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Instantaneous Sonophotocatalytic Degradation of Tetracycline over NU-1000@ZnIn₂S₄ Core-Shell Nanorods as a Robust and Ecofriendly Catalyst

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comprise a p-n heterojunction of 3D Zr(IV) metal-organic framework nanorods (NU-1000) and photoactive ZnIn₂S₄ (ZIS) nanostars. Among the obtained materials with varying content of ZIS (5, 10, 20, and 30%) on the surface of NU-1000, the NU@ ZIS20 nanocomposite revealed an ultrahigh catalytic performance



and recyclability in a quick visible-light-induced degradation of the tetracycline antibiotic in water under sonophotocatalytic conditions. Moreover, increased activity of NU@ZIS20 can be ascribed to the formation of a p-n heterojunction between NU-1000 and ZIS, and a synergistic effect of these components, leading to a high level of radical production, facilitating a Z-scheme charge carrier transfer and reducing the recombination of charge carriers. The radical trapping tests revealed that ${}^{\bullet}OH$, ${}^{\bullet}O_{2}^{-}$, and h⁺ are the major active species in the sonophotocatalytic degradation of tetracycline. Possible mechanism and mineralization pathways were introduced. Cytotoxicity of NU@ZIS20 and aquatic toxicity of water samples after tetracycline degradation were also assessed, showing good biocompatibility of the catalyst and efficacy of sonophotocatalytic protocols to produce water that does not affect the growth of bacteria. Finally, the obtained nanocomposites and developed photocatalytic processes can represent an interesting approach toward diverse environmental applications in water remediation and the elimination of other types of organic pollutants.

1. INTRODUCTION

The environmental pollution of different water bodies with organic contaminants currently represents a very serious environmental problem that justifies the development of novel water treatment protocols that consume less time and energy.^{1–3} Another source of aqueous contamination includes the pathogenic microorganisms that annually endanger public health with more than 2 million deaths worldwide.⁴ Thus, different drugs and pharma products are viewed as the increasing organic contaminants in water bodies that threaten people's health and environmental biodiversity.^{5,6} In particular, up to 2 \times 10⁵ tons of antibiotics are annually utilized worldwide to treat bacterial infections in humans and animals.^{7,8} Tetracycline (TC) is a widespread antibiotic that is used for treating infections in aquatic and terrestrial animals and humans.^{9,10} Excellent resistance to degradation explains a wide presence of TC in the environmental systems that requires appropriate remediation.^{11–14} However, majority of antibiotics do not respond to traditional biological wastewater treatment procedures. 15,16

In this regard, photocatalytic degradation of organic contaminants including antibiotics in wastewater and effluents represents an attractive and green method that can feature high performance, low cost, and sustainability.¹⁷⁻¹⁹ However, the removal of organic pollutants by photocatalytic processes alone might not be sufficient in some cases. Hence, many complementary methods such as sonochemical treatment were combined with photocatalytic processes to enhance overall process efficiency.^{1,20-22} One of the notable advantages of ultrasound includes the creation of high-pressure bubbles and elevated temperature zones that can lead to water sonolysis and the generation of 'OH and H' radicals capable of degrading organic contaminants.^{23–25}

Received: March 27, 2021 Published: June 23, 2021



Article



Scheme 1. Synthetic Scheme for H₄TBAPy



An additional and important challenge in photocatalytic pollutant degradation concerns the prevention of secondary pollution. Ideally, a complete transformation of pollutants into CO_2 and H_2O is most attractive.^{26,27} To develop such type of processes, there is a need for the design of high-performance photocatalysts.²⁸ Diverse semiconductor substances such as metal oxides, oxynitrides, sulfides, and metal-free semiconductors were tested for the photocatalytic degradation of antibiotics.^{29,30} However, metal sulfides with robust adsorption in the visible light zone are viewed as acceptable alternative photocatalysts for the degradation of antibiotics.³¹ In particular, a ternary chalcogenide, ZnIn₂S₄ (ZIS), features a reasonable band gap (2.30 to 2.46 eV) that matches the visible light adsorption,³² along with exhibiting polymorphs, light absorption up to 600 nm, and adjustable optical and electronic properties.³³ Prior research demonstrated a potential of ZIS polymorphs in photocatalysis with remarkable chemical stability.³⁴ Besides, a highly negative potential (-0.76 eV) of the conduction band (CB) of ZIS causes an effective reduction of O_2 to superoxide anion radicals ($^{\bullet}O_2$ -). However, a low positive potential (1.48 eV) of valence bond (VB) is not sufficient for oxidizing H_2O to [•]OH radicals (+4.4 eV vs NHE).^{35–37} Hence, photocatalysis with ZIS shows a moderate efficacy due to poor separation and lower migration ability of the photoinduced charge carriers.³⁸ However, the photocatalytic function of ZIS might be improved by combining it with another nanomaterial.³⁹⁻

MOFs (metal-organic frameworks) and PCPs (porous coordination polymers) belong to a very important family of crystalline compounds with significance in the design of advanced functional materials.42-45 Some MOFs reveal an encouraging semiconducting function and may be utilized in photocatalysis,⁴⁶⁻⁵⁰ including the degradation of organic contaminants. In comparison to conventional semiconductor photocatalysts, MOF-based photocatalytic systems represent some important characteristics, namely high porosity, surface area, structural versatility, and facile postsynthetic modification, along with appealing reagent/product diffusion properties.⁵¹⁻⁵³ Various procedures such as the noble metal deposition⁵⁴ and metal or ligand substitution^{55,56} were reported for improving the photocatalytic function of MOFs. In addition, one of the possible routes for separating the photogenerated charge carriers and enhancing the photocatalytic activity relies on the formation of heterostructures by coupling MOFs with the light-harvesting semiconductor substances. Put differently, the formation of a MOF-based composite decorated with a photoactive material can be very effective for reinforcing the features of distinct components in a hybrid photocatalyst.⁵

Based on the above discussion, it would be interesting to explore a porous and highly stable MOF material such as NU-1000 for designing a hybrid nanocomposite wherein the NU-1000 surface is decorated with a photoactive component such as $ZnIn_2S_4$ (ZIS). In our prior work, we dealt with the synthesis of $ZnIn_2S_4$ @MIL heterostructures that revealed notable synergistic effects in their functional properties.⁵⁸ However, there are still no reports on the preparation of the hybrid NU-1000@ZnIn_2S_4 (NU@ZIS) photocatalysts and their application in the degradation of antibiotics. Furthermore, suitable band positions of ZIS and NU-1000 can generate an appropriate p—n heterojunction, thus expanding the light adsorption ranges and promoting charge separation.

