In-situ photochemical synthesis of ZrO_2 NPs and fabrication of nanocomposites with EA/TPGDA Polymeric Matrices

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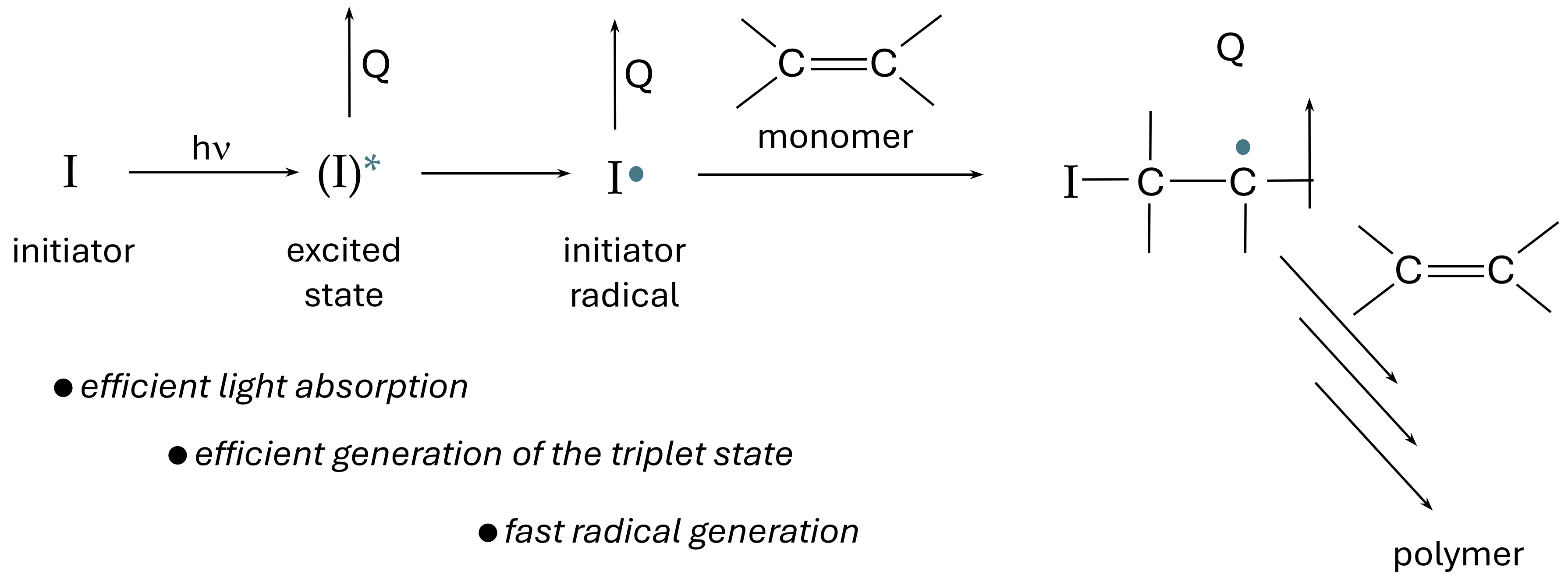
YTU CHEMISTRY DEPARTMENT

Photoinitiation of Free Radical Polymerization



- *efficient light absorption*
- *efficient generation of the triplet state*
- *fast radical generation*
- *high addition rate constant*

