Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Materials

Dual Cocatalysts Loaded Reverse Type-I Core/Shell Quantum Dots for Photocatalytic Antibacterial Applications

*Mohammad Reza Shariati [a], Abdolraouf Samadi-Maybodi *[a], Abasalt Hosseinzadeh Colagar [b]*

[a] Analytical Division, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran.

[b] Department of Molecular and Cell Biology, Faculty of Sciences, University of Mazandaran, Babolsar 47416-95447, Iran.

*Corresponding author: Tel: +98 1135302350; Fax: +98 1135302396; E-mail address: samadi@umz.ac.ir

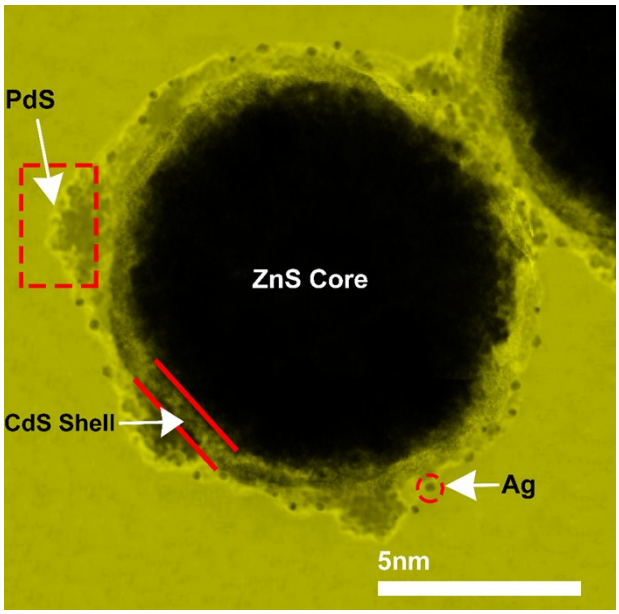

Figure S1: TEM image of Ag-PdS/ZnS/CdS nanohybrids.

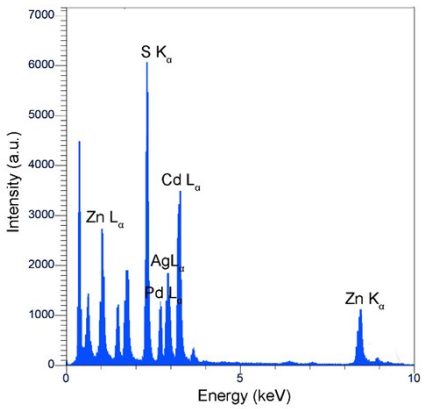

Figure S2: EDS spectrum of Ag-PdS/ZnS/CdS nanohybrids.

Table 1 Absorption band edges and emission maximum wavelengths of ZnS/CdS and Ag-PdS/ZnS/CdS together with the corresponding PL lifetimes.

	Absorption edge (λ_{max}, nm)	Emission peak (λ_{max}, nm)	PL lifetimes (ns)
ZnS/CdS	310, 425	500	111.3
Ag-PdS/ZnS/CdS	315, 430	515	125.0

Determination of MIC and MBC

A modification of the broth tube dilution method[1] for the determination of minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) was used. Briefly, photocatalysts were diluted into various concentrations in liquid LB broth in test tubes. A 1.0 mL volume of *E. coli* culture, 0.5 McFarland standard, was inoculated into test tubes containing 4.0 mL of the various concentrations of photocatalysts, 1.25 to 15.0 mg mL^{-1}, in liquid LB broth. Similarly, this was repeated for *S. saprophyticus*. After exposure to solar light for 30 min, the tubes were incubated at 37 ^{o}C for 3 h and thereafter observed for growth or turbidity. For determination of MBC, a loopful (50.0 μL) of broth from each test tube not showing growth, was inoculated into LB agar plate. The plates were incubated at 37 ^{o}C for 24 h. MBC corresponds to the lowest concentration showing no bacterial growth, which is different from the MIC. Experiments were performed in triplicate.