Hence, the present work reports the preparation, full characterization, and detailed catalytic exploration of a series of new hybrid NU@ZIS photocatalysts, constructed by decorating NU-1000 with varying amounts of ZIS (5-30%). NU-1000 was chosen as a model MOF because of its nontoxicity, high water- and photostability, along with excellent capability to absorb TC. The as-prepared NU@ZIS nanocomposites exhibit a very appealing sonophotocatalytic function for degrading TC in water under irradiation by visible light (λ > 430 nm). An excellent photocatalytic function of NU@ZIS results from an enhanced separation and transfer effectiveness of the photogenerated charge carriers. A shorttime and concise synthesis, as well as high sonophotocatalytic activity and reusability of NU@ZIS p-n heterojunction, disclose a high potential of this hybrid nanocomposite in the photocatalytic degradation of other organic molecules. Moreover, cytotoxicity of NU@ZIS p-n heterojunction and aquatic toxicity against E.coli of water samples after TC degradation were also evaluated, revealing good biocompatibility of the catalyst and sonophotocatalytic protocols with a potential significance in decontaminating different water resources.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All reagents and solvents (analytical grade) were used as received from commercial sources: 4-(methoxycarbonyl)-phenyl)boronic acid (Merck, 98%), 1,3,6,8-tetrabromopyrene (Aldrich, 97%), tetrakis(triphenylphosphine)palladium(0) (Merck, 97%), ZrCl₄ (Merck, 98.5%), indium(III) nitrate hydrate (In(NO₃)₃·XH₂O, Merck), zinc chloride (ZnCl₂, Merck), thioacetamide (TAA, Merck), K₃PO₄ (Aldrich), benzoic acid (Aldrich, 99.5%), ethanol (EtOH), methanol (MeOH), glycerol (GL), hydrochloric acid (HCl, Aldrich, 37%), and *N*,*N*-dimethylformamide (DMF, Merck).

2.2. Preparation of H₄TBAPy (1,3,6,8-tetrakis(p-benzoic acid)pyrene). A mixture of (4-(methoxycarbonyl)phenyl)boronic acid (5.80 mmol, 1.040 g), 1,3,6,8-tetrabromopyrene (0.97 mmol, 0.500 g), tetrakis (triphenylphosphine) palladium(0) (0.026 mmol, 0.030 g), and K_3PO_4 (5.30 mmol, 1.100 g) in 25 mL of dry dioxane was prepared in a 25 mL vial in a glovebox. The obtained mixture was

stirred under N_2 gas in an oil bath at 130 °C for 72 h. Then, the solvent was evaporated from the reaction mixture under vacuum, and the obtained solid residue was washed with water to remove an inorganic salt. The solid was treated with chloroform (50 mL, three

times) to extract a crude product, followed by drying the extract with magnesium sulfate. Then, the solvent was evaporated under vacuum. Finally, the obtained residue was boiled in tetrahydrofuran for 2 h and filtered off to separate the filtrate containing impurities. The obtained solid was isolated and dried to provide 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene (0.61 g, 84% yield).

In the next stage, a solution of NaOH (37.5 mmol, 1.5 g) in 75 mL of H_2O/THF (1:1) was introduced into a 200 mL round bottom flask containing 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene (0.78 mmol, 0.58 g), and the resultant suspension was stirred overnight under reflux. Then, solvents were evaporated under vacuum, and water was added to the residue, resulting in a transparent yellow solution. This was stirred at 25 °C for 3 h, and its pH value was set to 1.0 using concentrated HCl. Filtration was used to collect the resulting yellow solid that was abundantly washed with water several times. The crude product was recrystallized from DMF and filtered off. Furthermore, the product was washed with chloroform and dried under vacuum, resulting in H₄TBAPy (0.51 g, 92%) (Scheme 1).

2.3. Preparation of $[Zr_6(\mu_3-OH)_4(\mu_3-O)_4(OH)_4(H_2O)_4(\mu_8-TBAPy)_2]$ (NU-1000). NU-1000 was synthesized in compliance with a reported process.⁵⁹ In brief, benzoic acid (22 mmol, 2.70 g) and ZrCl₄ (0.30 mmol, 70 mg) were combined in DMF (10 mL) and then dissolved using an ultrasonic treatment. In the next stage, the obtained transparent solution was incubated in an oven at 80 °C for 1 h and cooled down to room temperature. To this solution, H₄TBAPy was added (0.06 mmol, 40 mg), followed by sonication for 20 min. The obtained yellow suspension was heated in an oven at 120 °C for 48 h and then cooled down to room temperature. The resulting suspension was filtered off, producing a yellow polycrystalline solid (35 mg after activation; 54% yield). Then, it was washed with DMF and consequently activated with HCl as shown by Feng et al.⁶⁰

2.4. Preparation of Hybrid NU@ZIS Nanocomposites. In this stage, a single-step solvothermal procedure was used to obtain hybrid NU@ZIS composites (ZIS = $ZnIn_2S_4$). In brief, specific content of the as-prepared NU-1000 powder (e.g., 2.75 g for NU@ZIS20) was mixed with glycerol (5.0 mL) and DMF (15.0 mL) under ultrasonication. Then, In(NO₃)₃·XH₂O (0.586 g), TAA (0.301 g), and $ZnCl_2$ (0.136 g) were added to the mixture which was shaken at 25 °C for 90 min. The obtained suspension was transferred to an autoclave (150 mL, stainless steel lined with Teflon) that was sealed and heated at 160 °C for 10 h. After cooling to ~25 °C, the autoclave was opened and the solid product was abundantly washed with EtOH and distilled H₂O several times and then dried at 60 °C. The obtained NU@ZIS samples included the materials with 5, 10, 20, and 30 wt % ZIS, which were labeled as NU@ZIS5, NU@ZIS10, NU@ZIS20, and NU@ZIS30, respectively. For comparative purposes, ZIS was also synthesized using a similar solvothermal procedure in the absence of NU-1000.

