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Plasmon enhanced degradation of methylene blue via photocatalysis (solar and ultraviolet) and sonocatalysis using hetero-nanocatalysts based on ZnO and gold nanoparticles

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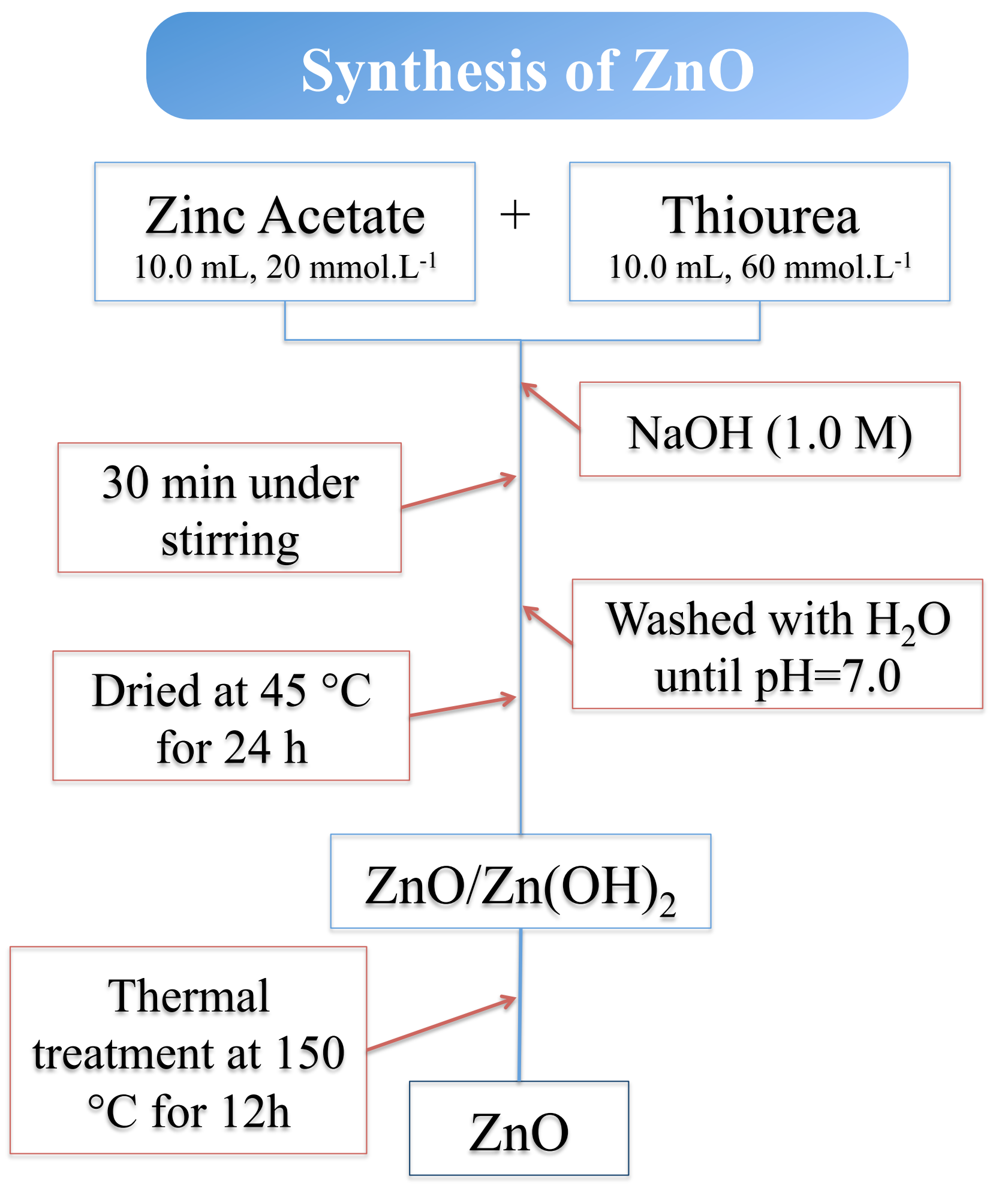
Introduction

Hybrid nanostructures based on the combination of metal oxide semiconductor and noble metal nanoparticles have been studied extensively due to the possibility of enhancing some functional properties, making them suitable and desirable for applications in diverse areas such as solar energy conversion, optoelectronics, chemical sensing, biological detection, environmental remediation and catalysis [1]. This behavior comes from the ability of metal nanoparticles to enhance the local incident field and the local density of states at semiconductor-metal interface by (1) promoting the creation of charge carrier pairs induced by the surface plasmon resonance (SPR) effect, (2) enhancing the charge carrier separation efficiency and (3) extending light absorption.