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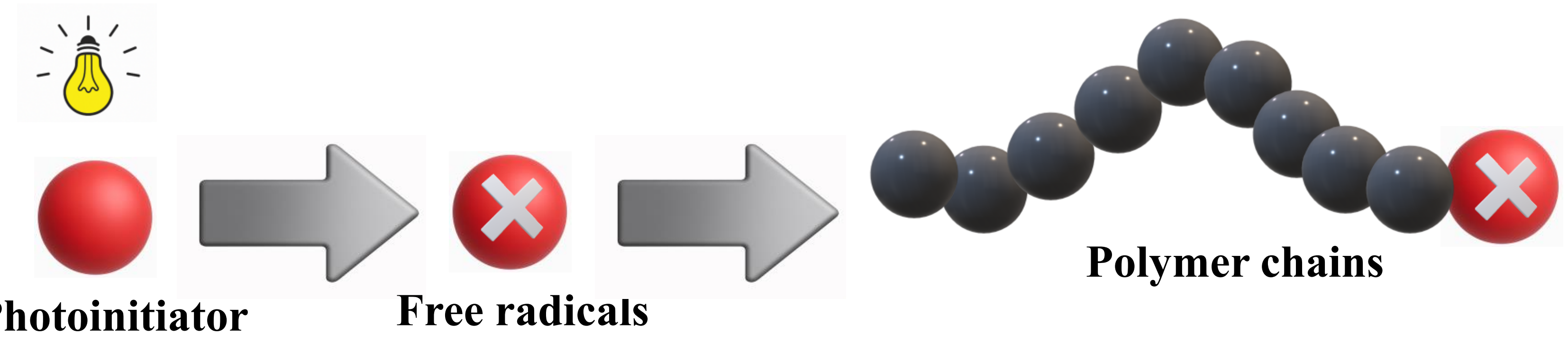
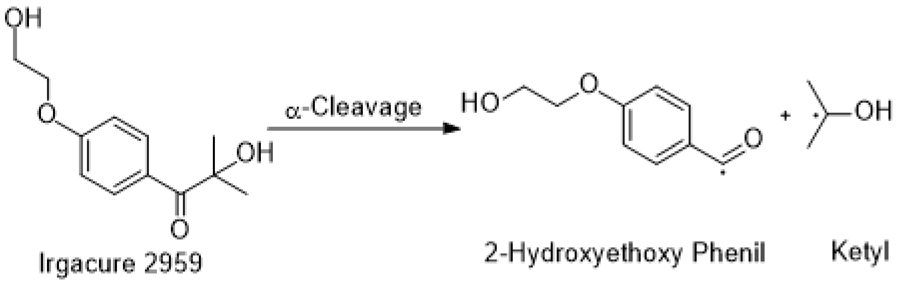
Photopolymerization Process



Type I



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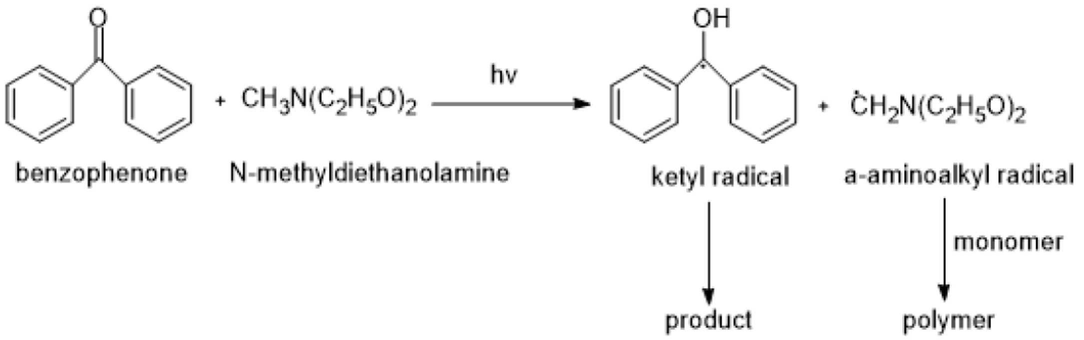

Advantages of UV-Curing Technique

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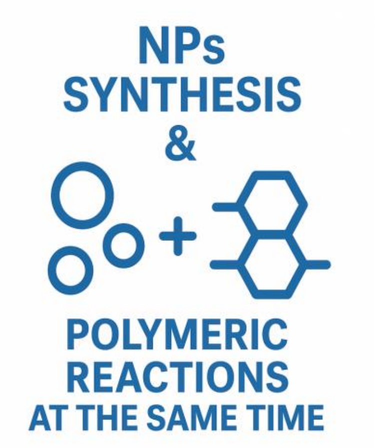

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Photoinduced Reduction of Metallic salts

