One-pot mild synthesis of 3D printed architectures as photocatalysts based on TiO_2, Fe_2O_3 and NiO for water decontamination

ORAL
Ph.D. Student: N
Journal: JECE

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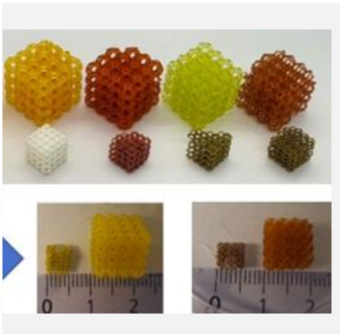

A 3D printing method is used to fabricate architectures based on TiO_2 modified with Fe_2O_3 and NiO. The different resins were prepared in the laboratory and the architectures were printed using the DPL technique. 3D TiO_2, TiO_2-Fe_2O_3, TiO_2-NiO and TiO_2 -Fe_2O_3/NiO architectures were fabricated. Their structural and optical properties were studied. The photocatalytic activity under white, UV and photo-Fenton irradiation using white light and H_2O_2 was evaluated. A 83% degradation of MB was achieved in 2h using TiO_2-Fe_2O_3/NiO, in a static system. Our work opens new horizons for 3D printed architectures, which can be used in water remediation and could be applied to drive other (photo/electro)catalytic processes in the future.

Introduction

Photocatalysis and photo-Fenton processes have been enhanced by integrating 3D printing technologies. Research has explored the use of photopolymerization-based 3D printing combined with photocatalysis, showcasing innovations in this field (Li et al., 2022). Additionally, studies have focused on the production and application of 3D printed photo-Fenton reactors for wastewater treatment, demonstrating the adaptability of 3D printing materials to the requirements of the photo-Fenton process (Esfahani et al., 2021). Studies have indicated the effectiveness of additive manufacturing in incorporating catalysts like TiO2 into 3D printable polymeric feedstock for evaluating photocatalytic treatments (McQueen et al., 2021). Leveraging advances in catalyst design and process optimization, the photo-Fenton process using 3D printing promises to address the challenges of contamination in various environments. The aim of the present study is to develop 3D printed photocatalytic architectures, using laboratory-prepared resist, that can be used by the photo-Fenton process in the degradation of pollutants.

Material and Methods

To prepare the titanium photoresists, a modified methodology of A. Vyatskikh (2020) was used. In a dark ball flask, titanium (IV) butoxide and acrylic acid were mixed gently in a 1:4 molar ratio to synthesize titanium (IV) acrylate, as DLP phptoiniciator we use phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO). Then, the resulting hybrid organic-inorganic TiO_2 precursor is combined with an acrylic monomer, pentaerythritol triacrylate (PETA), and the solution becomes transparent and orange. For the mixed architectures, Fe_2O_3 nanoparticles or NiO powder, were added to the resin just after the first step. Subsequently, the structure was printed, and washed away, using 2-methoxyethanol and isopropanol alcohol. The architectures were pyrolyzed in air at 550 °C for 1 h to create replicas of the original structures, with a reduction (~50%) in dimensions, made of titanium dioxide. The architectures were characterized by XRD, SSA, DRUV-Vis, SEM, TEM, and others. The photocatalytic activity was evaluated using methylene blue as model pollutant under white light, UV light and white light:H_2O_2 as photo-Fenton process. All of them, in a static system, there was no agitation. The decomposition reaction was tracked using a UV-Vis spectrometer from Avantes AvaSpec-ULS2048CL-EVO-RS. The λ = 664 nm was used as it corresponds to the maximum absorbance of MB.

Results and Discussion

Additive manufacturing of TiO_2 and modified TiO_2 3D architecture begins by using lab-prepared resins and nanoparticles suspended using the appropriate photoinitiator for DLP printing.

The graphical abstract shows architectures printed with TiO_2, TiO_2-Fe_2O_3, TiO_2-NiO and TiO_2-Fe_2O_3/NiO. Likewise, the size compaction due to annealing temperature is shown.

