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Doctor blade sol-gel deposition of a nano-composite copper-zinc oxide on borosilicate glass for advanced oxidative degradation of textille dye in water environment

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Abstract

Nano-composite copper-zinc oxide (NCCZO) was deposited on borosilicate glass using a novel sol-gel/doctor-blade technique. The photocatalyst was prepared from copper acetylacetonate, zinc acetylacetonate, monoethanolamine (MEA) and citric acid monohydrate at 75 ^{o}C, aged for 1 d and annealed at 650 ^{o}C. The properties of the NCCZO nano-composite were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Results showed that the NCCZO was dominated by zincate phase (83.9%) and tenorite phase (16.1%) after sintered at 650 ^{o}C. FESEM shows that NCCZO is nonocrystallines with an average size of 55 nm. Photocatalytic activities of NCCZO deposited on borosilicate glass were investigated in for degradation of an azo dye M5B contaminant in water. The NCCZO exhibit an excellent photocatalytic activity due to reducing the electron-hole pair recombination. Kinetic parameters have been investigated in terms of a first order rate equation. The rate constant is evaluated as a function of the initial concentration of dye.

Key words: Doctor blade, Sol-gel, Oxidative, Degradation, Nano-composite

Highlights

- Copper-zinc oxide nano-composite was deposited on borosilicate glass.
- Doctor blade-sol gel deposition was used for immobilization.
- Advanced oxidative degradation of textile dye in water environment was investigated.

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Introduction

The photocatalytic oxidation of organic pollutants in water has attracted many attentions because it works at ambient temperature and pressure (1-7). Different semiconductor photocatalysts has been used for photodegradation of organic contaminants by the photo-oxidation method (8-10). The semiconductor irradiated with light will produce electron/hole pairs with the ability of oxidizing the organic pollutants (11). Titania and zinc oxide are the most commonly used semiconductor for the degradation of organic pollutants with band gap energies of 3.3 eV (12) and 3.2 eV (13) respectively. The fine particles of the Titania and zinc oxide have been applied in a slurry form with an advantage of higher photoactivity due to more surface active sites (14). Immobilization of fine particle catalysts into an inert substrate reduces the amount of active sites and lower efficiency (15). This problem can be solved by coating of nano particles with high surface-to-volume ratio. Borosilicate glass is a good candidate for photocatalyst fixation because of its transparency which allows activation of nearly all photocatalyst particles (16). Electrophoretic coating on a glass substrate is expensive devices and there are needs for a simple coating method. Doctor blade is a versatile and simple technique used to produce coating for solar cells. It is reported that different nano materials fibers can be fabricated based on this doctor blade technique (17 and 18). Compared with other methods, this technique possesses many advantages such as ease of implementation, cost effectiveness, rapidity, and large film surface area preparation. To the best of our knowledge, the doctor blade-sol gel deposition of a nano-composite copper-zinc oxide on borosilicate glass for oxidative degradation of an azo dye in aqueous environment has not been studied.

In continuation of our research in semiconductor metal oxide thin film (19-21), here we report a new technique for coating nano-composite copper-zinc oxide on borosilicate glass by doctor blade-sol gel techniques. Nano-composite copper-zinc oxide was prepared by sol-gel method using zinc and copper acetylacetonates. The coating was characterized in detail by means of XRD and FESEM and the photodegradation of an azo dye was studied to evaluate the photocatalytic efficiency.

Materials and methods

All chemicals were analytic grade and used as received (Merck). The borosilicate glass slides were used as solid substrates. 1.9 mmol of copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and 3.8 mmol of zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ were dissolved in 20 mL ethanol. To the above solution, 2.5 mL monoethanolamine (MEA) and 5 mL citric acid monohydrate, $C_6H_8O_7$. H_2O and 0.5 M were added under magnetic stirring at 75 ^oC for 2 h with formation of a homogeneous sol solution which was aged for 1 d. The stable sol was slowly heated under magnetic stirring at 75 ^oC with formation of a hard homogeneous gel. The pyrolysis of the gel was performed at 650 ^oC for 2 h.

Characterization

Nano-composite copper-zinc oxide (NCCZO) deposited on borosilicate glass was characterized by XRD analysis using X-ray diffractometer (D8 Advance, BRUKER) in the diffraction angle range 2θ=20-60°, using Cu Kα radiation. Dye concentration was determined by its absorbance using a Cary 500 UV-vis spectrophotometer. Field emission scanning electron microscopy (FE-SEM, Hitachi, model S-4160 was used to observe the surface morphology of the zinc oxide nano-particles.

