A Safe by Design Approach for the Synthesis of a TiO_2-based Paint for the Photocatalytic Degradation of Pollutants under Visible Light

E. Koutsoumpari[1,2], K. Mavronasou[1], A. Grigoropoulos[1] and Ioanna Deligkiozi[1]

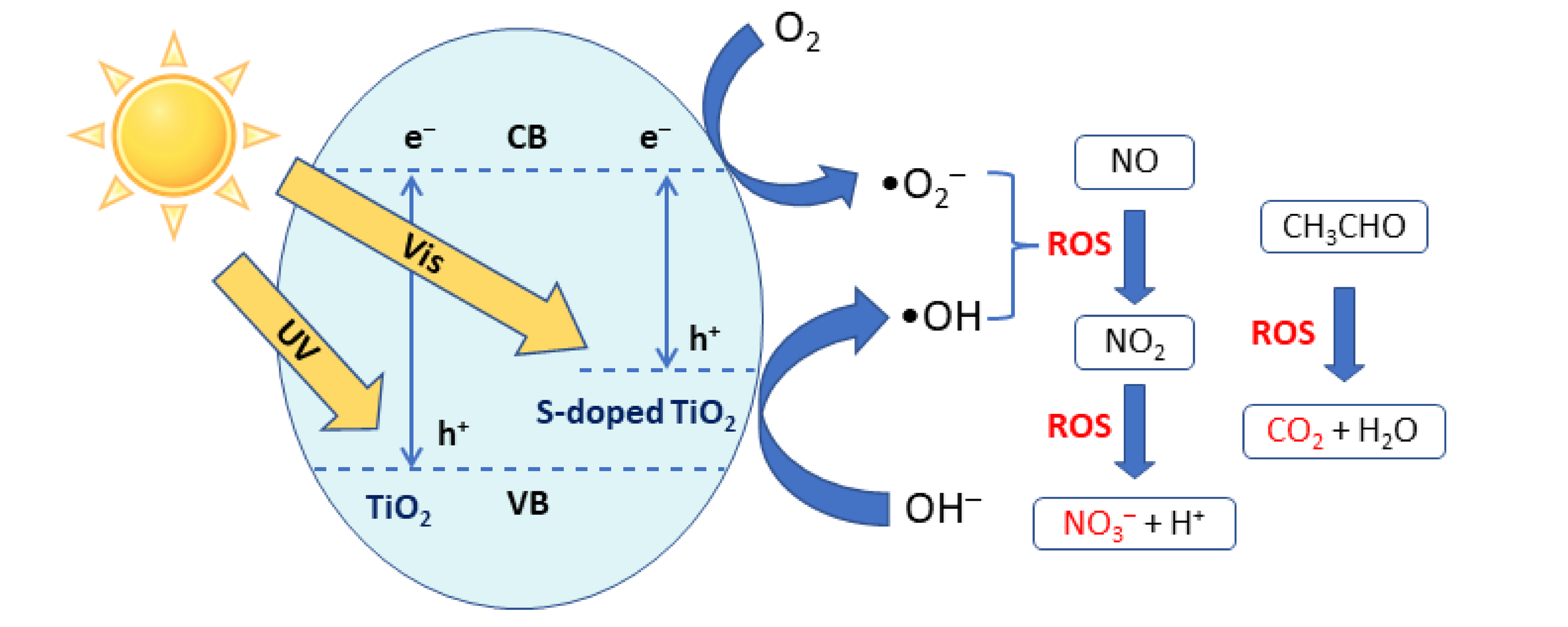
[1]Creative Nano PC, 4 Leventi Street, Peristeri, 12132 Athens, Greece

[2]Department of Material Science, School of Natural Sciences, University of Patras, 26504 Rio, Patras, Greece

e-mail: Efthimia.k@outlook.com.gr; a.grigoropoulos@creativenano.gr

INTRODUCTION

TiO_2 nanoparticles (NPs) are excellent photocatalysts for the photocatalytic degradation of indoor pollutants via the generation of surface Reactive Oxygen Species (ROS) due to light absorption.[1] However, pristine TiO_2 can only absorb the UV fraction of solar light. In addition, TiO_2 NPs were recently classified as a suspected carcinogen.[2] To address these challenges, Creative Nano is currently developing waterborne paints containing sulfur doped TiO_2 NPs to enable photocatalytic activity under visible light. Moreover, the S-doped TiO_2 NPs are entrained in a silica layer to produce **S-TiO_2/SiO_2 multicomponent NPs**, following a **"safe-by-design" (SbD) strategy** to restrict release of NPs into the environment.[3]



Scheme 1. ROS generation by TiO_2-based NPs and photocatalytic degradation of pollutants.