This work aims to prepare orange-emitting zinc oxide (ZnO) particles with a star-like morphology by a new room temperature methodology and their decoration with gold nanoparticles (GNPs). The degradation of aqueous MB solutions was investigated by solar photocatalysis (samples were exposed to sunlight from 11 a.m. to 4 p.m. during the autumn of 2016 (April-May) under an average radiant exposure of 2900 kJ m^{-2} at the time of experiments), UV-A photocatalysis (using a photochemical reaction apparatus equipped with two black light fluorescent lamps (25 W, λ range = 320-400 nm)) and sonocatalysis (performed in dark conditions using a ultrasonic bath operating with at a fixed frequency of 35 kHz and 100 W ultrasound power).

Experimental Details



Synthesis of ZnO

Zinc Acetate
10.0 mL, 20 mmol.L^{-1}
\+
Thiourea
10.0 mL, 60 mmol.L^{-1}

NaOH (1.0 M)

30 min under stirring

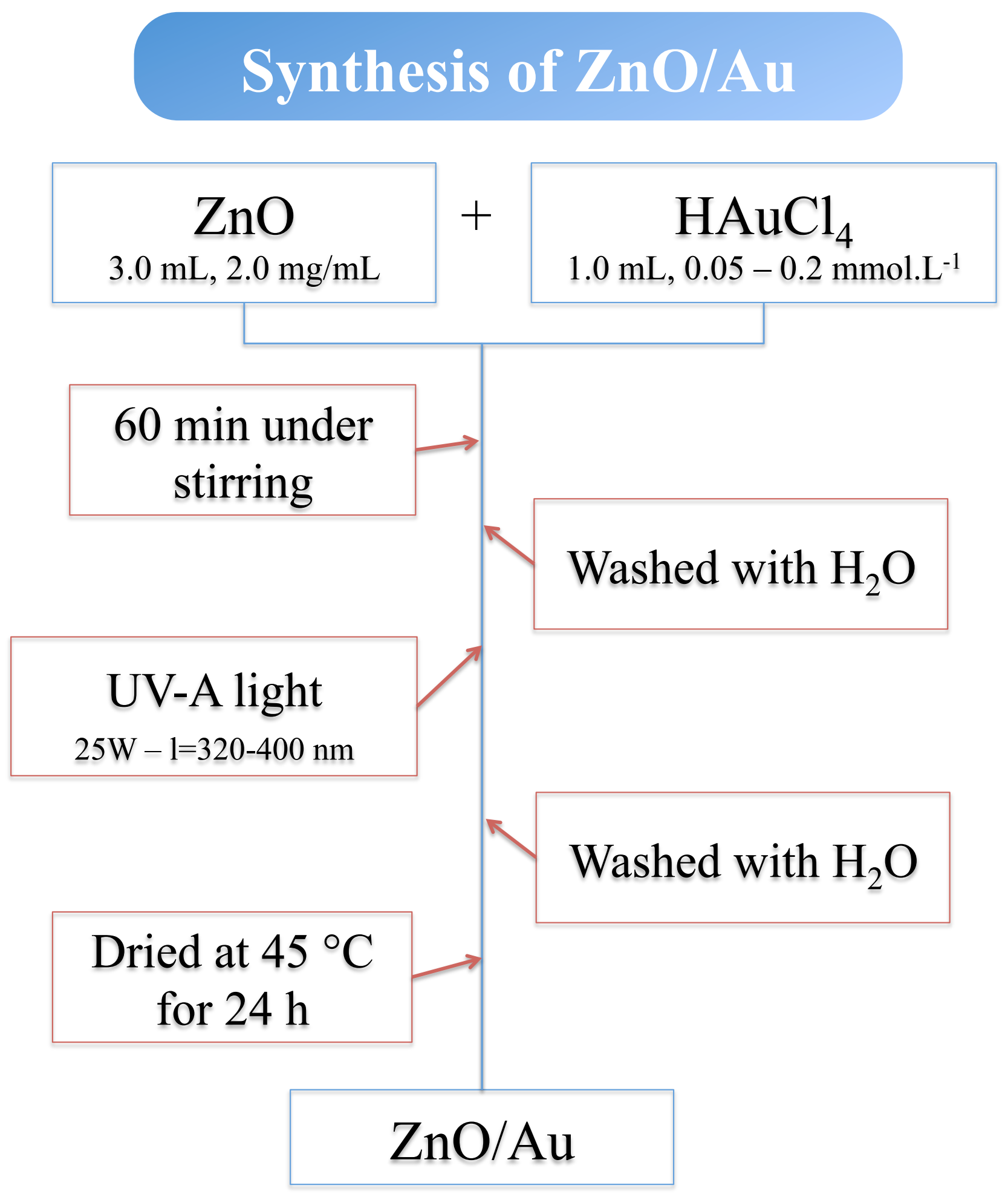
Washed with H_2O until pH=7.0

Dried at 45 °C for 24 h

$ZnO/Zn(OH)_2$