Photocatalytic Degradation of Textile Dye in Water Environment

Photocatalytic degradation of azo dye M5B was performed on a homemade photochemical reactor. The light source was a 250 W high-pressure mercury lamp. All photochemical experiments were performed in air at room temperature. In a typical experiment, NCCZO coated on borosilicate glass were placed in 25 mL freshly aqueous solution of MO. The initial M5B concentration for all experiments was fixed at 6.1 mg/L. The decolorization of M5B was evaluated by monitoring the absorbance change at 620 nm. Residual M5B concentration was then calculated according to the calibration curve of dye concentration versus absorbance (Fig. 1).

Results

Synthesis and Characterization of Photocatalyst

Fig. 2 shows XRD patterns of nano-composite copper-zinc oxide (NCCZO) coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC. It is obvious that five main diffraction peaks of the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) reflections are indexed to zincite ZnO (PDF No. 36-1451) and (1 1 1), (2 0 0) and (2 2 0) reflections are indexed to tenorite CuO (PDF No. 05-0661). The fact that no peak characteristic of any other phase or impurity is observed in the XRD pattern implies high purity of $ZnCuO_2$ crystalline phase synthesized in this work. The morphology of NCCZO samples coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC was investigated by FESEM in Fig. 3. This Fig. show that the samples are nearly in spherical shape with diameters of 55 nm.

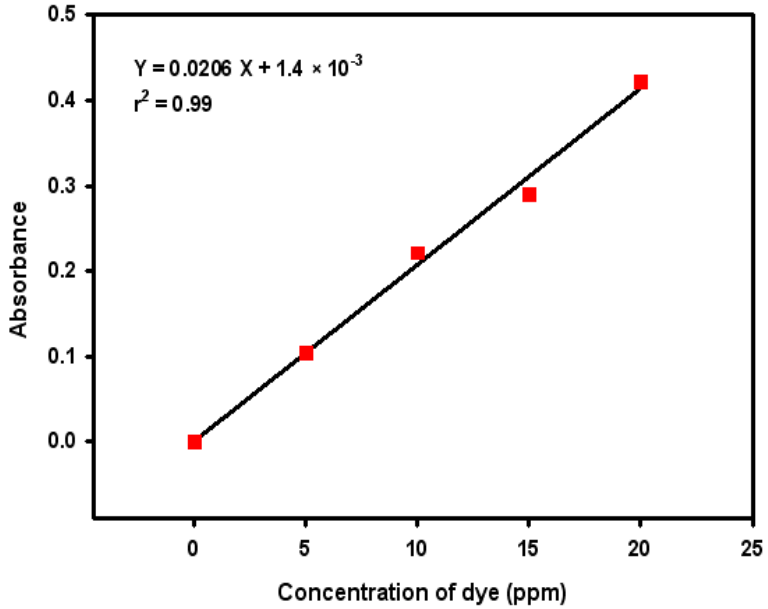

Fig. 1- Calibration curve of M5B dye concentration versus absorbance

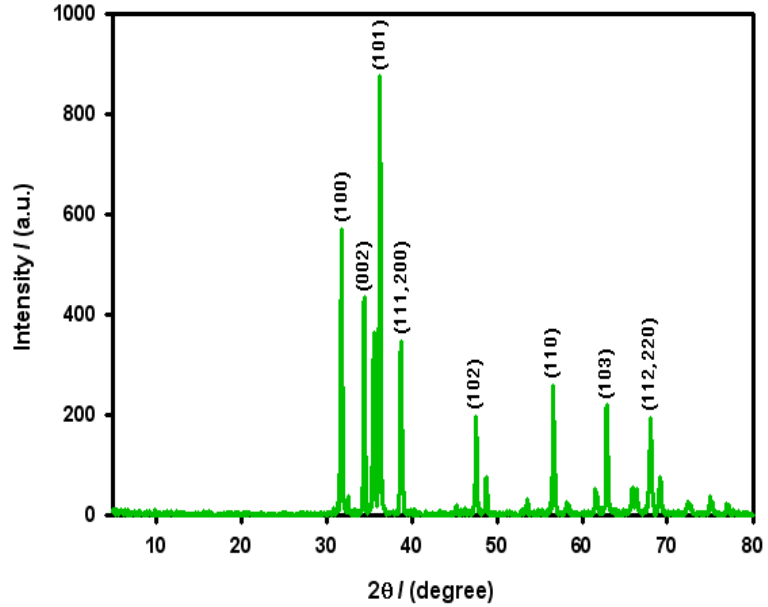

Fig. 2- XRD pattern of nano-composite copper-zinc oxide (NCCZO) coating fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC

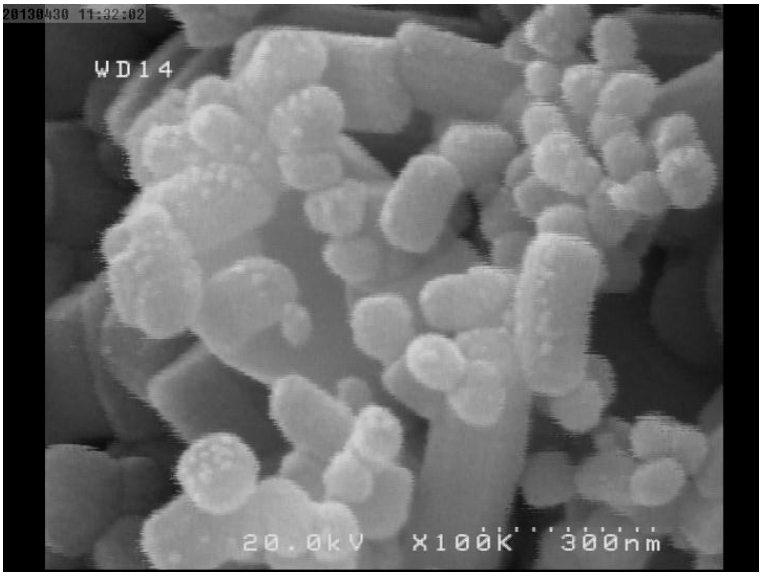

Fig. 3- FESEM image of nano-composite copper-zinc oxide (NCCZO) coating fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC

Application in Photocatalytic Degradation of Textile Dye in Water Environment

Fig. 4 displays the time-dependent absorption spectra of the M5B solution with initial concentration of 6.1 mg/L under UV-vis irradiation and using nano-composite copper-zinc oxide (NCCZO) coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC. For comparison, under dark conditions without light irradiation, the concentration of M5B almost does not change for every measurement in the presence of NCCZO sample. Light irradiation in the absence of any samples almost does not result in the photocatalytic decolorization of M5B, indicating that the photolysis of M5B can be ignored. Therefore, the presence of both light irradiation and NCCZO photocatalysts are necessary for the efficient degradation. Fig. 5 shows $Ln(C_0/C_t)$ vs. time (min) for the photocatalytic degradation of the M5B dye solution under UV-vis irradiation using nano-composite copper-zinc oxide (NCCZO) coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC. The degradation kinetics data were examined using first-order reaction kinetics. As shown, the effect of light on increasing decolorization rate of M5B is about 92%. When ZnO and CuO are coupled together, photons may be absorbed in both ZnO and CuO and form the e^- and h^+ pairs. The electrons at the CB bottom of CuO would migrate to that of the ZnO; whereas holes at the VB top of CuO would remain there. On the other hand, the holes at the VB top of the ZnO would migrate to that of CuO, with electrons at the CB bottom of ZnO remaining there. Such process is energetically favorable and the photogenerated e^- and h^+ pairs can be efficiently separated, which is regarded as the key factor for the enhancement of photocatalytic activities of the nano-composite copper-zinc oxide (NCCZO)

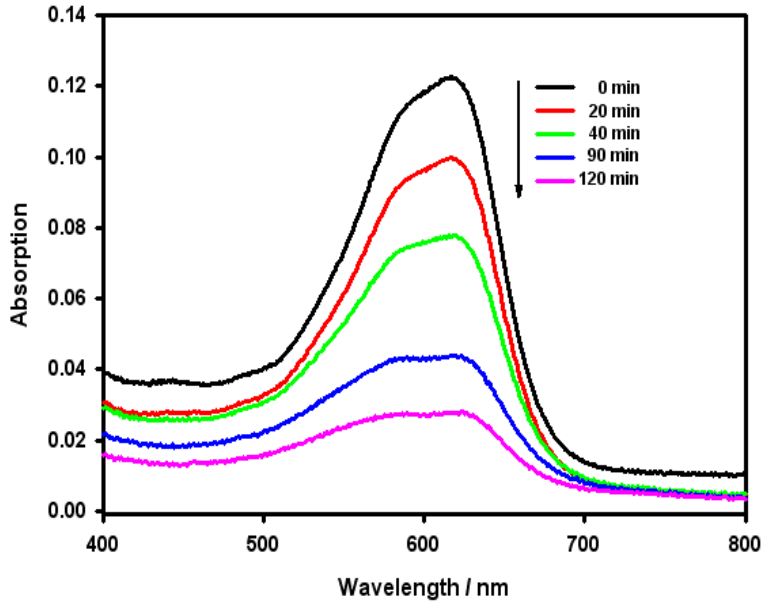

Fig. 4- Time-dependent absorption spectra of the M5B solution with initial concentration of 6.1 mg/L under UV-vis irradiation and using nano-composite copper-zinc oxide (NCCZO) coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC

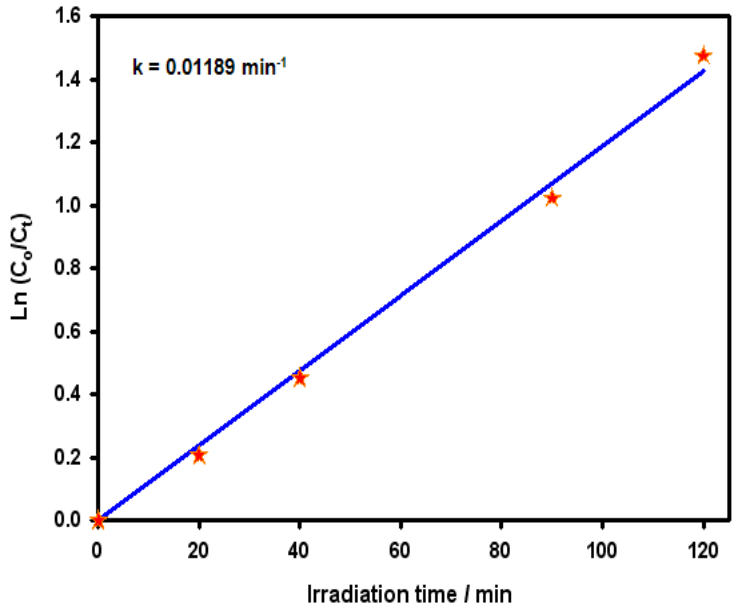

Fig. 5- $Ln(C_0/C_t)$ vs. Time (min) for the photocatalytic degradation of the M5B dye solution under UV-vis irradiation using nano-composite copper-zinc oxide (NCCZO) coated on glass fabricated via sol-gel and doctor blade route using copper acetylacetonate, $Cu(CH_3COCHCOCH_3)_2$ and zinc acetylacetonate, $Zn(CH_3COCHCOCH_3)_2$ as precursors with mol ratio 1:2 annealed at 650 ^oC

Discussion and conclusion

Nano-composite copper-zinc oxide (NCCZO) was deposited on borosilicate glass using a novel sol-gel/doctor-blade technique. Results of XRD showed that the NCCZO was dominated by zincate phase (83.9%) and tenorite phase (16.1%) after sintered at 650 ^{o}C. FESEM shows that NCCZO is nonocrystallines with an average size of 55 nm. Photocatalytic activities of NCCZO deposited on borosilicate glass were investigated in for degradation of an azo dye M5B contaminant in water. The NCCZO exhibit an excellent photocatalytic activity due to reducing the electron-hole pair recombination. The degradation kinetics data were examined using first-order reaction kinetics. As shown, the effect of light on increasing decolorization rate of M5B is about 92%. When ZnO and CuO are coupled together, photons may be absorbed in both ZnO and CuO and form the e^{-} and h^{+} pairs.

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پوشش شیشه با نانو کامپوزیت مس- روی اکسید با روش سل- ژل دکتر بلید برای تخریب اکسایشی پیشرفته پساب رنگ‌های نساجی

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چکیده

نانو کامپوزیت مس- روی اکسید بر روی شیشه با روش سل- ژل دکتر بلید پوشش دهی شد. این نانوفوتوکاتالیست از مس استیل استوناتو، روی استیل استوناتو، مونو اتانل امین و سیتریک اسید مونو هیدرات در دمای ۷۵ درجه سانتی‌گراد تهیه و در دمای ۶۵۰ درجه سانتی‌گراد کلسینه شد. خواص نانو کامپوزیت مس- روی اکسید با XRD و FESEM بررسی و نتایج نشان داد که ۸۳/۹ درصد فاز زینکت و ۱۶/۱ درصد فاز تنوریت در دمای ۶۵۰ درجه سانتی‌گراد تشکیل شده است. نتایج تصاویر میکروسکوپ الکترونی اندازه ذرات ۵۵ نانومتر را نشان داد. نتایج فعالیت فوتوکاتالیتیکی نشان داد که نانو کامپوزیت قابلیت تخریب اکسایشی پیشرفته پساب رنگ‌های نساجی را دارد.

واژه‌های کلیدی: تخریب اکسایشی پیشرفته، پساب رنگ‌های نساجی، نانو کامپوزیت، روش سل- ژل

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