2.5. Photocatalytic, Sonocatalytic, and Sonophotocatalytic Experiments. To evaluate the photocatalytic activity of the hybrid NU@ZIS nanocomposites in the visible-light-induced decomposition of TC in an aqueous solution, a 300 W halogen lamp with a UV filter was selected. In each test, aqueous TC solution (20 ppm, 300 mL) was added to a 500 mL beaker. The solution was set to an optimal pH of 9.0 by adding NaOH (1 M, 12 mL), followed by addition of the catalyst (0.2 g·L⁻¹). Initially, to attain equilibrium (adsorptiondesorption) between TC and the catalyst, the obtained suspension was subjected to vigorous magnetic stirring in darkness for 20 min. A cold water circulator was used to maintain a constant reaction temperature during the degradation process. As the light was turned on, aliquots (1.5 mL) were carefully taken out from the reaction solution at regular time intervals with a syringe. Prior to analysis, the suspension was filtered using syringe filter discs (0.45 μ m, polytetrafluoroethylene). Then, the absorbance of each sample was measured at 350 nm on a UV-vis spectrophotometer to investigate a decrease in TC concentration at different times. The degradation rate

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of TC (*D*, %) was obtained from eq 1, where C_0 and A_0 are the initial concentration and the absorbance of TC, while C_t and A_t refer to the respective parameters at a certain time (*t*).

$$D = \left[1 - \frac{A_t}{A_0}\right] \times 100 = \left[1 - \frac{C_t}{C_0}\right] \times 100 \tag{1}$$

For better comparison between photocatalytic, sonocatalytic, and sonophotocatalytic processes, the TC degradation using each of these three methods was separately investigated. Ultrasound waves were applied either in the absence (sonocatalytic process) or in the presence of irradiation by a 300 W halogen lamp (sonophotocatalytic process) by placing an ultrasound high-intensity probe (20 kHz frequency, 200 W power) into the reaction suspension. In recycling tests, the utilized catalyst was isolated, washed with distilled water, and dried at 60 °C prior to reuse in subsequent runs.

2.6. Experiments with Radical Scavengers. A scavenger (i.e., IPA, isopropanol; EDTA, ethylenediaminetetraacetic acid; or BQ, 4-benzoquinone) was added into TC solutions for probing the presence of [•]OH (hydroxyl radicals), h⁺ (positive holes), and [•]O₂⁻ (superoxide radicals), respectively. The following starting loadings of IPA (1 mmol), EDTA (1 mmol), and BQ (0.1 mmol) were used.

2.7. Cell Culture. Skin fibroblast cells (Hu02) were used to perform the cellular experiments. Hu02 cells for MTT assays were acquired from the National Cell Bank of Iran (NCBI). The cell cultures were grown and kept under 6% (v/v) carbon dioxide atmosphere in tissue culture flasks (T80 cm², Falcon) consisting of DMEM/L-glutamine, 7% (v/v) FBS, and 1.5% (v/v) penicillin/ streptomycin at 37 °C.

2.8. Cytotoxicity Examination. According to Mosmann's study,⁶¹ MTT assays were used to evaluate the Hu02 viability. This relies on a color change of yellow tetrazolium salt (soluble in H₂O) to purple formazan (insoluble in H₂O). Due to a decreased quantity of live mitochondrial cells, an amount of the formed formazan directly correlates with the number of live cells.⁶² 96-well plates were used to seed the cells and incubation was performed at 37 °C. Then, the NU-1000, ZIS, and NU@ZIS suspensions in PBS at 1 mg/mL concentration were sonicated for 2 h using an ultrasonic bath. The obtained samples were diluted with a growth medium and then poured into the seeded wells for yielding different concentrations (500, 400, 300, 200, 100, 50, and 0 $\mu g \cdot mL^{-1}$). Following incubation at 37 °C for 24 and 72 h, the medium used for growth was taken out from all of the wells and substituted by a fresh medium (100 μ L) and a solution of MTT (10 $\mu L;$ 0.5 mg per 1 mL of PBS). In the next stage, incubation of the well plates was done for 4 h until a purplecolored formazan product was produced. Then, 90 μ L of the test solution was taken out and 100 μ L of DMSO was poured into the wells for dissolving the formazan crystals. The well plates were incubated at 37 °C for 15 min, followed by centrifugation for 3 min at 1200 rpm. In addition, the supernatant (100 μ L) was transferred into a new well (96-well plate) and absorbance was determined at 530 nm with the use of a microplate reader (BioTek ELx808). Then, the cell survival was obtained as a relative percentage by comparing the absorbance in treated wells and control wells. Finally, the MTT experiments were repeated three times for all composite nanomaterials and the average values were used in this work.