Thermal treatment at 150 °C for 12h

ZnO



Synthesis of ZnO/Au

ZnO
3.0 mL, 2.0 mg/mL
\+
$HAuCl_4$
1.0 mL, 0.05 – 0.2 mmol.L^{-1}

60 min under stirring

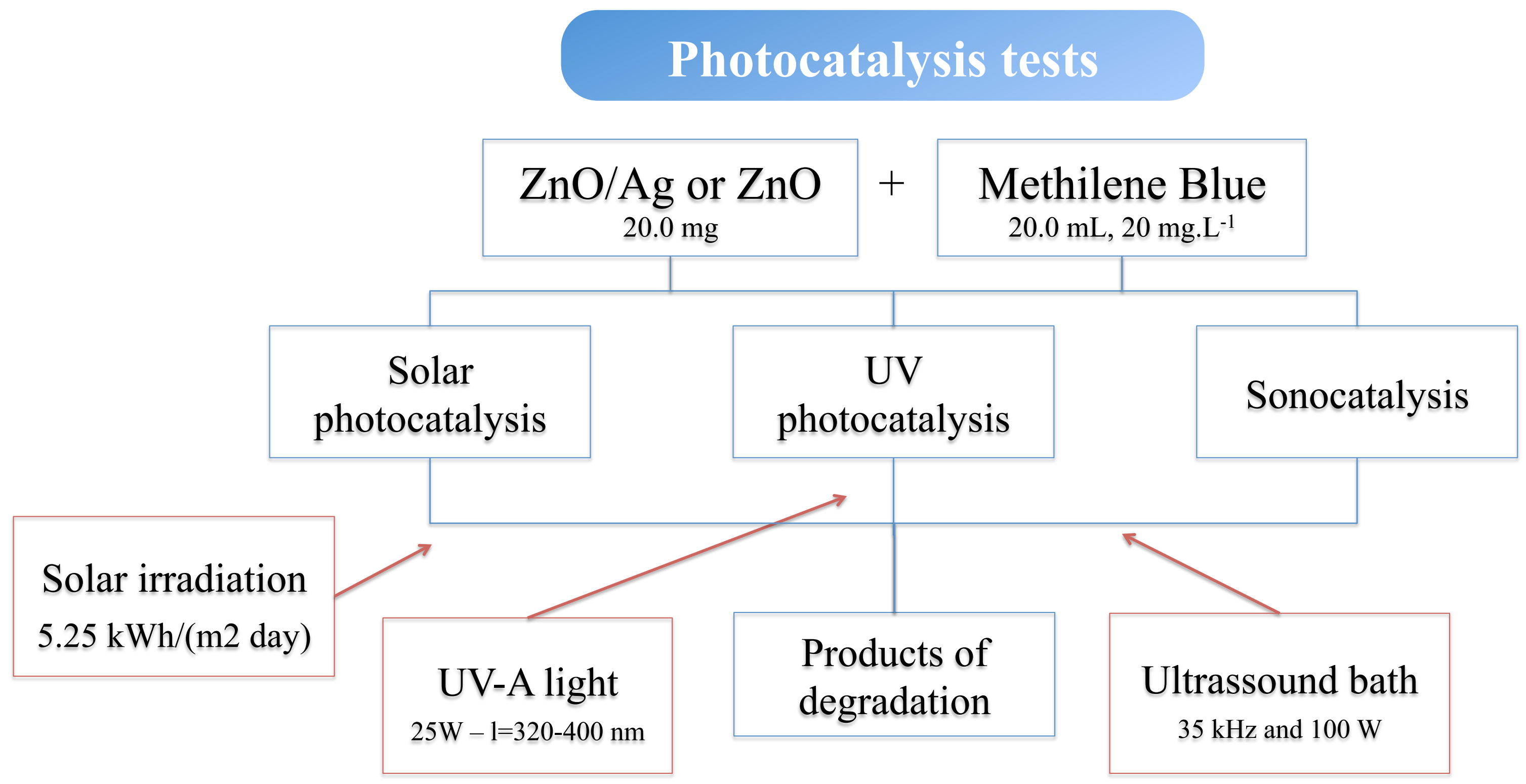
Washed with H_2O

UV-A light
25W – l=320-400 nm

Washed with H_2O

Dried at 45 °C for 24 h

ZnO/Au



Photocatalysis tests

ZnO/Ag or ZnO
20.0 mg
\+
Methilene Blue
20.0 mL, 20 mg.L^{-1}

Solar photocatalysis

UV photocatalysis

Sonocatalysis

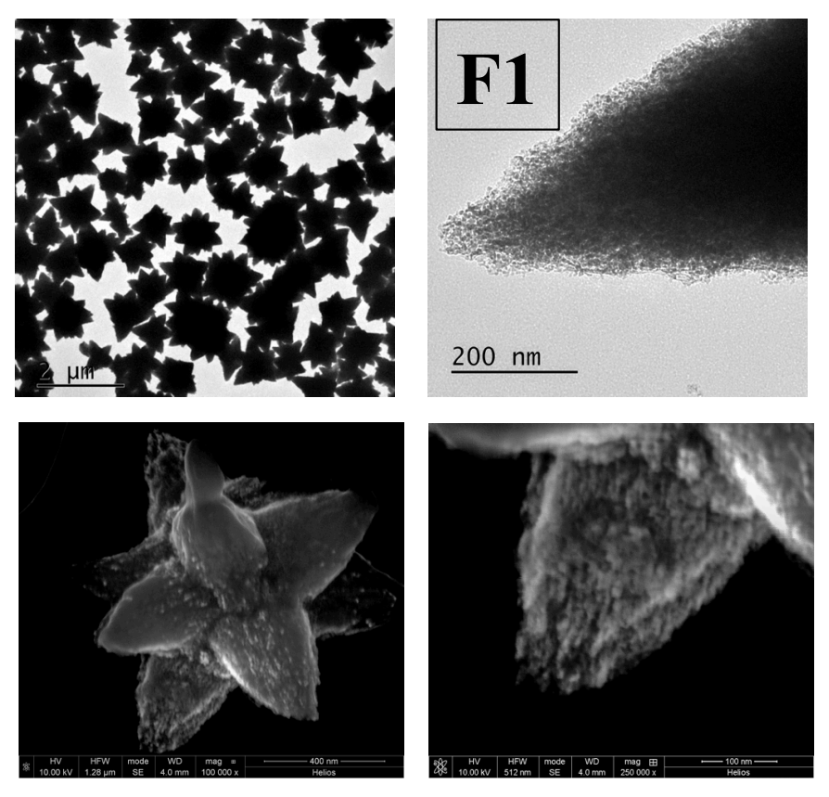
Solar irradiation
5.25 kWh/(m2 day)

