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Microwave-assisted photocatalysis of neurotoxin compounds using metal oxides quantum dots/nanosheets composites: Photocorrosion inhibition, reusability and antibacterial activity studies

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ABSTRACT

Water pollution caused by different pollutants is one of the challenging tasks for the scientific community. We have prepared and characterized a material for removal of pollutant compounds. ZnO quantum dots decorated CuO nanosheets and TiO_2 quantum dots decorated WO_3 nanosheets composites have been prepared using a hydrothermal method. The as synthesized catalysts were characterized by various techniques. The crystallite sizes of CuO NSs and WO_3 NSs were to be obtained 12.5 and 13.25 nm and when dopped with ZnO and TiO_2 size reduces to 3.2 and 3.9 nm, respectively. The energy band gap of the CuO NSs, WO_3 NSs, ZnO QDs/CuO NSs and TiO_2 QDs/WO_3 NSs composite are calculated to be 2.01, 2.61, 1.86 and 2.32 eV, respectively. The prepared catalysts are efficiently utilized for the photocatalytic degradation of two neurotoxin compounds under UV and UV coupled with microwave irradiation. The prepared catalyst composites reveal excellent photocatalytic degradation of neurotoxin compound by degrading it up to 75% under UV and UV/microwave irradiation. The photocalysis efficiency in UV/microwave system is higher than UV system. The result shows that the ZnO QDs/CuO NSs and TiO_2 QDs/WO_3 NSs composites have excellent photocorrosion inhibition and reusability properties. Thus, prepared samples with positive surface potential upon interaction with negative surface potential of *Enterococcus faecalis* and *Micrococcus luteus*.

1. Introduction

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and groundwater). This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds [1,2]. MPTP (1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine) is a prodrug to the neurotoxin MPP +, which causes rapid onset of Parkinsonism. MPTP as a lipophilic compound can cross the blood–brain barrier. Once inside the brain, MPTP is metabolized into the toxic cation 1-methyl-4-phenylpyridinium (MPP +) by enzymes. Tetanus toxin is an extremely potent neurotoxin and it's also called spasmogenic toxin, or TeNT. This toxin making it second only to Botulinum toxin (LD_{50} 2 ng/kg) as the deadliest toxin in the world [3,4].

Photocatalysis is a science of employing catalyst that is utilized for speeding up chemical reactions that requires or engages light. A photocatalyst is defined as a material that is capable of absorbing light, producing electron–hole pairs that enable chemical oxidation and reduction for transformations of the reaction participants and regenerate its chemical composition after each cycle of such interactions [5,6].

Tungsten oxide (WO_3) and copper oxide (CuO) is an n-type and p-type semiconductor which has low cost synthesis, non-toxicity, good thermal stability, photosensitivity, good electron transport properties [7,8].

Quantum dots (QDs) with narrow size distribution and high luminescent efficiency have attracted attention of researchers due to several properties. Recently, Titanium dioxide (TiO_2) and zinc oxide (ZnO) QDs are considered to be significant materials in the area of pollutant degradation due to their high photo catalytic efficiency. These materials are predominant semiconductor photocatalyst because of its stability, non-toxicity, low cost production and binding energy and band gap properties [9–18].

The main focus of the present investigation is to determine the photocatalytic performance of the synthesized products in degrading

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TeNT and MPTP in UV and microwave irradiation and the antimicrobial activity for different microbes can be investigated.

2. Materials and Methods

2.1. Materials

All the chemicals were obtained from Sigma-Aldrich Ltd., USA.

2.2. Preparation of CuO Nanosheets and ZnO Quantum Dots Decorated CuO Nanosheets

In a typical synthesis process, 0.01 M aqueous solution (50 mL) of copper nitrate was mixed with 0.01 M aqueous solution of hexamethylenetetramine (50 mL) under vigorous stirring. In order to maintain a pH = 12 of the solution, KOH was added drop by drop with continuous stirring. After stirring, the suspension was transferred to Teflon-lines stainless steel autoclave and heated to 180 °C for 8 h. The product formed was filtered, washed with ethanol-water mixture solution and finally dried at 70 °C for 4 h in oven.

200 mg Zinc acetate and 500 mg of the as-prepared CuO nanosheets was added into 50 mL distilled water. The reaction was carried out by dropwise addition of KOH solution to zinc acetate solution with constant stirring. The final pH of the solution was maintained at 10. The obtained suspension was transferred into a 100-mL Teflon-lined stainless-steel autoclave, and then was heated to 180 °C for 10 h. After natural cooling to room temperature, the product was collected and washed with ethanol-water mixture solution.

2.3. Preparation of WO_3 Nanosheets and TiO_2 Quantum Dots Decorated WO_3 Nanosheets

10 mL of 65% nitric acid was dissolved in distilled water (40 mL) and stirred for 10 min. 1 g $Na_2WO_4{\cdot}2H_2O$ were dissolved homogeneously in 20 mL distilled water and were slowly added under continuous magnetic stirring. After stirring for another 30 min, the suspension was putted into a 100 mL Teflon-lined stainless-steel autoclave, sealed and heated to 180 °C for 3 h. Then, the product was centrifuged and washed with distilled water and ethanol several times. The sample was dried in vacuum at 60 °C for 12 h.