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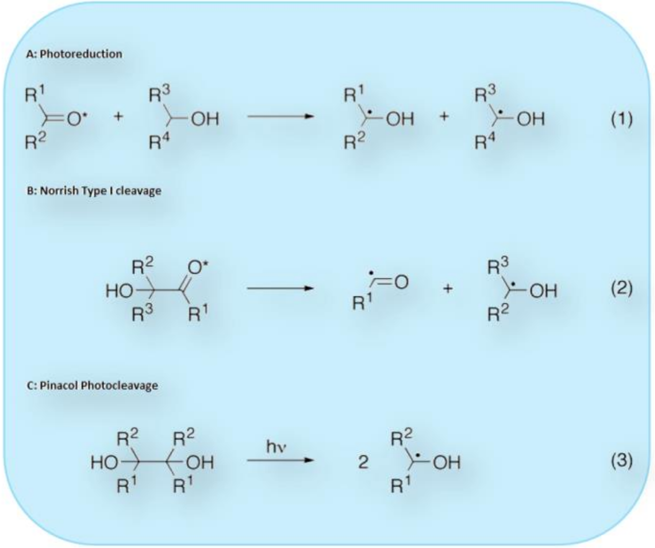
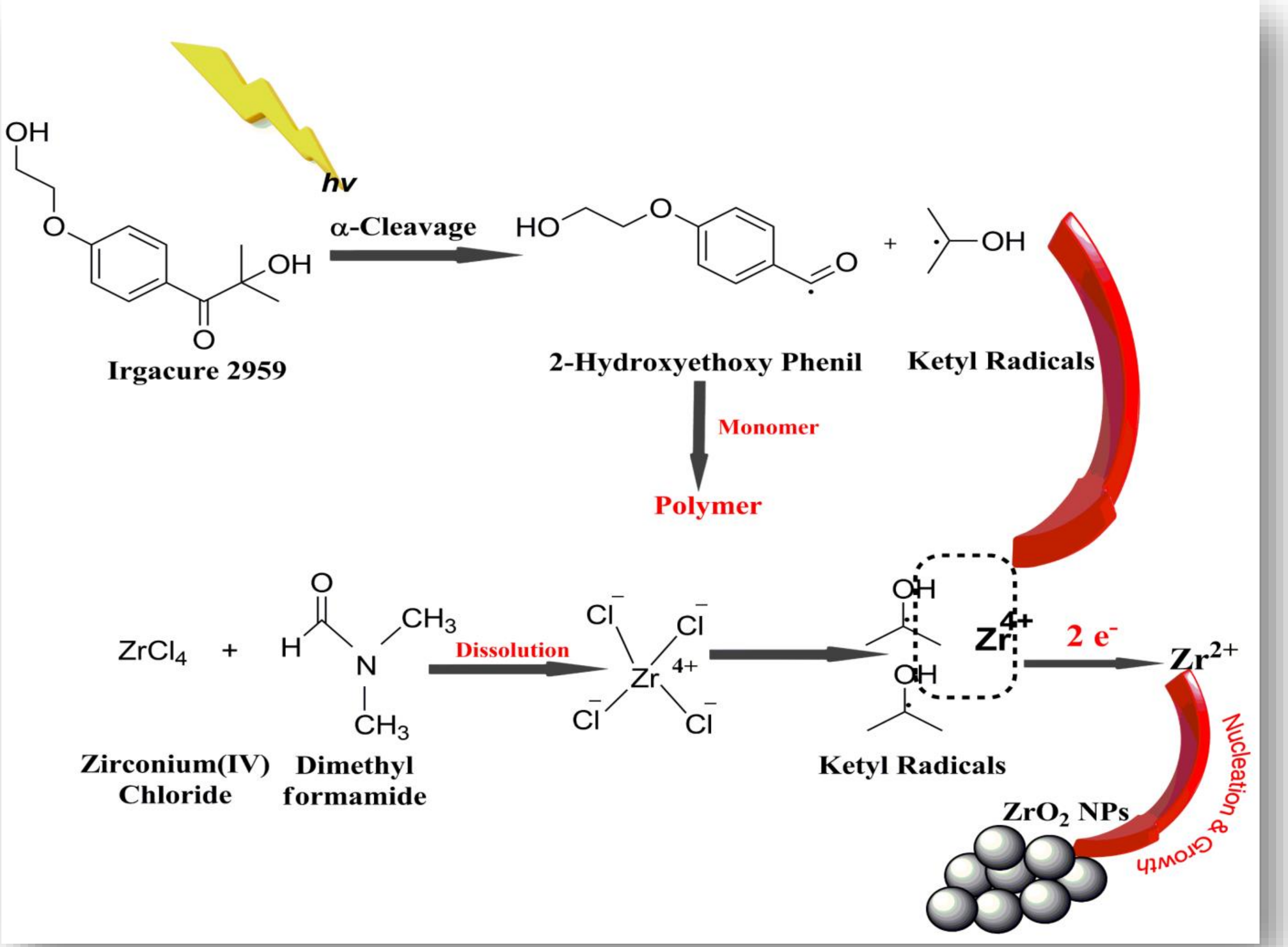
Ketyl radicals, which can be easily produced photochemically, are generally used to reduce metal salts.