2.9. Aquatic Toxicity. Aquatic toxicity of the reaction solutions against *E. coli* was assayed prior to and following the sonophotocatalytic degradation of TC. In the first method,⁶³ Petri dishes were prepared by mixing adequate volumes of agar and nutrient broth. Then, the obtained mixture was boiled resulting in the formation of a gel within not less than 1 h. *E. coli* (50 μ L; stock solution with ~1 × 10⁸ CFU/mL) was spread on the agar surface. A control experiment was assembled with the agar formed using water from sonophotocatalytic experiments (performed during 4 h) for ensuring that the antibacterial test result is caused by an antibiotic degradation instead of potential catalyst leaching or change in H₂O chemistry. In addition, we utilized the aqueous solutions obtained after sonophotocatalytic procedures (at 0, 15, and 30 min of the reaction time) to prepare agar and evaluate the level of changes in the bacterial growth. *E. coli* growth

Scheme 2. Preparation of the Hybrid NU@ZIS Nanocomposites by Self-Assembly Method



Figure 1. FE-SEM images of (a) ZIS, (b) NU-1000, and (c) NU@ZIS20 nanocomposite. (d,e) TEM images of NU@ZIS20 and (f) elemental mapping of NU@ZIS20.

was monitored after incubation for 24 h at 37 $^\circ$ C. Furthermore, the agar-well diffusion procedure was employed for visualizing changes in bacterial growth prior to and following the catalytic treatments.⁶⁴ In

this method, when the surface of the agar was covered by *E. coli*, holes with a diameter of 5 mm were made in the agar through punching and then the reaction solution (50 μ L) was poured into holes. Then, the

Petri dishes were kept in an incubator for 24 h at 37 °C. Afterward, we applied a test kit (Toxtrac kit) for quantitative assessment of aquatic toxicity of samples against bacteria following the manufacturer's protocol.⁶⁵ This method involves a solution color change (monitored at 605 nm) due to a reduction of resorufin. Finally, eq 2 was used to calculate the *E. coli* growth inhibition (2)⁶⁶

% inhibition =
$$\left(1 - \frac{\Delta A_{\text{sample}}}{\Delta A_{\text{control}}}\right) \times 100$$
 (2)

herein ΔA refers to (initial absorbance) – (final absorbance).

3. RESULTS AND DISCUSSION

3.1. Characterization of NU-1000, ZIS, and Hybrid NU@ZIS Nanocomposites. The assembly process of the NU@ZIS nanocomposites is shown in Scheme 2. We utilized FE-SEM to study the morphology of the as-prepared ZIS, NU-1000, and NU@ZIS samples. According to Figure 1, ZIS exhibits a flower-like structure (~0.4–0.7 μ m length), tending to be stacked layer by layer. The NU@ZIS nanocomposite morphology underwent a significant change if compared to parent precursors. As seen, the NU@ZIS thickness is lower than that of ZIS. Put differently, nanosheets of ZIS have no tendency to stack together but self-assemble into a hierarchical structure on the surface of the NU-1000 nanorods. With regard to the TEM images for NU@ZIS20 as the most promising photocatalyst, there is a more homogeneous distribution of ZIS (Figure 1d,e). The elemental mapping obtained by EDX (Figure 1f) shows a uniform distribution of elements (In, Zn, Zr, S, N, O, and C) in the composite material. Moreover, according to the ICP measurements, the Zr/Zn/In/S molar ratios are close to the stoichiometry used while preparing the hybrid NU@ZIS nanocomposites.

In the next stage, X-ray powder diffraction (PXRD) was used to analyze the structures (Figure S1). The important diffraction peaks of the pure ZIS are indexed to a hexagonal phase (JCPDS card 03-065-2023) with some impurity phases, including indium sulfide and zinc sulfide with (006), (102), (104), (106), (108), (110), (116), and (022) crystal planes at 20 of 21.52, 27.97, 30.16, 33,64, 39.88, 47.08, 53.02, and 55.38°, respectively.⁶⁷ Moreover, each diffraction peak of the obtained NU-1000 does not completely match with a pattern simulated from single-crystal data, showing the scattering angles of 2.68, 5.22, 7.36, 8.73, and 10.46° that are in agreement with the crystal planes (101), (201), (300), (311), and (400), respectively.⁵⁹ In addition, PXRD data demonstrate retention of the NU-1000 structure after its modification with ZIS. Consequently, the diffraction peaks of NU-1000 and ZIS are visible in the composites (Figure S1), but their intensity is weakened due to a decrease in crystallinity. All these observations along with the FE-SEM data suggest that the NU@ZIS nanocomposites are not a simple mixture of ZIS and NU-1000 but indeed a p-n heterojunction of the two components.68,69

Additionally, FT-IR spectra were analyzed to explain the interactions between the two components in NU@ZIS (Figure S2). Both ZIS and NU-1000 display the same spectral features as described earlier in the literature.^{43,70} Hence, the characteristic broad bands with maxima at 3440–3495 cm⁻¹ in NU@ZIS correspond to ν (OH/H₂O) vibrations due to the presence of hydroxo and aqua ligands of NU-1000 as well as surface-absorbed water. Two most intense bands at 1614 and 1416 cm⁻¹ (red star label, Figure S2) are attributed to ν_{as} (COO) and ν_{s} (COO) vibrations, respectively, of the μ_{s} -TBAPy

carboxylate groups.^{71,72} Additionally, three peaks at 792, 721, and 663 cm⁻¹ (blue star label) correspond to the longitudinal and transverse vibrations of Zr–O. As a result of the p–n heterojunction between NU-1000 and ZIS, some new bands

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appear in the spectra of NU@ZIS. Finally, the bands at 598 and 584 cm⁻¹ are likely associated with the stretching In–S and Zn–S vibrations, respectively.⁷³ The specific surface area (BET) of all materials was measured (Figure S3). The surface area of NU-1000 (2137 m² g⁻¹) is greatly superior to that of ZIS (34 m² g⁻¹). The obtained hybrid NU@ZIS nanocomposites essentially preserve

high surface areas of NU-1000, the gradual decline of which follows the trend of increasing the loading of ZIS from 5 to 30%. As expected, the significantly higher specific surface areas of NU@ZIS in comparison with ZIS would greatly affect the photocatalytic performance of these materials. The data on surface areas, pore volumes, and pore size distributions for all samples is given in Table S1 (Supporting Information).

3.2. Sonophotocatalytic Degradation of TC. The degradation of TC in water was investigated under sonophotocatalytic conditions using the hybrid NU@ZIS nanocomposites as photocatalysts. For comparison, NU-1000 and ZIS were also studied. Several reaction parameters were evaluated, including the loading amount of ZIS, initial TC concentrations, and reaction pH values. In addition, the stability and performance of the recycled catalyst were studied.