Initially 5.0 mL of TTIP and 500 mg WO_3 nanosheets was added into in 150 mL of isopropanol in a 500 mL beaker. Then, the mixed solution was stirred for more than 1 h. 0.01 mol of aqueous CTAB was added drop-wise into the mixed solution. The obtained suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave, and then was heated to 180 °C for 10 h. The finely ground sample was calcinated at 350 °C for 30 min.

2.4. Characterization Instruments

A Transmission Electron Microscope (TEM) (Zeiss EM-900) was used to examine the particle size and morphology of prepared samples and X-ray diffractometer (XRD) Philips X'Pert was measured for evaluation of crystalline information. X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD) and UV–vis spectroscopy studies (TEC Avaspec 2048) were performed for evaluation of optical information. Infrared spectrum was recorded by Bruker Hyperion 3000 FTIR spectrometer. Absorption spectra were recorded on Cary 100 BIO UV–visible spectrophotometer. Zeta potential measurements of the dilute dispersions (0.1 mg mL^{-1}) of the various samples were performed with a Brookhaven NanoBrook Omni Instrument at 25 °C.

2.5. Photocatalytic Activity

In order to evaluate the photocatalytic efficiency of the prepared samples, photocatalytic measurements were done by dispersion was put in the side-arm glass cell with an optical length of 1 cm. After the glass cell was purged with Ar, it was placed into the ellipsoidal microwave applicator for irradiating the solution in the cell by microwaves. The temperature of the solution was kept by irradiating microwaves of 1.5 W. A spectroscopic cryostat was used to maintain the solution temperature. The sample was irradiated with a 300 W Xe lamp equipped with a UV mirror module ($\lambda < 400$ nm). For the measurement, a suspension of 10 mg of the as prepared photocatalyst powder and 100 mL of an aqueous solution of the TeNT and MPTP having a concentration of 1 mg/L were mixed and stirred in a dark place for about 30 min to reach the adsorption desorption equilibrium condition between the photocatalyst with TeNT and MPTP molecules. The TeNT and MPTP concentration was distinguished with the aid of a two dimensional Gas Chromatography (GC∗GC) (Kimia Shangarf Pars Research CO., Iran). The column set used a first column 30 m × 0.25 mm i:d: × 0.25 μm film thickness 5% phenyl-methyl siloxane phase serially coupled to a second column 1 m × 0.1 mm i:d: × 0.1 μm film thickness 50% phenyl equivalent phase. Both columns which were temperature programmed from 70 to 320 °C. The injector temperature was 250 °C (injection volume of 1 mL) was employed in the split less mode. Helium was used as the carrier gas (2 mL/min).

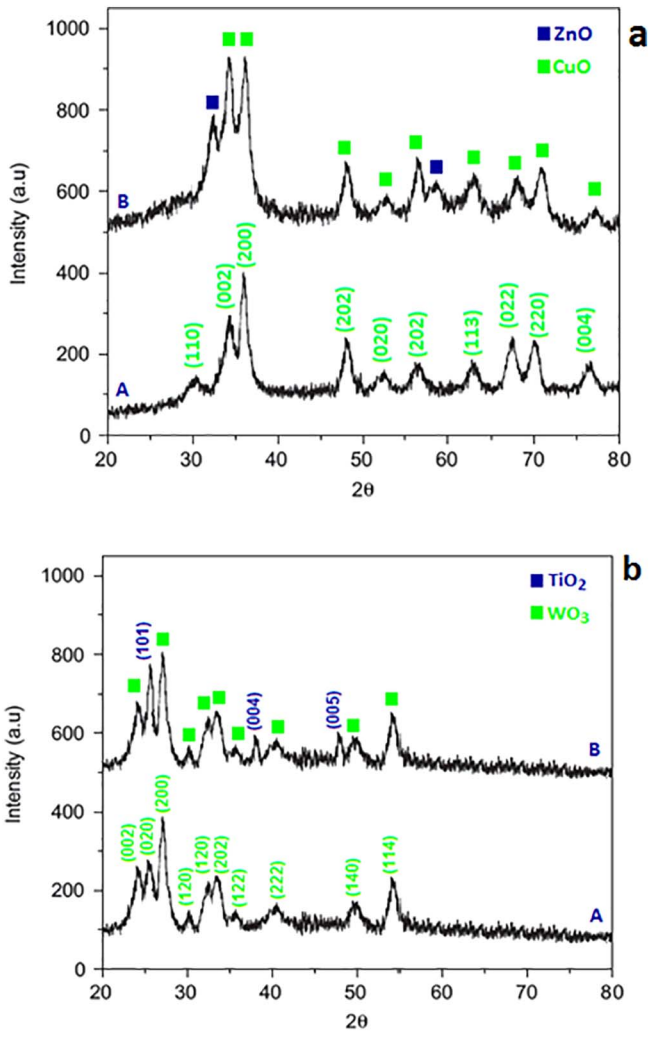

Fig. 1. XRD patterns of the prepared (a) CuO NSs (A) and ZnO QDs/CuO NSs (B), (b) WO_3 NSs (A) and TiO_2 QDs/WO_3 NSs (B).

2.6. Antibacterial Activity

The antibacterial activity was investigated by two bacterial strains, namely *Enterococcus faecalis* (gram positive) and *Micrococcus luteus*