METHODOLOGY

Four different **S(x)-TiO_2/SiO_2** NPs were prepared by sol-gel synthesis, followed by calcination at 500 °C and high-energy ball milling. The nominal S/Ti molar ratio was varied (**x = 0, 2, 5, 7**) to investigate the effect of sulfur-doping, using thiourea as the sulfur precursor. After an optimal sulfur-doping level was identified (**x = 5**), the nominal Si content (**wt% Si = 0, 3, 4, 6**) was varied, using TEOS as the silica precursor. The photocatalytic activity was evaluated in the degradation of Methyl Orange (MO) and MeCHO **under visible light irradiation**. Finally, the best performing nanopowder was incorporated in a waterborne paint formulation.[4]

RESULTS

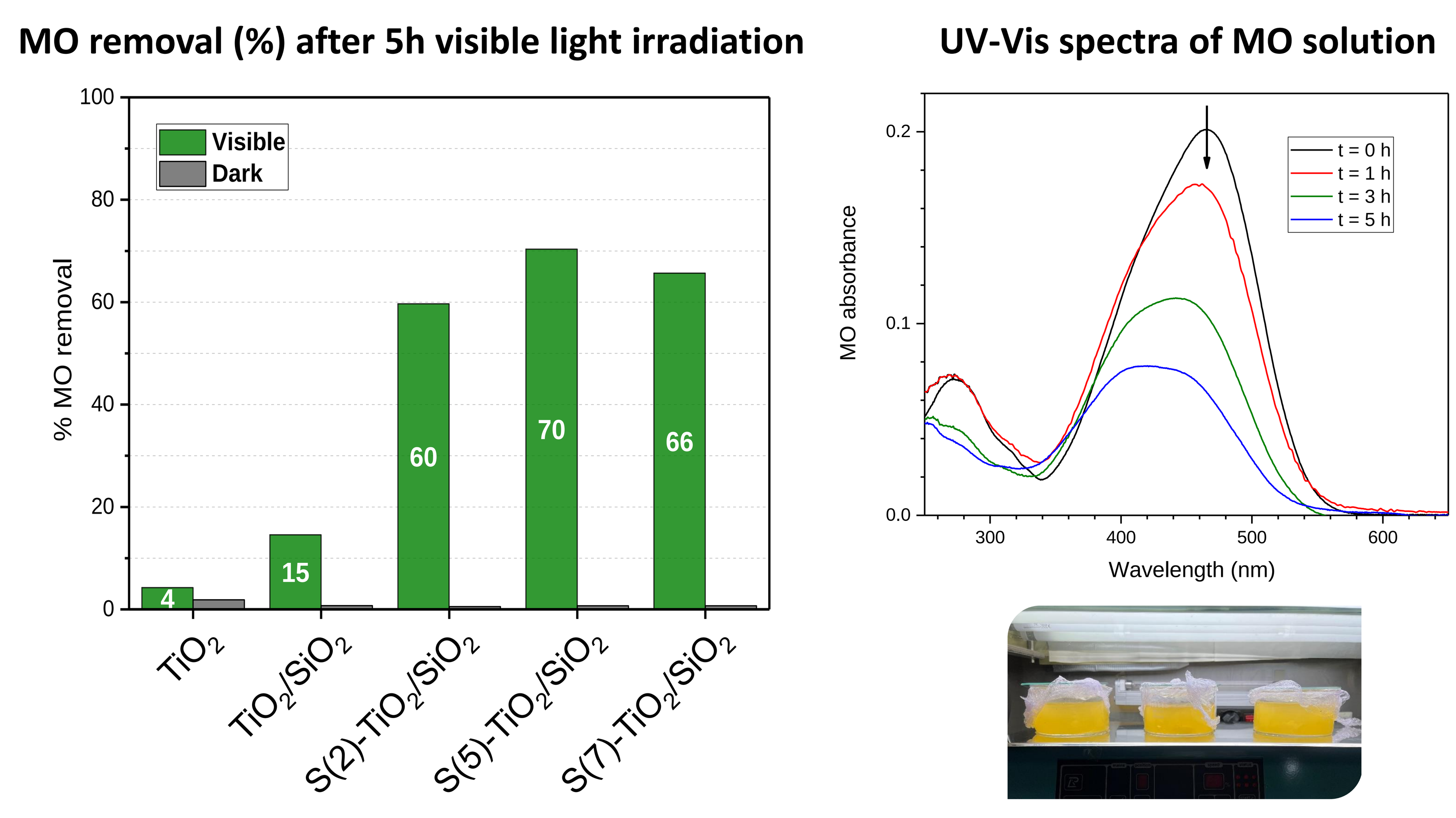


Figure 1. MO photocatalytic degradation in water under visible light, $[MO]_0$ = 2 ppm.

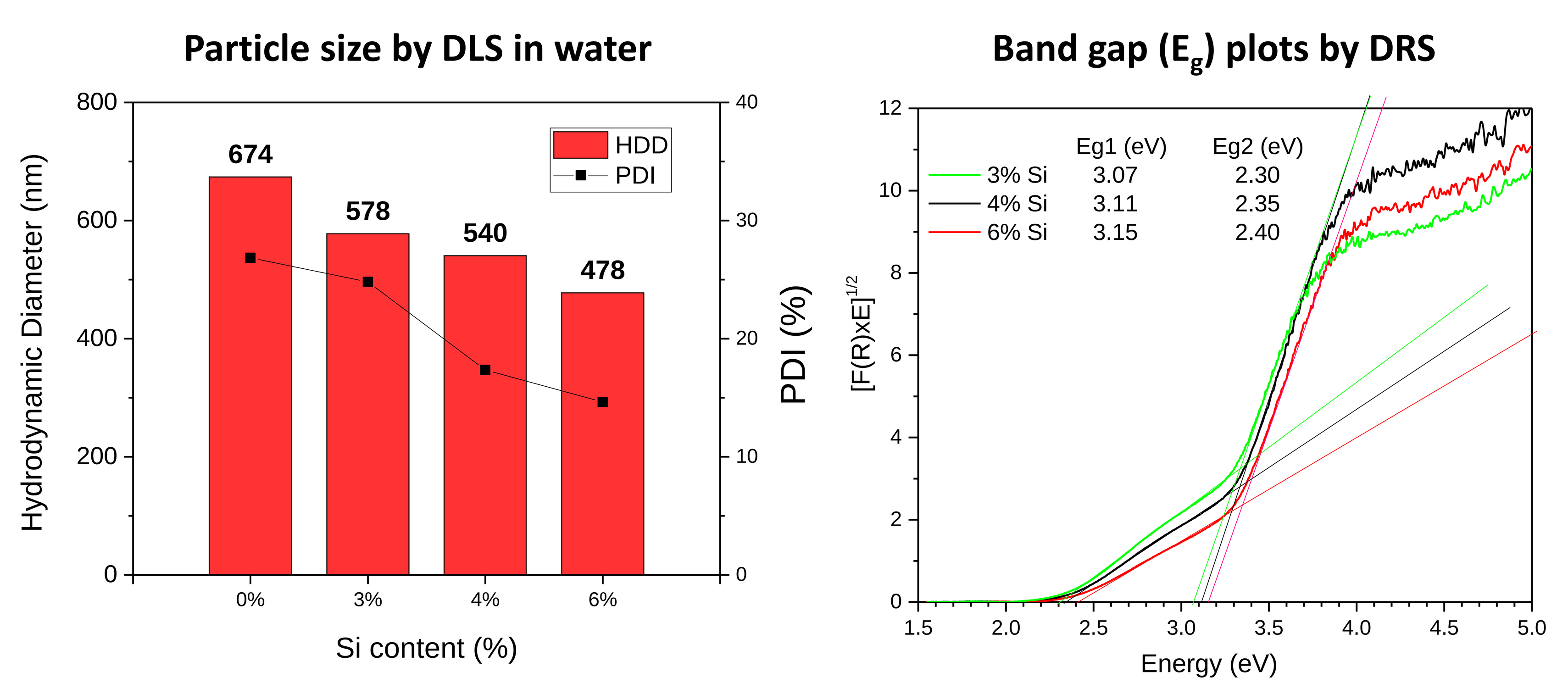


Figure 2. Hydrodynamic diameter (left) and Tauc plots (right) of S(5)-TiO_2/SiO_2-wt% Si NPs.

