Multifunctionality of Photocatalytic Semiconductor Nanocrystals in Nanocomposites

[1]Tom Naor, [1]Shira Gigi, [1]Nir Waiskopf, [2]Gila Jacobi, [2]Sivan Shoshani, [3]Sanjit Mondal, [3]Michael Volokh, [1]Shlomo Magdassi, [3]Menny Shalom, [2]Ehud Banin and [1]Uri Banin

[1]*The Institute of Chemistry and the Center for Nanoscience and Nanotechnology, the Hebrew University of Jerusalem*

[2]*The Mina and Everard Goodman Faculty of Life Sciences and the Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan*

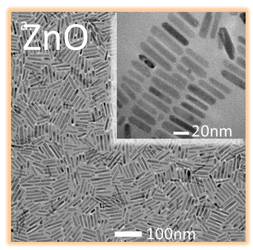
[3]*Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva*

Abstract

Nanocomposites are constructed from a matrix material combined with a nano-sized property modifying filler. This diverse and flexible combination yields the powerful ability to tailor the desired thermodynamic, mechanical, optical, electrical, and antimicrobial material properties. Semiconductor nanocrystals (SCNCs) are highly interesting potential fillers as they showcase size, shape, and composition controlled properties and are easily embedded in diverse matrices. While their optical functionality has been already addressed in several studies, the utilization and multifunctional outcomes of photocatalytic SCNCs in such nanocomposites has not been sufficiently addressed. This research presents the multifunctionality of photocatalytic SCNCs in two main composite systems: First, as quantum photoinitiators (QPIs) in biocompatible acrylate based polymers, where they act as a radical catalytic initiator and endow the system with mechanical, photocatalytic and antimicrobial properties. Second, as sensitizers and co-catalysts for photo-electrochemical water splitting in carbon-nitride (CN)-based photoelectrodes. This is done by first synthesizing highly active, heavy metal-free, Zn-based SCNCs, embedding them in different matrices, and demonstrating the improved features of the final product. These discoveries would label SCNC systems as a leading candidate for property modifying fillers in nanocomposites for renewable energy applications and future biomedical solutions, where specific and purpose-oriented characteristics are required.

A. Synthesis of Zn-based nanocrystals

One–step, large–batch, environmentally–friendly synthesis of antimicrobial ZnO nanorods for photocatalytic polymerization



Length: 40 ± 10 nm
Diameter: 9 ± 1 nm

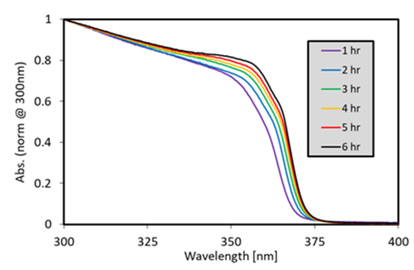
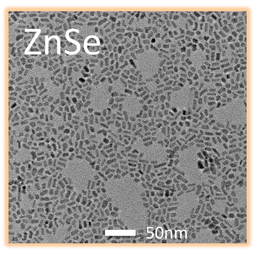


Photo-activated @ 365nm

Synthesis of visible light activated photocatalytic ZnSe nanorods for photoelectrochemical water splitting



Length: 12 ± 2 nm
Diameter: 5 ± 1 nm

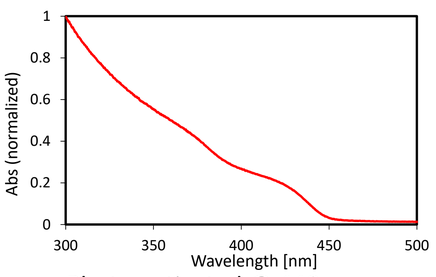
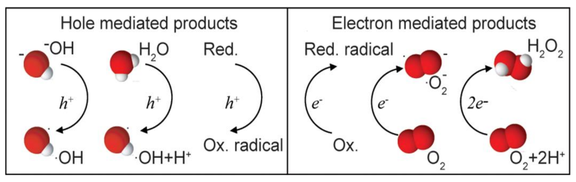


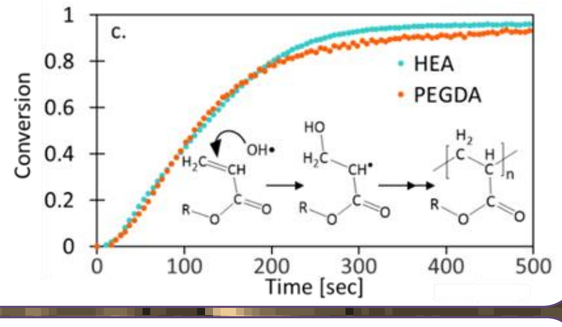
Photo-activated @ 440nm

Photocatalytic radical polymerization

Photopolymerization of two biocompatible monomers, 2-Hydroxyethyl acrylate (HEA) and poly(ethylene glycol) diacrylate (PEGDA) using ZnO QPIs