Applications Areas of ZrO_2 Nps

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Photocatalysis
High band gap & fluorescence

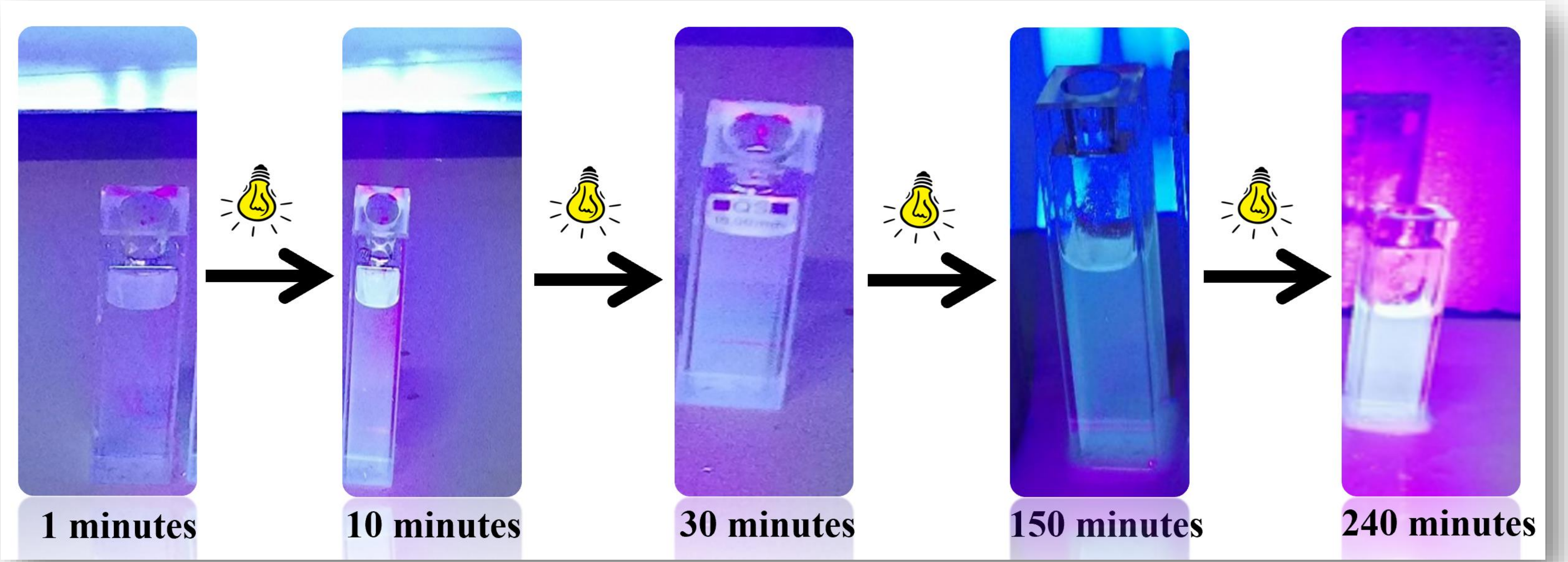
Biomedical Imaging
Cancer cell bio-mapping