DISCUSSION

The S(5)-TiO_2/SiO_2 nanopowder with a nominal S/Ti molar ratio of x = 5 showed the highest activity in MO photocatalytic degradation. All S-doped samples achieved higher MO removal under visible light irradiation compared to TiO_2 and TiO_2/SiO_2 (Fig.1). The particle size decreased and the band gap increased with increasing Si content (Fig.2). The introduction of SiO_2 led to significantly more porous NPs. TEM images suggested the formation of an external SiO_2 layer (Fig.3). This resulted in a **4-fold enhancement of MeCHO** photocatalytic degradation under visible light (Fig.4) compared to S-TiO2 (no SiO_2 modification). Finally, the synthesis of S(5)-TiO_2/SiO_2 was scaled up to 50 g to produce 1 Kg of a waterborne paint that is active in the photocatalytic degradation of pollutants (Fig.5).

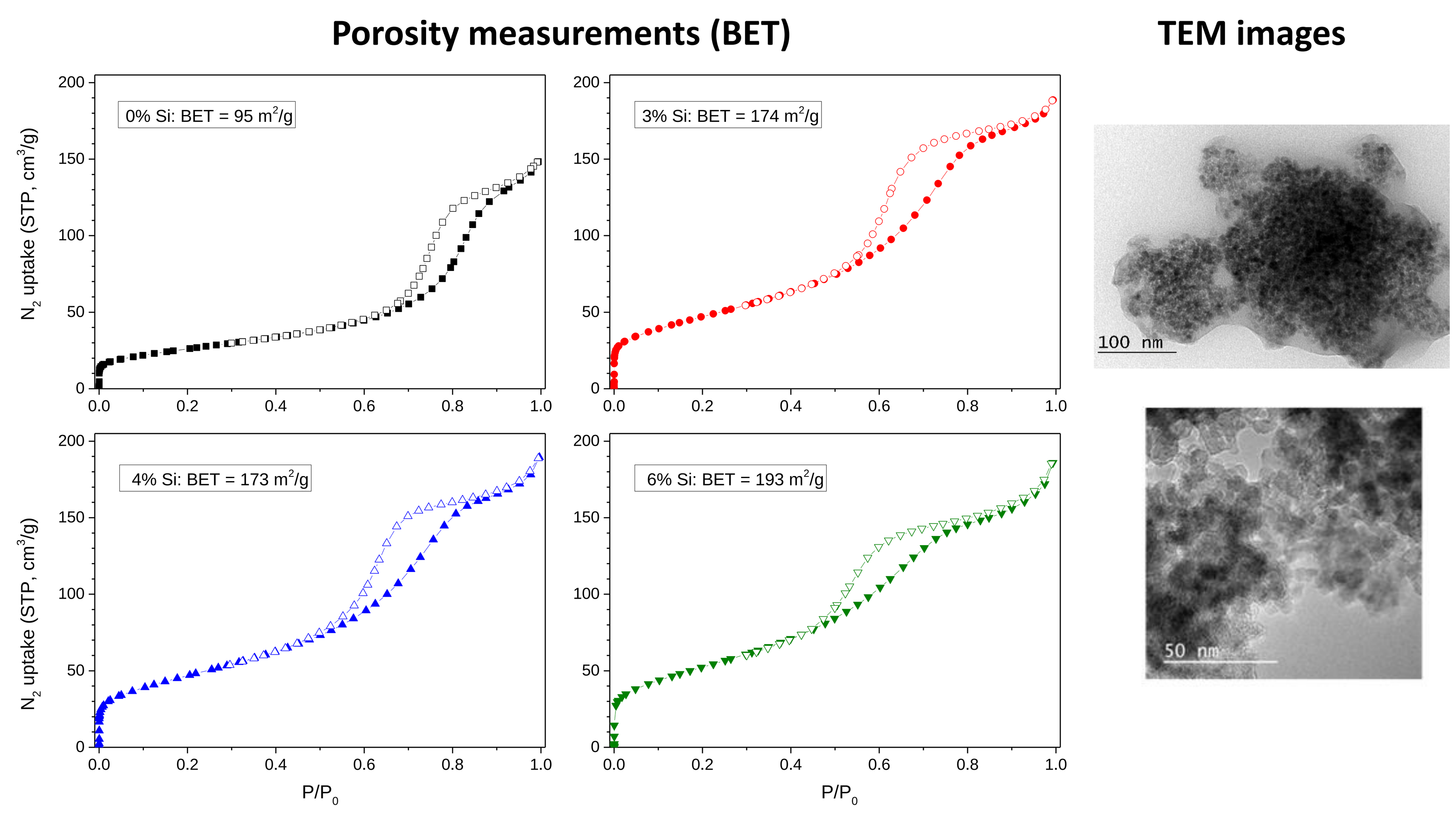


Figure 3. N_2 uptake for different SiO_2 content (left) and TEM images for 4 wt% Si (right).