The main reactive species that may form by direct charge transfer from the nanocrystals upon light excitation in water

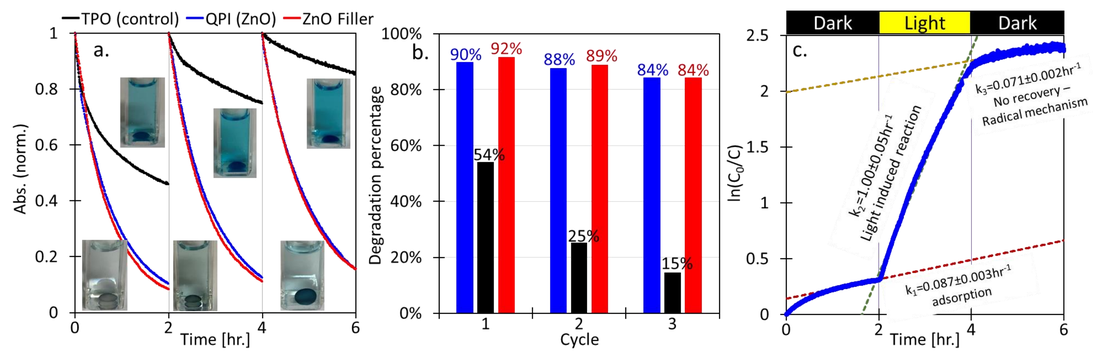


B. Post-polymerization photocatalytic activity of QPI-based nanocomposites

Comparison between three PEGDA hydrogel systems:

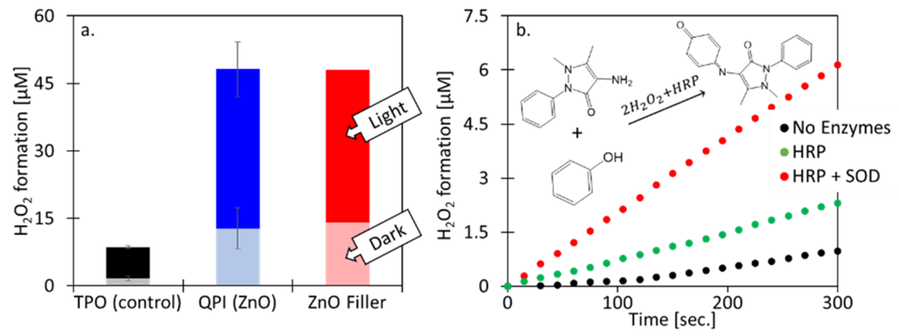
1. Control – 0.1$_{wt}$% TPO
2. Filler – 0.1$_{wt}$% of TPO and 1$_{wt}$% ZnO
3. QPI – 1$_{wt}$% of ZnO

Methylene blue degradation in water under illumination



Efficiency lost after 3 rounds: QPI – 7 % ; Filler – 9 % ; TPO – 72 %

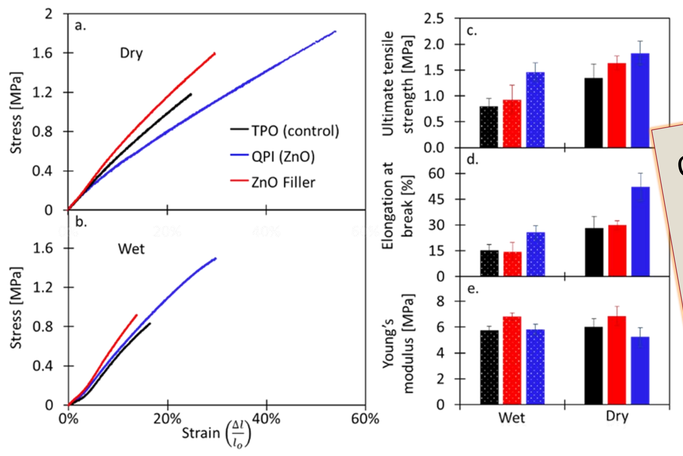
HRP and SOD assay: hydrogen peroxide (H_2O_2) and superoxide (O_2^-) formation measurement through the absorption of Quinone-imine dye @500nm