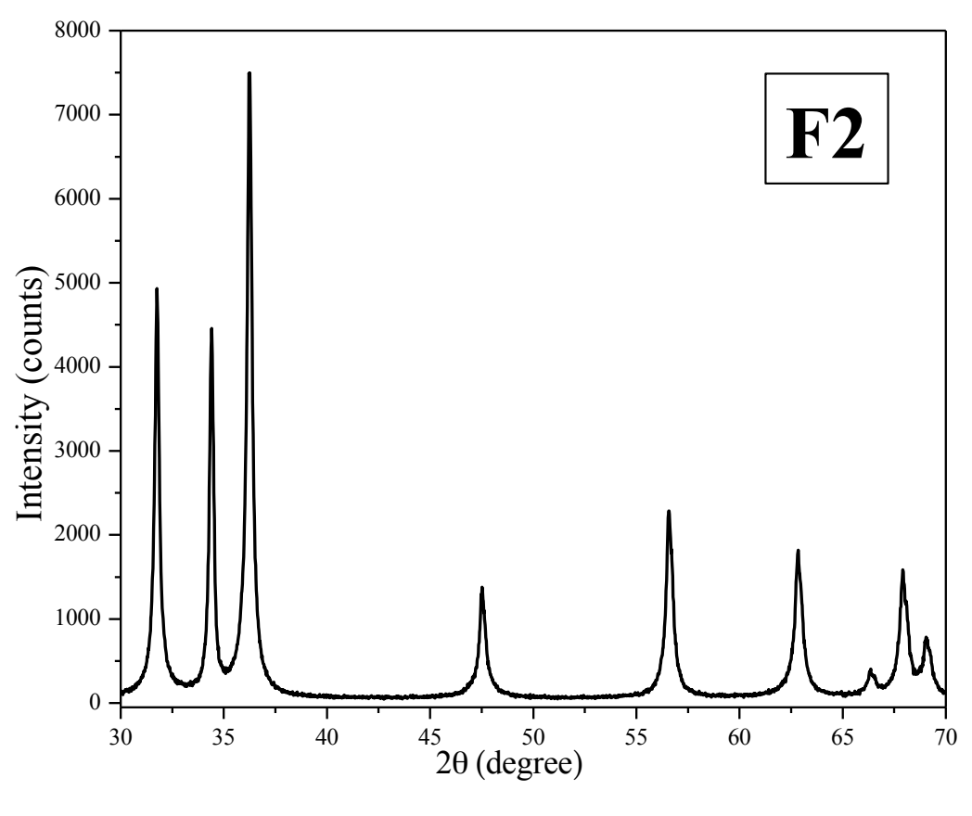
UV-A light
25W – l=320-400 nm

Products of degradation

Ultrassound bath
35 kHz and 100 W

Results and Discussion



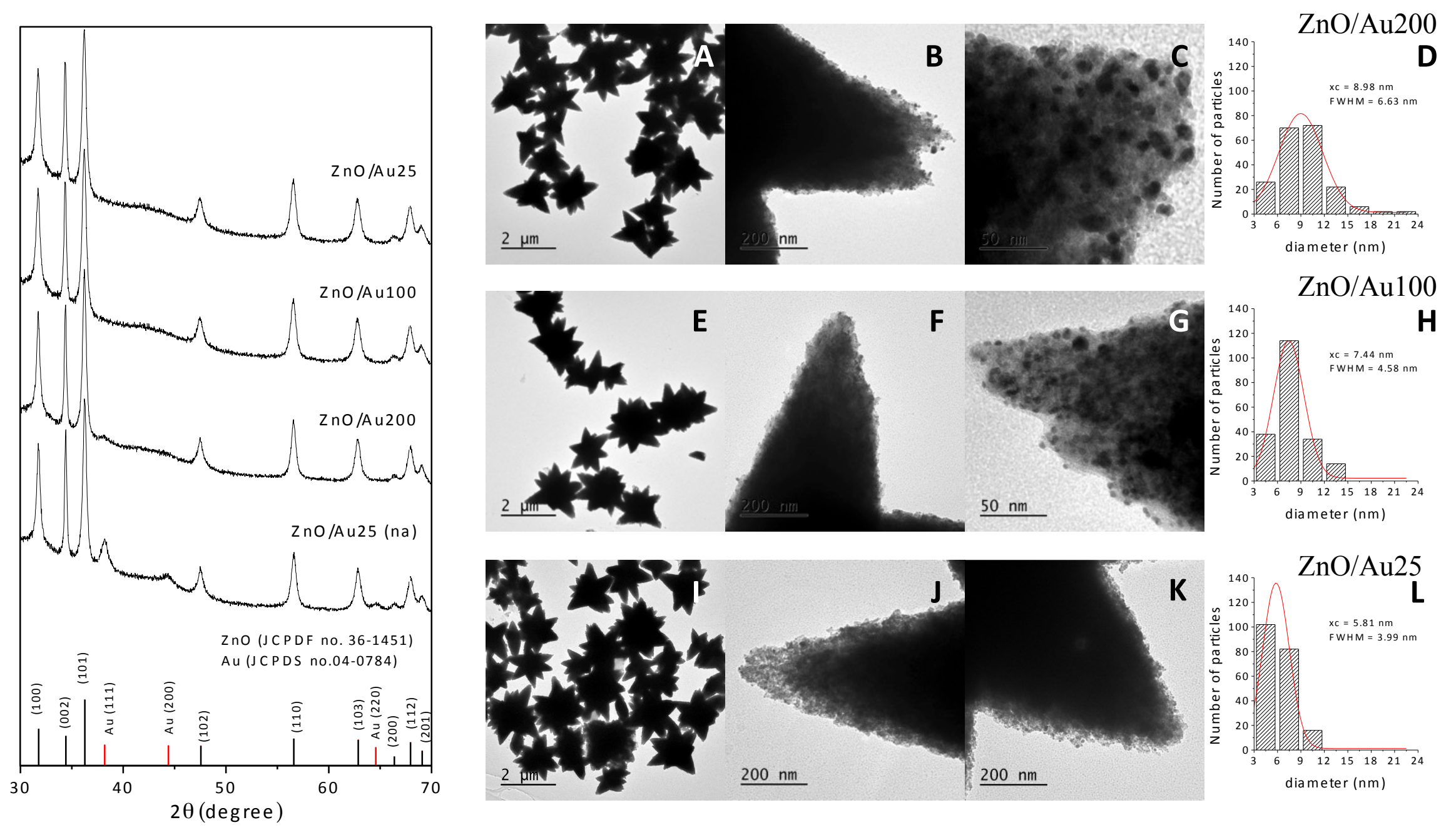


XRD, TEM and SEM analyses showed the presence of hexagonal wurtzite ZnO particles with a star-like shape.