Figure 2 shows the sonophotocatalytic degradation of TC in water using various NU@ZIS nanocomposites exposed to a



Figure 2. Sonophotocatalytic activity of NU-1000, ZIS, and NU@ ZISX nanocomposites (X = 5-30 wt %) in the degradation of TC under a 300 W halogen lamp irradiation after 35 min (catalyst loading = 0.2 g·L⁻¹, $C_0(TC) = 20$ mg·L⁻¹, pH = 7).

300 W halogen lamp irradiation. It should be noted that in the control test, that is, direct photolysis without the presence of a catalyst, poor photolysis occurred with a TC degradation efficiency of only 4.6%. The TC degradation rates for the catalysts tested stay in the following order: NU@ZIS20 > NU@ZIS30 > NU@ZIS10 > NU@ZIS5 > ZIS > NU-1000. As expected from the catalyst design, the sonophotocatalytic performance is increased through the decoration of a surface of NU-1000 by ZIS nanostars, leading to 60-85% TC degradation efficiency over 35 min for different NU@ZIS nanocomposites. The NU@ZIS20 photocatalyst revealed the

highest efficiency (85%). It can be concluded that the amount of ZIS in the hybrid nanocomposite plays an important role in the TC photodegradation process. Consequently, NU@ZIS20 was used as a model photocatalyst for further optimization of the process. Prior to the investigation of other important parameters, it was necessary to evaluate the capability of ZIS, NU-1000, and NU@ZIS20 for removing TC in the absence of ultrasonic waves and light. As shown in Figure S4, none of these catalysts features a high adsorption capacity in the absence of light and ultrasonic waves; the absorption capacity declines in the order of NU-1000, NU@ZIS20, and ZIS. As a result, the removal of TC is very substantial under light and by using ultrasonic waves, especially at shorter reaction times.

It is recognized that the initial concentration of a pollutant might be an important parameter that affects the surface adsorption and degradation performance of the photocatalyst. To evaluate the TC degradation at its different initial concentrations, $C_0(TC) = 5-50$ mg/L, several experiments were performed in the presence of the NU@ZIS20 nanocatalyst (Figure S5). An initial concentration of antibiotic does not have a significant effect on the adsorption process in the darkness, leading to 4, 5, 7, 10, 12, and 13% of absorbed TC at $C_0(TC)$ of 5, 10, 20, 30, 40, and 50 mg/L, respectively. During 35 min of irradiation in the presence of the NU@ZIS20 photocatalyst, TC with initial concentrations ranging from 5 to 50 mg/L is degraded with an efficiency varying from 92 to 52% (Figure S5), respectively. Therefore, to achieve full degradation efficiency, the $C_0(TC)$ was set to 50 mg/L along with other parameters in further experiments.

To justify the need for all three factors involved in the TC degradation process (i.e., light, ultrasound, and catalyst), a series of control experiments were carried out at neutral pH (Figure S6). Analysis of Figure S6 indicates the following trend in the degradation efficiency for different processes catalyzed by NU@ZIS20: sonophotocatalytic (blue curve) > photocatalytic (red curve) > sonocatalytic (purple curve). The TC degradation increases over the reaction time, reaching 81% after 15 min of sonophotocatalytic reaction. At the same time, the degradation rates of the TC solution exposed to sonolysis and photocatalysis are in the 14-32% range. In the next step, in order to determine the role of different intensities of ultrasonic waves, we tested three different frequencies (30, 40, and 60 kHz). The antibiotic degradation was improved slightly as the frequency increased from 20 to 40 kHz. At the 60 kHz frequency, the reaction efficiency greatly reduced to 7%. The results of TEM analysis (Figure S7, Supporting Information) revealed that the catalyst changed its morphology from rod to spherical state at this frequency and the agglomeration increased sharply; according to the literature,⁷⁴ these factors can play a substantial role in catalytic performance. Hence, in standard sonophotocatalytic experiments, we used a lower 20 kHz frequency which, along with the synergistic effect of ultrasonic waves, was sufficient to achieve excellent performance of the catalyst within 35 min.

As a result, the sonophotocatalytic reaction with approximately 97% TC degradation over 30 min represents the most effective method for removing TC from an aqueous solution. Besides, a control experiment by using a physical mixture of NU-1000 and ZIS as a catalyst (Figure S6, yellow curve) reveals a modest performance that resembles that of ZIS. This test thus highlights the importance of the p-n heterojunction of both components in NU@ZIS20 to attain high catalytic efficacy.

Prior research revealed that the pH of the solution can have a significant influence on thephotodegradation of organic contaminants.⁷⁵ Also, pH may greatly affect the adsorption capacity, the distribution of electric charges on the surface of the catalyst, the degree of contaminant degradation, and the VB oxidation potential.⁷⁶ We found that pH has a major influence on TC degradation. In fact, the maximum and minimum degradation efficiency is observed at pH values of 9 and 3, respectively (Figure S8), which is consistent with the results of previous research.⁷⁷ It is known that the increase of the solution pH leads to an enhancement in the quantum efficiency of TC. Having an amphoteric character, TC possesses several functional groups that can ionize.^{15,78} At different pH values, these groups have varying acidity in H₂O and thus may play dominant roles in photocatalytic degradation.^{12,79,80} In the sonophotocatalytic process catalyzed by NU@ZIS20 (Figure S8), at pH = 3, only 50% of the TC degradation efficiency is observed after 30 min, while it reaches 99% at pH = 9. This might be associated with an increased generation of radical species at elevated pH.⁸¹⁻⁸⁴ In photocatalytic processes involving semiconductor compounds, at alkaline and neutral pH values, hydroxyl radicals are the most important oxidizing agents formed when hydroxide ions react with positive holes.⁸⁵ On the other hand, at acidic pH, the main oxidative species are present in the positive pores.⁸⁶ Also, in acidic aqueous solutions, the accessible surface area of the nanocomposite for absorbing TC and optical photons is reduced due to an aggregation of the nanocomposite, which can explain the lower TC degradation efficiency. Under these conditions, the amount of OH⁻ ions is low which prevents the generation of hydroxyl radicals. Accordingly, the photocatalytic transformations are more efficient under alkaline or neutral conditions. Figure S9 shows that all degradation data fit well to a quasi-first-order dependence $[\ln(C_0/C_t) = \kappa t]$. The photocatalytic rate constant for NU@ZIS20 is 0.043 min⁻¹, which is 4.2- and 2.3-fold superior to that for NU-1000 and ZIS, respectively.