Disc diffusion assays

The antibacterial activities were also evaluated by the paper disc diffusion method. The disc diffusion assay was performed by placing 5.0 mm paper discs attached with ZnS, CdS, ZnS/CdS and Ag-PdS/ZnS/CdS photocatalysts slurry (5.0 mg mL^{-1}) onto an agar plate seeded with microorganisms. As a control, a disc without any sample was also included. After irradiation under solar light for 30 min, the plates were incubated (37 °C, 16 h). All experiments were accomplished in triplicate, and the obtained results were averaged.

Detection of •OH radicals

An aqueous solution containing 0.01 mol L^{-1} NaOH, 0.3 mmol L^{-1} H_2O_2, 0.1 mol L^{-1} KCl and 3.0 mmol L^{-1} TPA was prepared, and then 17.5 mg of photocatalyst was introduced in 3.5 mL of this solution. The sample cell (1.0 cm × 1.0 cm quartz cuvette) was placed on a stirrer and illuminated using a 150-W xenon lamp (spectral distribution: 185 nm to 2000 nm) for 0.0-30.0 min. Fluorescence spectra of the supernatant liquid were recorded with a fluorescence spectrophotometer.

Detection of $O_2^{\bullet-}$ by chemiluminescence technique

$O_2^{\bullet-}$ was detected by the luminol chemiluminescence (CL) method,[2] and the experimental procedure was as follows. A glass tube (10.0 mm ID) containing 3.5 mL of 0.01 mol L^{-1} NaOH and 5.0 mg mL^{-1} of catalysts was placed on a magnetic stirrer in a dark box, and the suspension was stirred before the measurement. During stirring process, the solution was irradiated by 150-W xenon lamp (spectral distribution: 185 nm to 2000 nm) for 0.0-30.0 min. Immediately after the irradiation, luminol solution (350.0 μl, 10.0 mmol L^{-1}) was injected into the tube, then, the CL response was recorded over an interference filter (λ = 425 nm) by a photon counting system for 120 s.

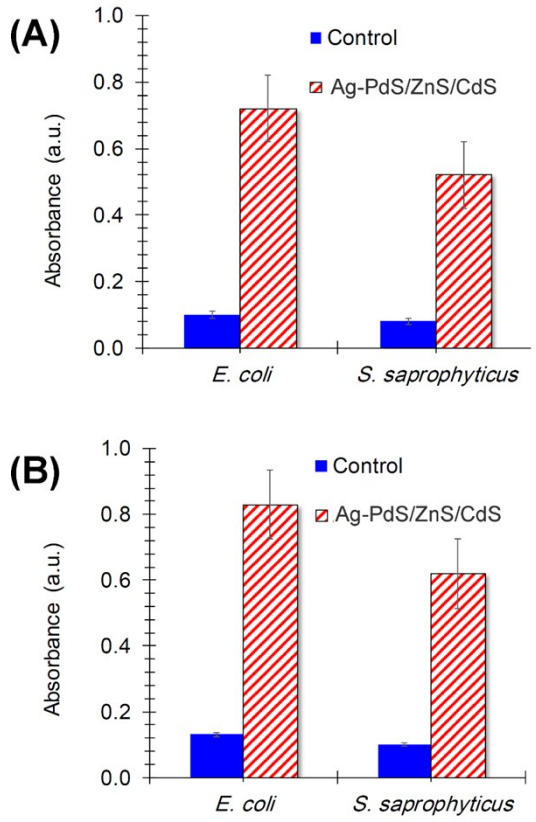

Figure S3: Changes in oxidative damage to lipids (A) and proteins (B) in cells after exposure to 5.0 mg mL^{-1} Ag-PdS/ZnS/CdS (at 30.0 min after irradiation) compared with the control.