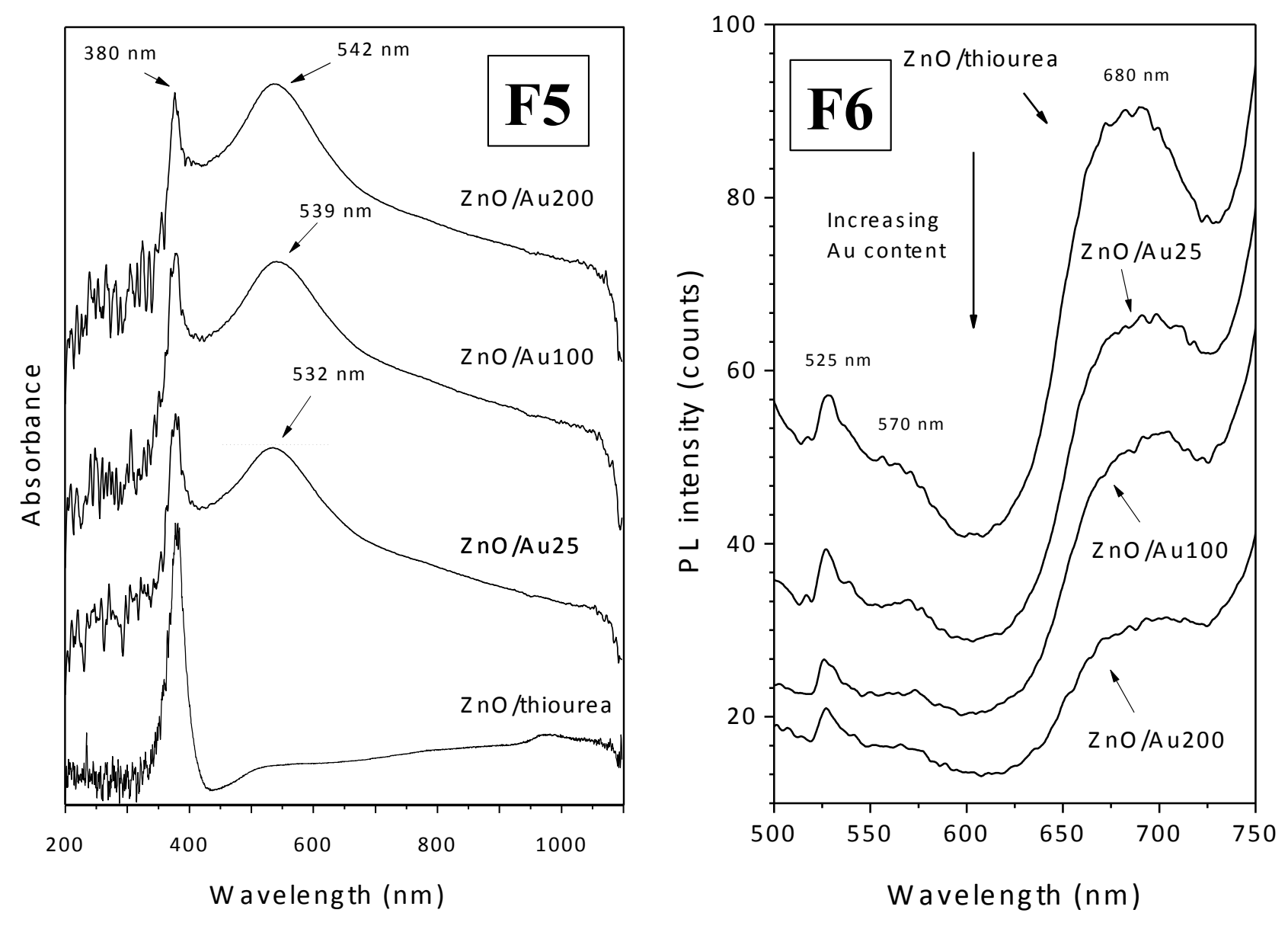
F1. TEM and SEM images of bare ZnO
F2. Powder XRD patterns for bare ZnO

Results and Discussion

The XRD pattern for ZnO/GNP hybrid structures further supports the formation of GNPs due to the presence of a peak at 2θ = 38.44°, was assigned to the (111) plane of gold with face centered cubic structure. A slight increase in average sizes and size distribution is observed when the concentration of $HAuCl_4$ is changed, as seen in TEM images.