C. ZnO-based QPI as mechanical properties modifier

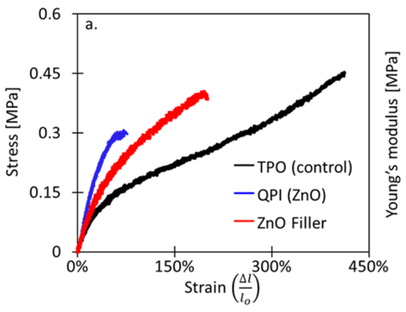
Tensile test results for nanocomposite polymers

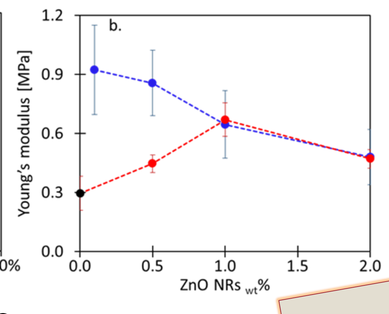
PEGDA hydrogels containing 50$_{wt}$% water tested in both wet (swollen) and dry conditions

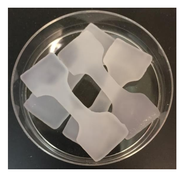


QPI-driven nanocomposites show
Higher tensile strength
Better elongation
Same Young's modulus

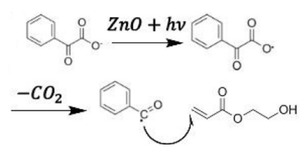
Solvent-free HEA photopolymers with 1$_{wt}$% of benzoylformic acid salt (BAS)







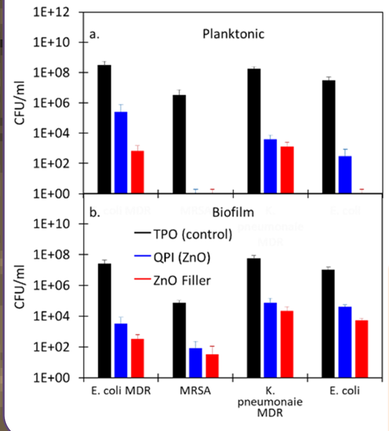
Polymerization with BAS



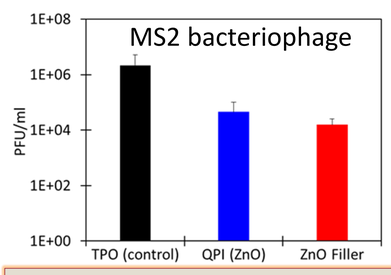
Transformation from ductile to brittle polymer when using ZnO NRs as PI or as fillers

D. Antimicrobial activity of QPI-based PEGDA nanocomposites

Antibacterial activity

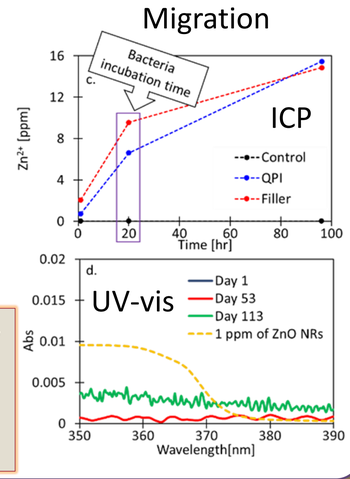


Antiviral activity



Significant antimicrobial activity was shown for the ZnO-contained samples, mainly through the release of Zn^{2+} ions

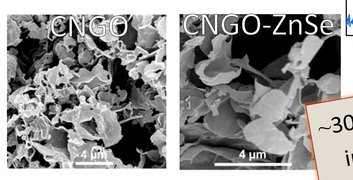
Migration

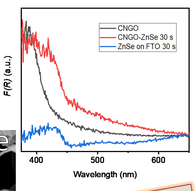


E. SCNC-embedded Nanocomposite Electrode for Water Splitting

Electrophoretic deposition of ZnSe NPs on CNGO electrode

SEM and UV-vis characterization

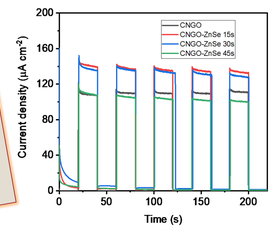




~30% enhancement in photocurrent with ZnSe

PEC measurements

Potential= 1.23 V vs. RHE
Electrolyte 0.1 M KOH (aqueous)



Summary

Herein, we presented the multifunctionality of SCNCs as mechanical property modifiers, antimicrobial agents and photocatalytic sensitizers in nanocomposites. First, as an all-in-one solution in biocompatible photopolymers, and second, as a solar energy-harvesting enhancer in photoelectrochemical water splitting towards hydrogen generation.

This research was supported by the Israel Science Foundation (Grant No. 1363/18)