Monitoring of lipid peroxidation

The free-radical modulation activity of Ag-PdS/ZnS/CdS catalysts was also determined using a lipid peroxidation assay.[3,4] The analysis was performed with fresh cells and with cells subjected to 30 min of irradiation with solar light using 5.0 mg mL^{-1} catalysts. Briefly, 330.0 µL of catalyst exposed cells were mixed well with 3.0 mL of TBA reagent (TBA reagent: a mixture of 1.0 vol. of 0.8% TBA and 3.0 vol. of 20.0% TCA). Then, the reaction mixture was kept in a boiling water bath for 60 min. The mixture was cooled and

centrifuged (6000 rpm, 5 min). Finally, the absorbance of the supernatant was measured at 532 nm via a UV-visible spectrophotometer. Experiments were performed in triplicate.

Monitoring of protein carbonyl

The reaction between DNPH is a well-established strategy to detect protein carbonyls. The reaction generates a Schiff base to produce the proteinhydrozone which can be analyzed spectrophotometrically at 370 nm.[5]

The proteomic analysis was performed with fresh cells and with cells subjected to 30 min of irradiation with solar light using 5.0 mg mL^{-1} catalysts. Briefly, the exposed cells were sonicated in cold phosphate buffer (50.0 mmol L^{-1}, pH 6.7, containing 1.0 mmol L^{-1} EDTA) and centrifuged at 10000 rpm for 10 min. Two aliquots (1.0 mL) of supernatants were placed in two 12.0-mL glass tubes. To one tube 4.0 mL of 0.01 mol L^{-1} DNPH in 2.5 mol L^{-1} HCI was added, while to the other tube only 4.0 mL of 2.5 mol L^{-1} HCI solution was added. Tubes were left for 60 min of incubation in the dark at room temperature with vortexing every 15 min. Then, 5.0 mL of 20% w/v TCA solution was introduced to both DNPH and HCI samples. The tubes were left in an ice pail for 10 min and centrifuged to collect the protein precipitates. The supernatants were thrown away. Afterward, one aliquot of 10.0% TCA solution (4.0 mL) was added, and then the protein pellets were broken mechanically using a glass rod. Eventually, the pellets were washed 3 times with ethanol/ethyl acetate mixture (1.0:1.0, v/v, 4.0 mL) to get rid of the lipid contaminants and extra DNPH. The obtained precipitates were dissolved in 6.0 mol L^{-1} guanidine hydrochloride solution (2.0 mL) and centrifuged at 10000 rpm for 10 minutes to remove

any left-over debris. The supernatant was recovered, and absorbance was measured at 370 nm against the sample treated with 2.5 mol L^{-1} HCl (second tube). Experiments were performed in triplicate.

References

(1) Wiegand, I.; Hilpert, K.; Hancock, R. E. W. Agar and Broth Dilution Methods to Determine the Minimal Inhibitory Concentration (MIC) of Antimicrobial Substances. Nat. Protoc. **2008**, 3, 163-175.

(2) Nosaka, Y.; Takahashi, S.; Sakamoto, H.; Nosaka, A. Y. Reaction Mechanism of Cu(II)-Grafted Visible-Light Responsive TiO_2 and WO_3 Photocatalysts Studied by Means of ESR Spectroscopy and Chemiluminescence Photometry. J. Phys. Chem. C **2011**, 115, 21283-21290.

(3) Nair, V.; Turner, G. E. The Thiobarbituric Acid Test for Lipid Peroxidation: Structure of the Adduct with Malondialdehyde. Lipids **1984**, 19, 84-95.

(4) Hosseinzadeh Colagar, A.; Memariani, H.; Sohbatzadeh, F.; Valinataj Omran, A. Nonthermal Atmospheric Argon Plasma Jet Effects on Escherichia Coli Biomacromolecules. Appl. Biochem. Biotechnol. **2013**, 171, 1617-1629.

(5) Oliver, C. N.; Starke-Reed, P. E.; Stadtman, E. R.; Liu, G. J.; Carney, J. M.; Floyd, R. A. Oxidative Damage to Brain Proteins, Loss of Glutamine Synthetase Activity, and Production of Free Radicals During Ischemia/Reperfusion-Induced Injury to Gerbil Brain. Proc. Natl. Acad. Sci. U.S.A. **1990**, 87, 5144-5147.