concentrations of SDZ, including before and after irradiation were analysed using PG Instrument T60UV-Visible Spectrophotometer at 262 nm within 24 hrs of sample collection. This wavelength was determined to be the maximum wavelength of SDZ through a full-range scanning of 10 mgL⁻¹ SDZ as shown in appendix A (figure A1) at 200 – 800 nm using Agilent Cary 100 UV-Visible Spectrophotometer. The photocatalytic degradation performance was calculated by the following equation:

\[
\text{Degradation} = \frac{C_i}{C_0} \tag{1}
\]

C₀ is the initial concentration of SDZ and Cᵢ the concentration of SDZ at time i.

3. Results and Discussion
The white coloured powder of ZnO shows rod-like structure under SEM as shown in figure 2. Preliminary study was done at various reaction pH at 7, 8 and 11 [15]. At pH of 7, it was found that the ZnO possess hexagonal rod-like structure in clumps at approximately 10 μm. At pH 8, the ZnO possess nanorod-like structure at ~2 μm. At pH 11, the ZnO possess inconsistency in shapes and sizes. The SEM images of pristine ZnO at different pH are shown in figure 2. Based on this preliminary study, pH 8 were chosen to be the synthesise parameter to conduct further steps.
Figure 2. SEM image of pristine ZnO with reaction (a) pH 7 at 5 k magnification, (b) pH 8 at 20 k magnification and (c) pH 11 at 25 k magnification.

Figure 3. Colour of x wt% CuVA-ZnO. (a) ZnO, (b) 10 %, (c) 30 %, (d) 50 %, (e) CuVA.

Successful introduction of CuVA QDs onto ZnO was confirmed through EDX analysis. The details of EDX analysis are included in appendix B. In-situ reaction method had shown to be an effective method in incorporating CuVA onto ZnO. As shown in appendix B, as the targeted weight percentage increased, the composition of copper and vanadium increased linearly while zinc decreased linearly. The powder also progressively became greener as the weight fraction of CuVA increased (figure 3).

Figure 4. FT-IR Spectra of ZnO, 10, 30, 50 wt% CuVA-ZnO and CuVA.
In the FTIR spectra spectrum (figure 4) of 10, 30 and 50 wt% CuVA-ZnO, the broad band corresponding to ZnO from 2800 cm\(^{-1}\) to 3400 cm\(^{-1}\) was decreased consistently compared to that of pure ZnO. At 734 cm\(^{-1}\), the peak shows a downward trend in sharpness consistently. The double peak around 1360 cm\(^{-1}\) that present in ZnO also became less pronounce as the percentage of CuVA increased. Thus, this confirms that the incorporation of CuVA at their respective percentage is successful.

**Figure 5.** Photocatalytic degradation efficiencies of SDZ over different photocatalysts.

The degradation of 10 mgL\(^{-1}\) SDZ under visible light irradiation (figure 5) was monitored over CuVA-ZnO. After irradiation for 120 min, SDZ showed the greatest degradation at 17.01% under the presence of 30 wt% CuVA-ZnO, higher than that of ZnO, CuVA, 10 and 50 wt% CuVA-ZnO by a fair margin. Compared to negligible degradation of 10 wt% CuVA-ZnO over two hours of light time and 50 wt% CuVA-ZnO degrading 9.18%, 30 wt% CuVA were the optimal loading in CuVA-ZnO in terms of degradation of SDZ. Moderate CuVA concentration provides enough photoactive species and at the same time, it does not block the ZnO surface for initiation of oxidation reaction [10]. Apart from CuVA, all the samples showed no observable adsorption of SDZ before light on. This implies that at the absence of light, the catalyst was unable to decrease the concentration of SDZ in any observable manner.

4. **Conclusion**

The synthesis of ZnO through hydrothermal process and synthesis of different weightage of CuVA-ZnO (10, 30 and 50 wt%) through in-situ reaction has been achieved in this work. In-situ reaction method is particularly attractive because (i) it took relatively short amount of time to prepare and (ii) with ZnO acting as the nucleation point, the QDs were able to directly grow on ZnO surface evenly. Further studies are necessary to identify the catalytic mechanisms of the heterojunction composites as well as the optimal parameter to be used to degrade SDZ to improve the performance (sample loading amount, pH of SDZ solution and SDZ concentration).
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Appendix A

![Figure A1](image)

Figure A1. Full-range scan of 10 mgL\(^{-1}\) SDZ using double-beam UV-Vis spectrophotometer.

From Figure A1, the maximum local peak of SDZ is found to be 262 nm. Moreover, SDZ does not appear to absorb any visible light (380 – 800 nm).

Appendix B

| Element | Wt%  | At%  |
|---------|------|------|
| CK      | 30.63| 55.49|
| OK      | 20.85| 28.36|
| ZnK     | 48.52| 16.15|
| Matrix  | Correction | ZAF |

Figure B1. EDX Spectrum and percentage distribution of ZnO.
**Figure B2.** EDX Spectrum and percentage distribution of 10 wt% CuVA-ZnO.

**Figure B3.** EDX Spectrum and percentage distribution of 30 wt% CuVA-ZnO.

**Figure B4.** EDX Spectrum and percentage distribution of 50 wt% CuVA-ZnO.
High carbon content in the analysis were due to the sample being placed above a carbon tape during analysis. From figure B1 – B5, it is observed that as the intended mass loading of CuVA increased, the observed percentage of Cu and V increased in a linear matter while presence of Zn also decreased linearly.

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