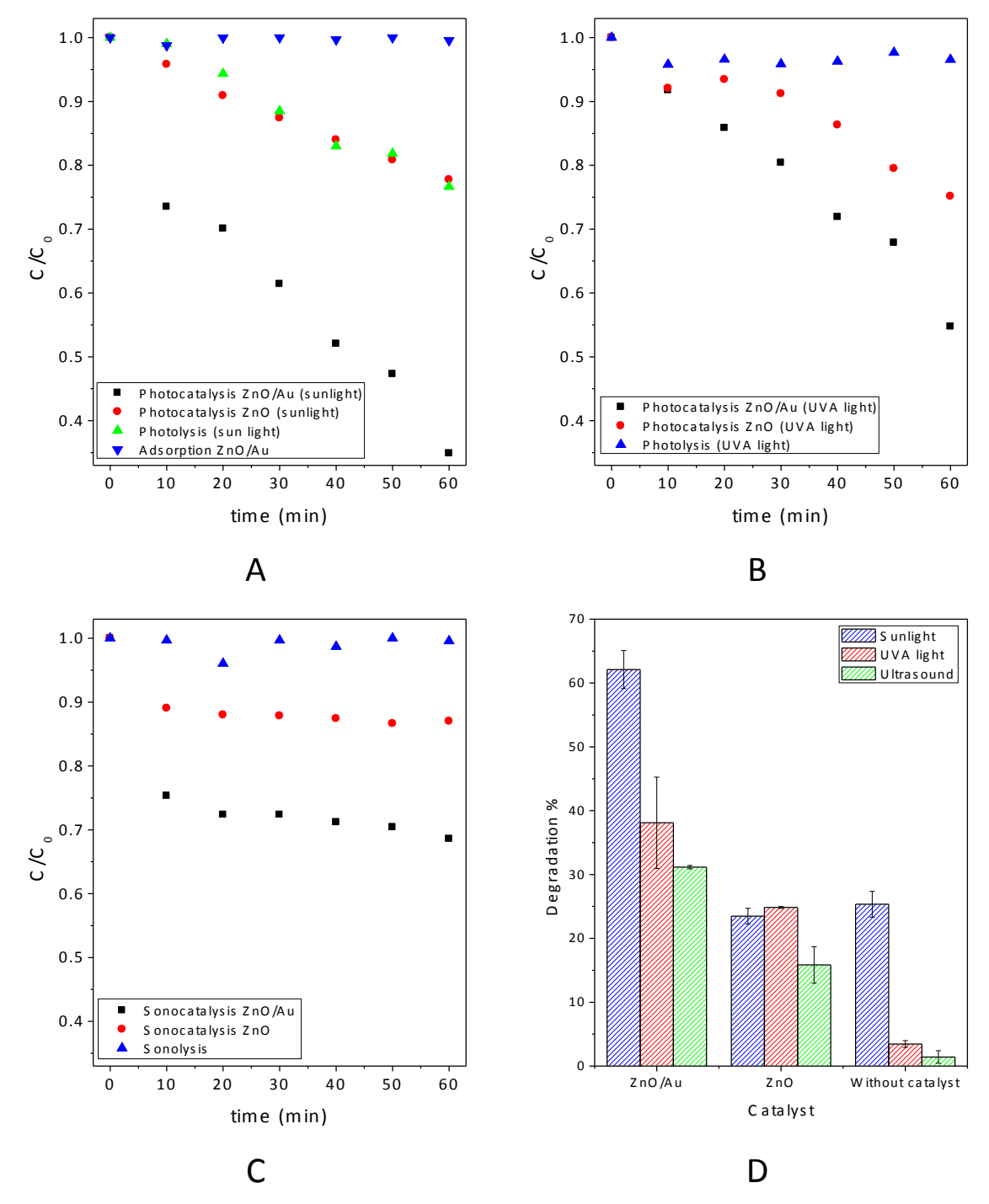
F3 and F4. XRD and TEM images of samples ZnO/GNP