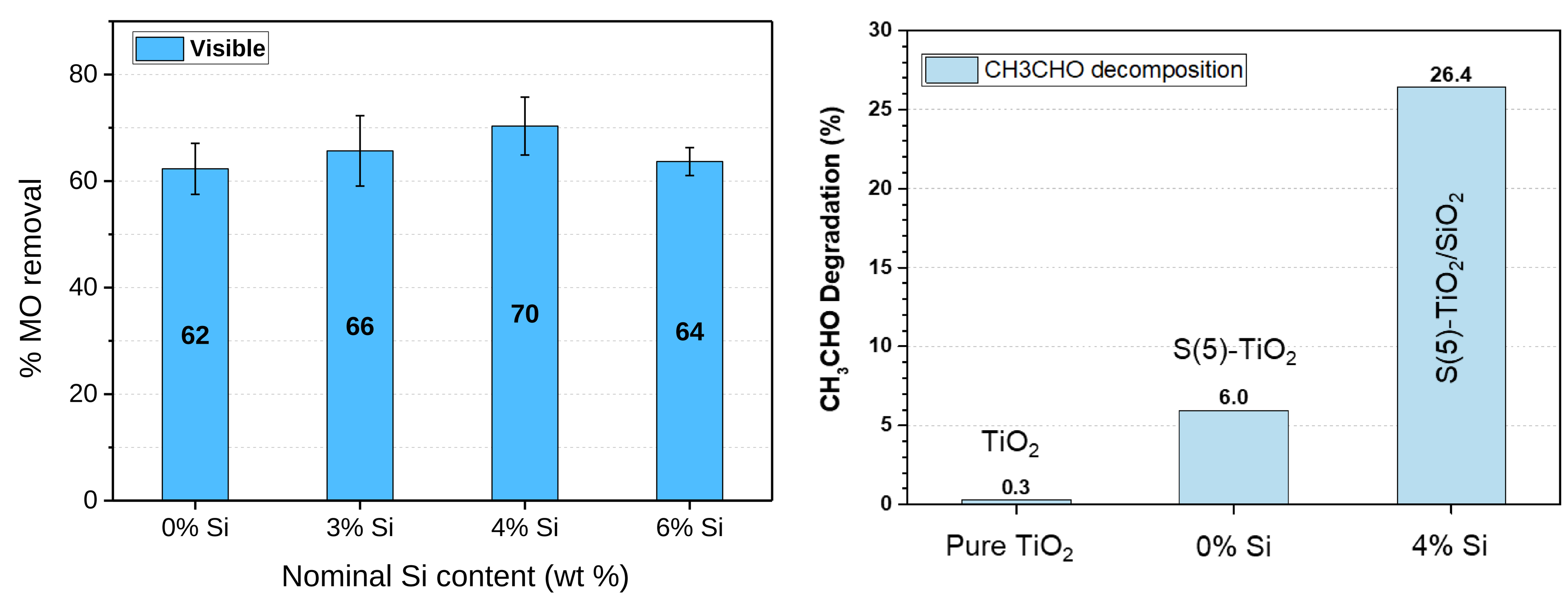


Figure 4. MO (t=5h) and aldehyde (t=1h) photocatalytic degradation under visible light.