To access the possible practical application of NU@ZIS20, the reusability and stability of this photocatalyst in the sonophotocatalytic degradation of TC was investigated for five consecutive reaction cycles. After each cycle, the catalyst was centrifuged, washed, and dried before being reused in the next cycle. After five recycles (Figure S10a), the sonophotocatalytic activity of NU@ZIS20 is 92%, showing that this photocatalyst remains stable. This is also confirmed by the match of PXRD diffraction patterns (Figure S10b) and FT-IR spectra (Figure S10c) of the NU@ZIS20 samples before and after catalytic experiments. Moreover, SEM and TEM analyses after five cycles of the sonophotocatalytic process showed that the employed nanocomposite did not undergo significant morphological and structural changes, as can be seen in Figure 3. These results show that NU@ZIS20 is a highly efficient, stable, and recyclable photocatalyst with good potential for use in real conditions.

Before examining the reaction mechanism, the absorption of NU-1000, ZIS, and NU@ZIS nanocomposites was investigated by UV-vis diffuse reflectance spectroscopy in the 200-800 nm range (Figure S11). An absorption edge of ZIS at 581 nm indicates intense absorption in the visible light region. The absorption edge of the NU@ZIS nanocomposites is comparable to that of pure NU-1000. After the incorporation of ZIS into NU-1000, the resulting NU@ZIS materials show a red shift in the visible light region (this shift is more

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Figure 3. SEM image and (b) TEM image of NU@ZIS20 nanocomposite after five recycles.

pronounced for NU@ZIS20 and NU@ZIS30). The generation of a hybrid nanocomposite, an upward shifted position of the VB edge, and a band gap reduction can explain this phenomenon. The energy gap was determined using the Kubelka–Munk protocol (eqs 3 and 4)⁸⁷

$$A(h\nu) = C(h\nu - E_{\rm g})^{n/2}$$
(3)

$$A^{n/2}(h\nu) = A(h\nu - E_{g})$$
(4)

where $h\nu$ is the energy of the photon; α is the semiconductor absorbance; *C* and *A* are the constants; and n indicates the transfer properties in the structure of a semiconductor. The band gap was established as shown in Figure S12. Energy gaps for NU-1000 and ZIS are 2.85 and 2.26 eV, respectively. Due to an appropriate band gap between these two semiconductors, the charge carriers produced by the light can be effectively separated and thus lead to more reactive species. Also, the oxidation potential of the edge of the CB (conduction band) and the VB (capacitance band) can be determined by applying equations 5 and 6.⁸⁷

$$E_{\rm VB} = XE_{\rm e} + 1/2E_{\rm g} \tag{5}$$

$$E_{\rm CB} = E_{\rm VB} - E_{\rm g} \tag{6}$$

herein, the definitions are as follows: X (electronegativity), E_e (free electron energy, 4.5 eV), and E_g (band gap). According to equations 5 and 6, the E_{CB} and E_{VB} values of NU-1000 are -0.65 and +2.20 eV, respectively, while these values for ZIS are -0.72 and +1.54 eV, respectively.

To clarify the recombination of photoexcited electronholes, the photoluminescence spectra of NU-1000, ZIS, and NU@ZIS were recorded using the excitation wavelength of 345 nm (Figure S13). A lower recombination rate of carriers is exhibited by all NU@ZIS nanocomposites compared to pure NU-1000 and ZIS. Furthermore, for the NU@ZIS20 nanocomposite, the recombination rate of carriers is the lowest among the other samples. Thus, the highest photocatalytic activity might be expected for NU@ZIS20, as experimentally observed in photocatalytic studies. This result indicates that a considerable p–n heterojunction formed in the NU@ZIS nanocomposites is advantageous for separating and migrating the electron-hole pairs. A decreased probability for charge carrier recombination might be beneficial for photocatalytic redox reactions.⁸⁸

To get further insight into the mechanistic information, several trapping experiments were performed (Figure 4) to shed light on the main species that are involved in a



Figure 4. Scavenger effect on the sonophotocatalytic degradation of TC over NU@ZIS20 nanocomposite under a 300 W halogen lamp irradiation (catalyst loading = $0.2 \text{ g}\cdot\text{L}^{-1}$, $C_0(\text{TC}) = 50 \text{ mg}\cdot\text{L}^{-1}$, pH = 9).

sonophotocatalytic degradation. Thus, isopropanol (IPA), 4benzoquinone (BQ), and ethylenediaminetetraacetic acid (EDTA) were, respectively, applied as scavengers for ${}^{\circ}O_{2}^{-}$, ${}^{\circ}OH$, and h⁺. After adding IPA to the reaction system, there is a significant reduction in the degradation efficiency from 99 to 15%, revealing the major role of ${}^{\circ}OH$ radicals as oxidizing species in this study. Similarly, when BQ is present, the degradation efficiency decreases from 99 to 19%, suggesting that ${}^{\circ}O_{2}^{-}$ is also involved in TC degradation. When EDTA is used as a scavenger, a decrease in the degradation efficiency from 99 to 35% is observed, confirming that h⁺ also plays a significant role in the TC degradation experiments. Therefore, it can be concluded that all three types of active species ${}^{\circ}OH$, ${}^{\circ}O_{2}^{-}$, and h⁺ are present in TC degradation catalyzed by NU@ ZIS20.