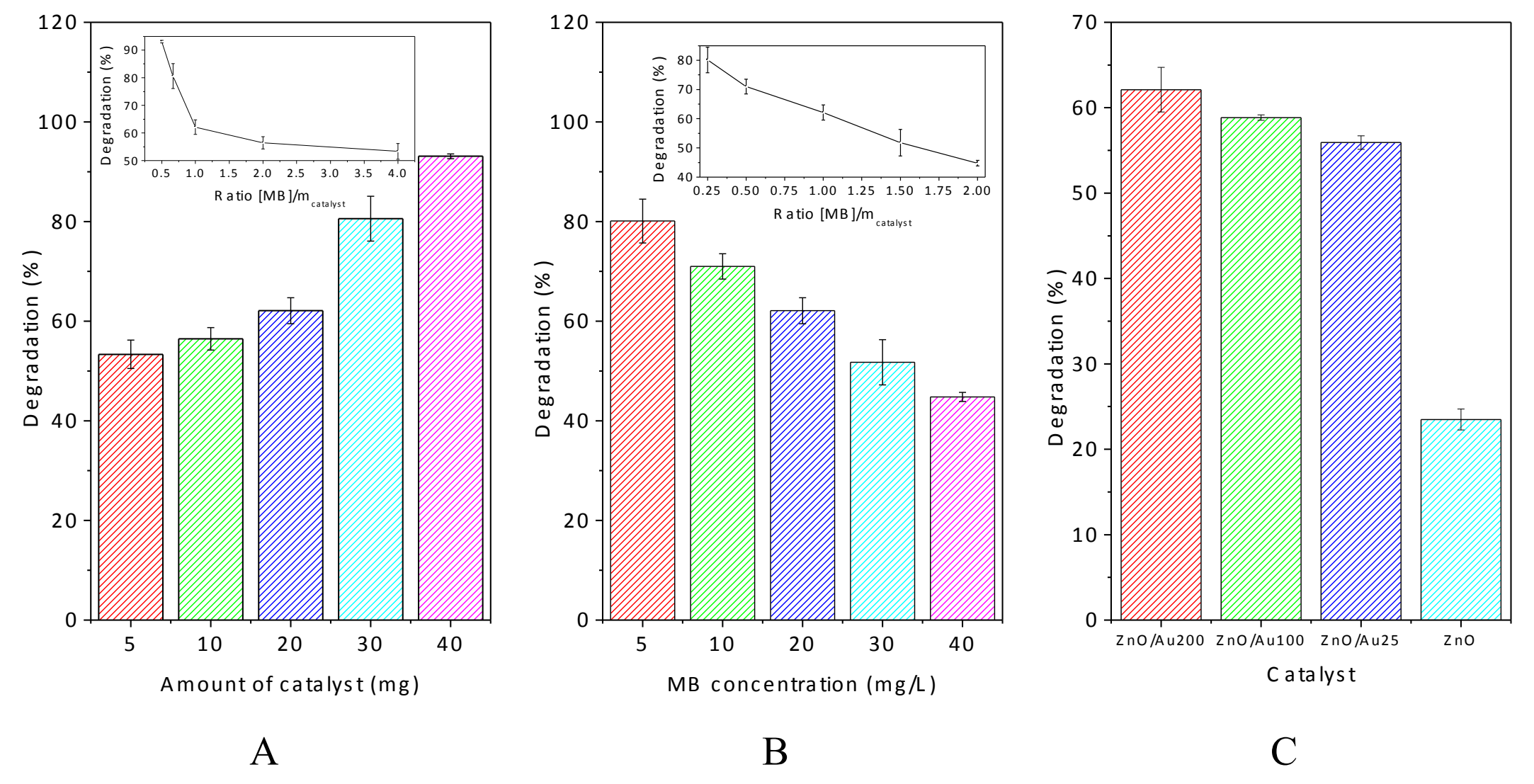
F5 and F6. UV/vis and PL spectra of samples ZnO/GNP

A slight red shift in the LSPR band is observed with the increase in the amount of the Au precursor, as a consequence of particle growth (see F5). When GNPs are associated with ZnO, a systematic decrease of the fluorescence intensity is observed (see F6), suggesting that the metal nanoparticles contributed to the relaxation processes of ZnO.

Figure F7 shows the degradation of MB via 3 methods: solar photocatalysis, UV photocatalysis and Sonocatalysis. Among all methodologies, photocatalysis performed under solar irradiation using hybrid ZnO/GNPs nanocatalysts showed enhanced results for discoloring aqueous solution of the dye.



F7. Degradation of MB using ZnO/Au200.



F8. Degradation of MB under different conditions.

Figure F8 shows other experimental conditions, such as catalyst amount, initial concentration of the dye and the use of samples ZnO/Au25 and ZnO/Au100.

Conclusions

Overall, these results indicate that star-shaped ZnO can be easily prepared by a facile one-pot method and gold nanoparticles can be loaded onto its surface by a photochemical reaction. The presence of metal nanoparticle improved photocatalytic activity of pure ZnO toward degradation of methylene blue. The solar photocatalysis showed improved results, which is a sustainable alternative as it uses a clean, simple, economical and renewable energy source

Bibliography

[1] X. Hou, L. Wang, *RSC Adv.* **2014**, *4*, 56945–56951.
[2] W. He, H.-K. Kim, and coworks. *J. Am. Chem. Soc.* **2014**, *136*, 750–757.

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