The surface areas obtained in the architectures were 179, 115, 115 and 177 m^2/g for TiO_2, TiO_2-

Fe_2O_3, TiO_2-NiO and TiO_2-Ni/Fe respectively, which indicates porous materials. The XRD pattern (no shown) demonstrates the typical diffraction pattern of anatase TiO_2 crystallographic phase after annealing, there is no evidence of the presence of Fe_2O_3 or NiO due to the low concentration of these in the structure.

The optical properties of TiO_2, TiO_2-Fe_2O_3, TiO_2-NiO and TiO_2-Fe_2O_3/NiO architectures are measured using UV–Vis DRS in **Figure 1** to estimate and compare the bandgap. Eg values were calculated from their DRUV-Vis spectra, 3.11, 3.13, 3.00, and 2.94 eV were obtained for TiO_2, TiO_2-Fe_2O_3, TiO_2-NiO and TiO_2-Fe_2O_3/NiO, with a slight redshift observed for the NiO-containing samples.

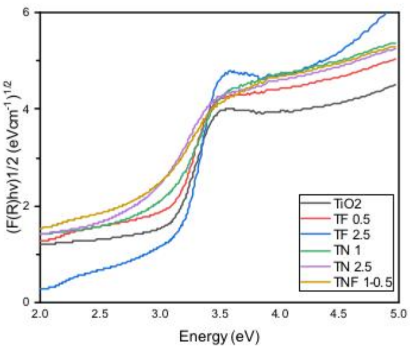

Figure 1. Optical properties of TiO_2, TiO_2-Fe_2O_3, TiO_2-NiO and TiO_2-Fe_2O_3/NiO using DRUV-Vis.

The photocatalytic activity evaluation test using the 3D architectures, was carried out under white light, UV light and white light and H_2O_2, as a photo-Fenton process. In **Figure 2,** only the results of the photo-Fenton process are shown, where the blue bars are for 2h of reaction and the orange bars are for 4h of reaction.

The MB degradation averages using white light were, at 2h about 55% and at 4h about 70%, the best performance was obtained with the TiO_2-Fe_2O_3/NiO architecture, which reached 79% degradation. Better results were obtained with UV light, which were very similar to the photo-Fenton process, where at 2h an average of 75% and at 4h 90% MB degradation was obtained. The highest degradation percentages were obtained using TiO_2-Fe_2O_3, and TiO_2-Fe_2O_3/NiO. It is important to remember that the system was static, as there was no agitation, so a very good performance was obtained for the different architectures, with special interest for those of TiO_2-Fe_2O_3, and TiO_2-Fe_2O_3/NiO.

Figure 2. Photocatalytic activity evaluation test using the 3D architectures of

Conclusions

This work presents a DPL printing method that enables the production of 3D TiO_2 architectures with Fe_2O_3 and NiO loadings. We demonstrate that our DPL approach is compatible with laboratory prepared resin. The functionality of the 3D TiO_2 architectures is evaluated during MB degradation with white light, UV light and photo-Fenton. A 83% degradation of MB was achieved in 2h using TiO_2-Fe_2O_3/NiO, in a static system. Our work opens new horizons for 3D printed architectures, which can be used in water remediation and could be applied to drive other (photo/electro)catalytic processes in the future.

Acknowledgments

N.A. Ramos-Delgado acknowledges to CONACyT-Mexico the support for a sabbatical stay. M.A.Gracia-Pinilla acknowledges to UANL the support for a sabbatical stay.

References

[1] Li, J., Boyer, C., & Zhang, X. (2022). Macromolecular Materials and Engineering, 307(8).
[2] Esfahani, K., Zandi, M., Travieso-Rodriguez, J., Graells, M., & Pérez-Moya, M. (2021). International Journal of Environmental Research and Public Health, 18(9), 4885.
[3] *McQueen, A., Ballentine, M., May, L., Laber, C., Das, A,..... & Kennedy, A. (2021). Acs Es&t Water, 2(1), 137-147.*
[4] Vyatskikh A, R.C. Ng, B. Edwards, R.M. Briggs, and J.R. Greer. Nano Lett. 2020, 20, 3513-3520.