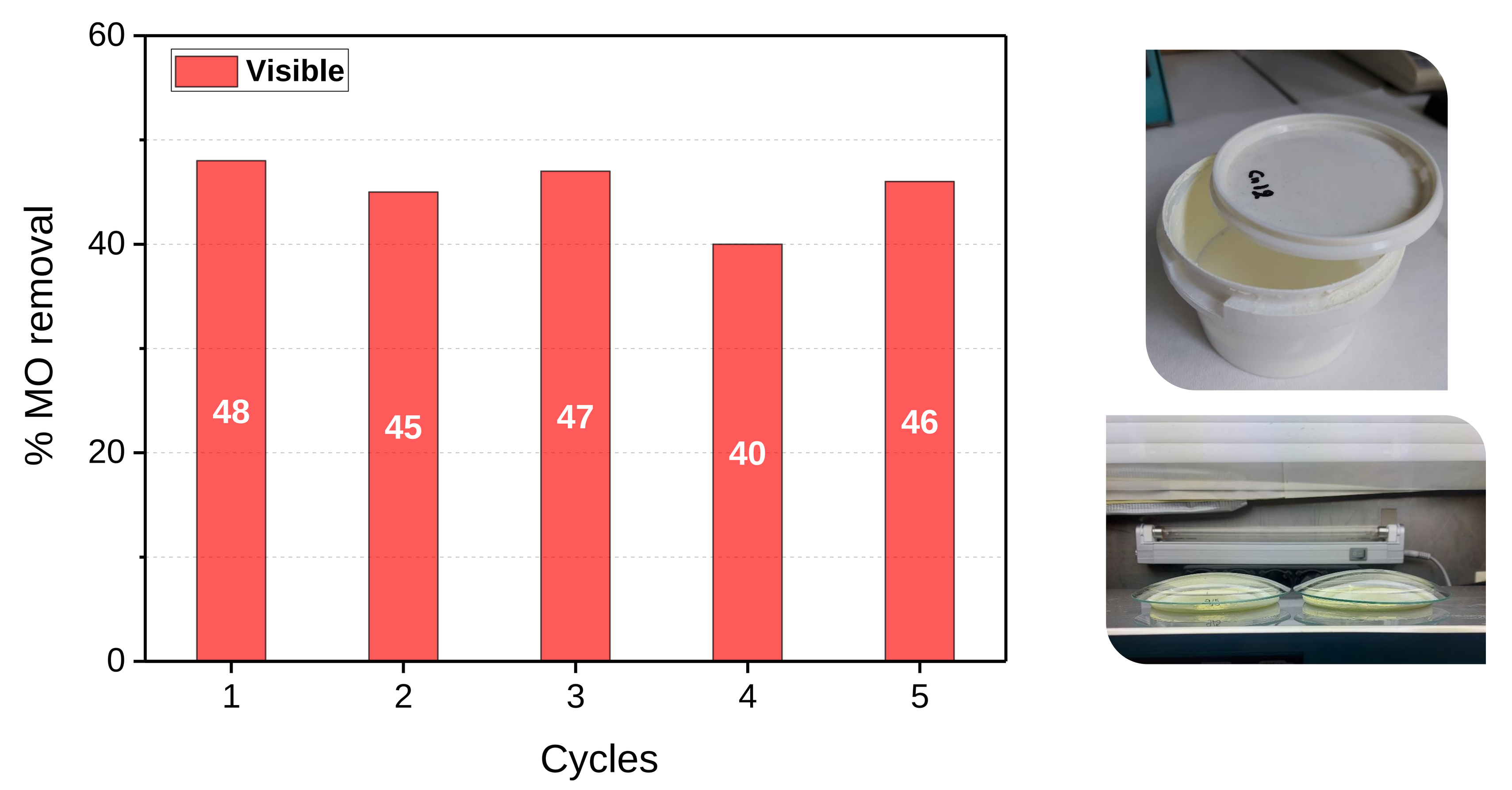


Figure 5. MO degradation under visible light over waterborne photocatalytic paint.

CONCLUSIONS

1) A series of S(x)-TiO_2/SiO_2-wt% Si NPs were synthesized and evaluated for the photocatalytic degradation of MO in solution.
2) An optimal S/Ti molar ratio (x = 5) and SiO_2 modification (4 wt% Si) was found.
3) The introduction of SiO_2 restricts TiO_2 particle growth and increases porosity, therefore enabling the photocatalytic degradation of MeCHO.
4) The best performing nanopowder S(5)-TiO_2/SiO_2 was incorporated in a photocatalytically active waterborne paint.

REFERENCES

1) S. Banerjee et al. *J. Phys. Chem. Lett.* **2014**, *5*, 2543
2) Commission Delegated Regulation (EU) 2020/217
3) R. Bengalli et al. *Nanomaterials,* **2019**, *9*, 1041
4) T. Kalampaliki et al., *Nanomaterials,* **2021**, *11*, 2543

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862195, "SbD4Nano".