To better understand the involvement of •OH as the main oxidizing species, a photoluminescence probing method with terephthalic acid was run, which permits the estimation of the quantity of forming hydroxyl radicals.¹ Figure 5a displays a photoluminescence (PL) signal of 2-hydroxyterephthalic acid generated by irradiating (300 W halogen lamp) a solution of terephthalic acid with NU@ZIS20. As the reaction time increases, the PL signal of the produced 2-hydroxyterephthalic acid becomes more intense (Figure 5a). A control experiment revealed that under irradiation in the absence of a photocatalyst, no PL signal of 2-hydroxyterephthalic acid was observed at 429 nm. These results are consistent with the experiments in the presence of radical scavengers, confirming the main role of •OH in TC photodegradation.

Nitrotetrazolium blue chloride (NBT) reduction method as an O_2 probe can determine the production of ${}^{\bullet}O_2^{-.89}$ According to Figure 5b, absorption intensity of NBT, monitored by UV-vis spectroscopy at 259 nm, significantly decreased after adding the NU@ZIS20 photocatalyst. However, no significant changes were observed in the peak absorption intensity of the control sample. This result confirms that NU@ZIS20 can lead to the production of ${}^{\bullet}O_2^{-}$ in the photocatalytic process. Nevertheless, the control sample that has no photocatalyst could not form ${}^{\bullet}O_2^{-}$. Considering the experimental findings, a mechanism explaining the enhanced sonophotocatalytic activity of the NU@ZIS nanocomposites could be suggested (Scheme 3). Generally, the synergistic



Figure 5. (a) Evolution of PL emission over time for 2-hydroxyterephthalic acid formed by irradiating terephthalic acid (basic medium) over NU@ ZIS20 nanocomposite (λ_{ex} = 290 nm). (b) Evolution of NBT absorbance over time in UV–vis spectra in the presence of NU@ZIS20 nanocomposite.





effect of the photocatalyst and sonolysis plays an important role in the efficiency of sonophotocatalytic reactions. The p-n heterojunction structure could be created at the interface of NU-1000 and ZIS.

When compared to photocatalytic and sonocatalytic processes, the degradation of TC in the sonophotocatalytic reaction is significantly more efficient due to the following main factors: (1) enhanced generation of oxidizing species through sonolytic hydrolysis, (2) prevention of catalyst agglomeration, thus maintaining a large active surface area due to cavitation, (3) increase of the transfer of TC molecules to catalyst surface using diffuse shock waves, and (4) continuous cleaning of the catalyst surface aided by ultrasonic waves which, in turn, increases the catalyst performance.¹ Cavitation also enhances the pyrolysis of water and formation of °OH radicals because the collapse of bubbles creates reactive °OH and °H species. Also, the reaction of °H with dissolved O_2 leads to the formation of HO₂° (eqs 7 and 8).⁹⁰ These radicals attack TC, provoking its degradation.

$$H_2O + ultrasound H + OH$$
 (7)

$$^{\bullet}H + O_2 \rightarrow HO_2^{\bullet} \tag{8}$$

Then, the cavitation bubbles remove the degradation products from the photocatalyst surface, creating more active

sites on the nanocomposite surface for the adsorption and degradation of other TC molecules. Therefore, the use of both ultrasonic and photocatalytic (sonophotocatalytic) processes increases the degradation rate of TC by increasing the production of $^{\circ}$ OH. Based on the total organic carbon (TOC) analysis, a 45% mineralization efficiency for TC can be achieved for the NU@ZIS20 photocatalyst after 30 min irradiation. It should be noted that the mineralization efficiency (45%) is inferior in comparison with the degradation efficiency (99%), indicating that complete mineralization is not achieved due to the generation of some organic intermediates. Therefore, it is essential to determine the type of this species in the next phase.

Hence, the TC degradation mechanism was further investigated by high-performance liquid chromatography– mass spectrometry by analyzing the intermediates present in the reaction mixtures of the sonophotocatalytic processes. In the TC molecule, double bonds and amino and phenolic groups are the functionalities with an increased electronic density, which are more prone to a radical attack in the sonophotocatalytic reaction.⁹¹ The mass spectra of the reaction mixtures in the sonophotocatalytic degradation of TC catalyzed by NU@ZIS20 were analyzed at a reaction time of 0, 10, and 30 min (Figure S14). The structures of possible TC



Figure 6. Hu02 cell viability after treatment for 24 and 72 h with NU-1000, ZIS, and NU@ZIS20 at concentrations of 0 (control), 50, 100, 200, 300, 400, and 500 μ g/mL.



Figure 7. Aquatic toxicity of water solutions against *E.coli* obtained after sonophotocatalytic degradation of TC over NU-1000, ZIS, and NU@ZIS (a) Petri dish experiments, (b) agar-well diffusion experiments, and (c) inhibition % determination (Toxtrac kit).

degradation intermediates (Figure S15) were established based on the HPLC-MS and literature data.

In the hydroxylation reaction, [•]OH radicals attack various sites of the TC molecule, forming three possible intermediates with m/z = 461. These are further oxidized into derivatives with m/z = 477 (Figure S15, pathway a).^{92–94} Several fragments are also observed due to the N-demethylation caused by the h⁺ attack (Figure S15, pathway b). In general, the oxidation of TC (m/z = 445) is performed by °OH, ⁺h, and ${}^{\circ}O_2^{-}$ to provoke a ring-opening reaction giving a new species (m/z = 467). Then, through oxidation and deamination processes, another compound (m/z = 437) is formed which, in turn, leads to a derivative with m/z = 301. As the reaction time increases, ions with m/z = 329, 283, and 246 are detected as a result of the removal of several functional groups. The six-membered ring is then oxidized and opened to form an intermediate with m/z = 267, which turns into a new compound with m/z = 223. In this photocatalytic degradation

reaction, ${}^{\bullet}O_2^{-}$ and H_2O_2 can also be present along with highermolecular-weight fragments (m/z = 525, 496, and 451). Hence, an alternative degradation pathway (Figure S15, pathway c) may be identified. First, ${}^{\bullet}O_2^{-}$ and H_2O_2 attack the aromatic ring and lead to a ring-opening fragment (m/z =525); this is oxidized into a derivative with m/z = 496. The next step involves further oxidation of the $C(O)NH_2$ group and the formation of an intermediate with m/z = 451, which is further converted to a ketone derivative (m/z = 351). Eventually, all of the above intermediate fragments undergo oxidation to carboxylic acid (m/z = 255), which then degrades into H₂O and CO₂. Finally, before examining the cytotoxicity, we compared NU@ZIS20 with other recently reported MOFbased catalysts for degrading TC (Table S2, Supporting Information). These data show that the NU@ZIS20 nanocomposite can lead to higher rates of TC degradation and shorter reaction times.

3.3. In Vitro Cellular Cytotoxicity. We utilized MTT assay to determine the cytotoxicity of ZIS, NU-1000, and NU@ZIS20 nanocomposites.⁶² The Hu02 cell line (fibroblast cells) was used as a model for evaluating cell viability after 24 and 72 h in the presence of ZIS, NU-1000, and NU@ZIS20 in a 5–500 μ g·mL⁻¹ concentration range (Figure 6). Altogether, the cell viability decreases in a dosage-dependent manner for each of the tested nanomaterials. Moreover, NU-1000 revealed the weakest cytotoxicity, followed by NU@ZIS20 and ZIS. Nonetheless, at the highest experimented concentration of 500 μ g/mL, mitochondrial activity moderately declined for NU@ZIS20 as an optimal sample with a cell viability of 55 ± 2.5%.

3.4. Aquatic Toxicity of Water Solutions after TC Degradation. According to TOC analysis, total mineralization of TC was not attained after 30 min of sonophotocatalytic degradation. Hence, possible aquatic toxicity of water solutions after TC degradation was assayed against E. coli (for details, see the Experimental Section; Figure 7). In a positive control experiment, significant inhibition of E. coli growth was observed when using a TC solution prior to the sonophotocatalytic treatment. Petri dishes containing water after the sonophotocatalytic experiments using ZIS and NU-1000 as catalysts show some impact on bacterial growth (Figure 7a), although a complete bacterial growth inhibition is not observed. In contrast, Petri dishes with water from the TC degradation experiments in the presence of NU@ZIS show a significant level of bacteria development, thus indicating that TC is no longer present and its degradation products do not exert a notable antibacterial activity (Figure 7a). The agar-well diffusion method was applied to further confirm the obtained findings (Figure 7b), showing reduced or absent inhibition zone diameters when using water from the TC degradation experiments catalyzed by NU@ZIS20.

Moreover, Figure 7c represents the percentage inhibition (PI) of bacterial growth determined with the Toxtrac kit for water samples before (positive control) and after TC degradation in catalytic experiments with NU-1000, ZIS, and NU@ZIS20 during two periods of time (15 and 30 min). A high PI of the TC solution toward *E. coli* growth (~97%) can be observed prior to the degradation experiments. However, after 30 min of the sonophotocatalytic TC degradation, PI declines from 97% to 79, 41, and 3% for water solutions upon the catalysis with NU-1000, ZIS, and NU@ZIS20, respectively. These findings indicate that NU@ZIS20 is an efficient catalyst for the sonophotocatalytic degradation of TC in an aqueous medium, producing water samples which, despite the possible presence of TC degradation intermediates, exert no aquatic toxicity on bacteria.

4. CONCLUSIONS

In summary, we used a simple hydrothermal method for the synthesis of a series of hybrid NU@ZIS nanocomposites, composed of the 3D Zr(IV) MOF (NU-1000) and ZnIn₂S₄ (ZIS) components. These materials were fully characterized and applied as highly efficient photocatalysts for the degradation of TC in an aqueous medium. The degradation processes were tested under photocatalytic, sonocatalytic, and sonophotocatalytic conditions, revealing a clear advantage of the latter protocol. Particularly impressive catalytic efficiency (up to 99% TC degradation), stability, and recyclability were displayed by the NU@ZIS20 nanocomposite when compared to other catalysts in the present research and previously published photocatalysts. In addition, the presence of both

NU-1000 and ZIS in a hybrid NU@ZIS nanomaterial provided an appealing Z-scheme system with a larger specific surface area, a high number of active sites, and remarkably augmented visible light adsorption potential. Furthermore, NU@ZIS20 features effective protection of ZIS against photocorrosion due to a proper band structure between ZIS and NU-1000 components, thus allowing increased photocatalytic stability. Finally, appealing activity of the NU@ZIS20 catalyst is credited to its heterogeneous hierarchical structure and the synergistic effect of ZIS and NU-1000, leading to a high level of radical production, facilitating a Z-scheme charge carrier transfer and reducing the recombination of charge carriers. The radical trapping tests and HPLC-MS data also demonstrated the presence of ${}^{\bullet}OH$, ${}^{\bullet}O_2^{-}$, and h^+ as the main active species in the sonophotocatalytic degradation of TC. Cytotoxicity of NU@ZIS20 and aquatic toxicity of water samples after TC degradation were also evaluated, showing good biocompatibility of the catalyst and sonophotocatalytic protocols with potential significance in decontaminating different water resources. We believe that the obtained hybrid NU@ZIS nanocomposites, as well as the developed sonophotocatalytic degradation protocols, would open up new perspectives for the design of new advanced materials and processes for efficient removal of organic pollutants in water bodies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00951.

PXRD patterns, FT-IR spectra, isotherms of nitrogen adsorption/desorption, effect of TC initial concentration, solution pH effect, reaction kinetics, catalyst reusability and stability, UV–vis diffuse reflectance spectra, band edges, PL spectra, and mass spectra (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Tarbiat Modares University, Iran's National Elites Foundation, and Iran National Science Foundation (project number: 98026339). A.M.K. acknowledges the FCT (LISBOA-01-0145-FEDER-029697) and RUDN University (this paper has been supported by the RUDN University Strategic Academic Leadership Program).

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