Dental & Prosthetics
High mechanical strength

Semiconductors
Excellent electrical conductivity

Solar Cells & Sensors
Gas and solvent detection

In-situ photochemical synthesis of ZrO_2 NPs



In-Situ Photochemical Preparation of ZrO_2 NPs in DMF

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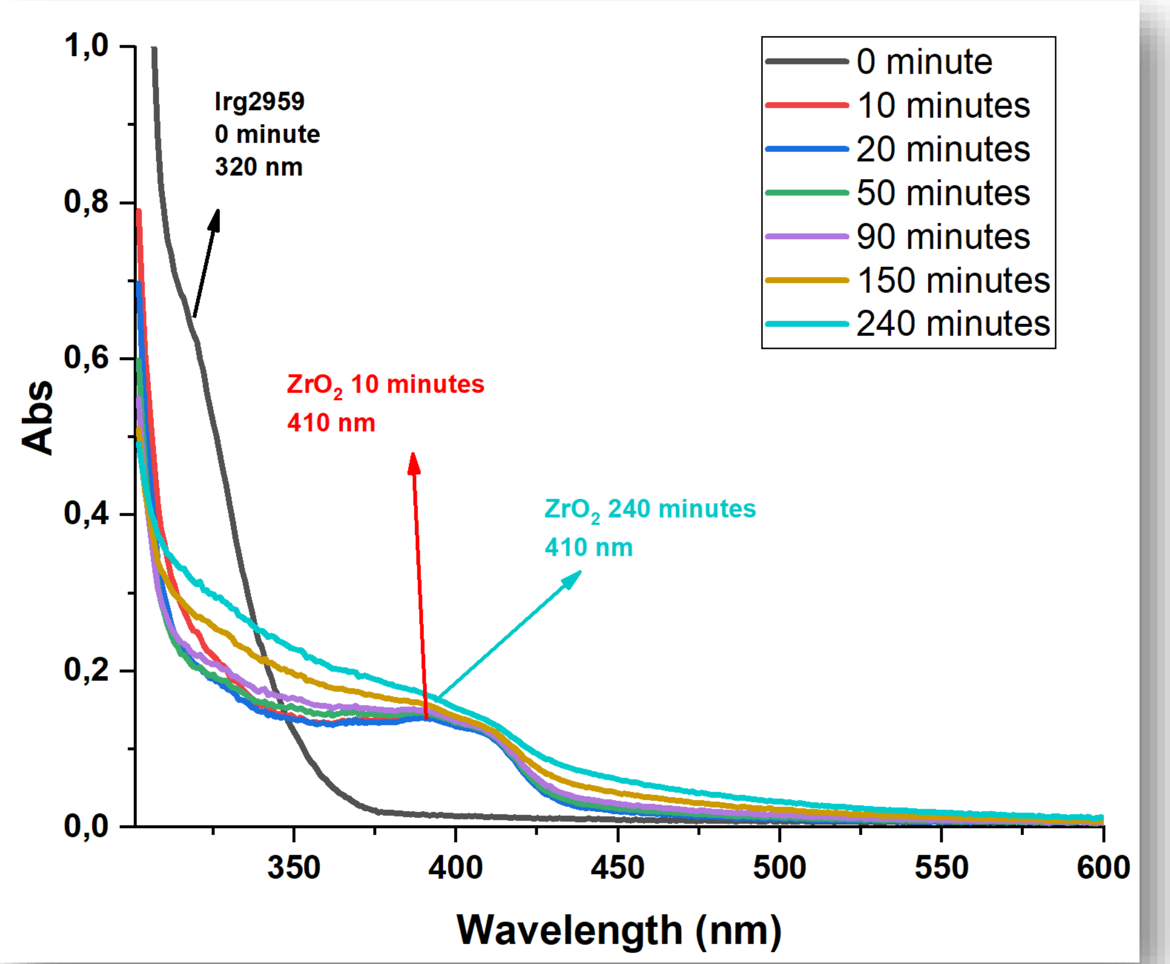
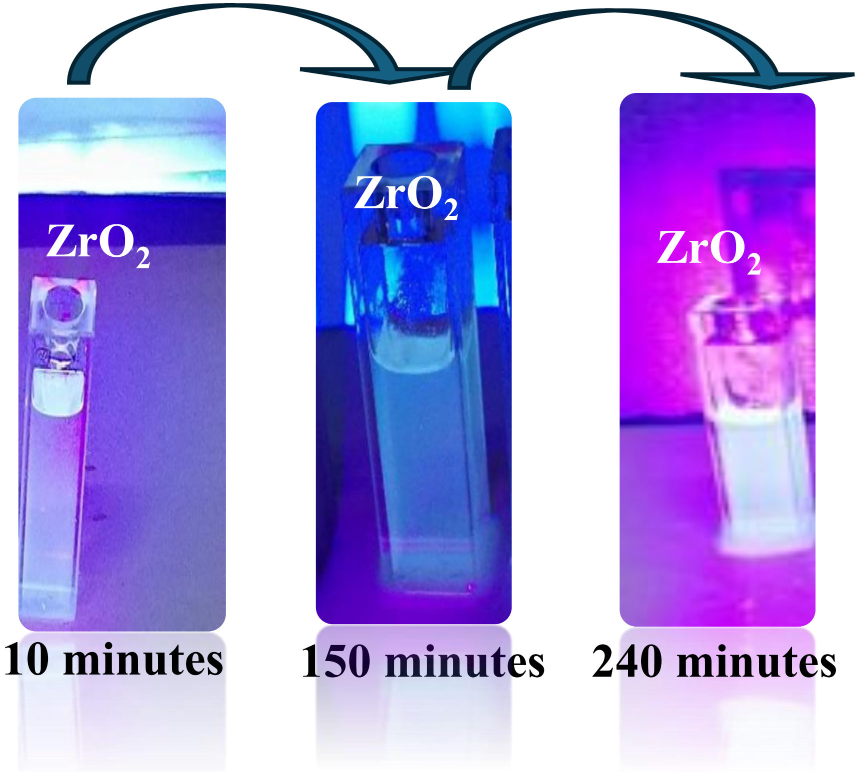
Solution 1:

3.8×10^{-3} M $ZrCl_4$

2.7×10^{-3} M Irg 2959

in DMF





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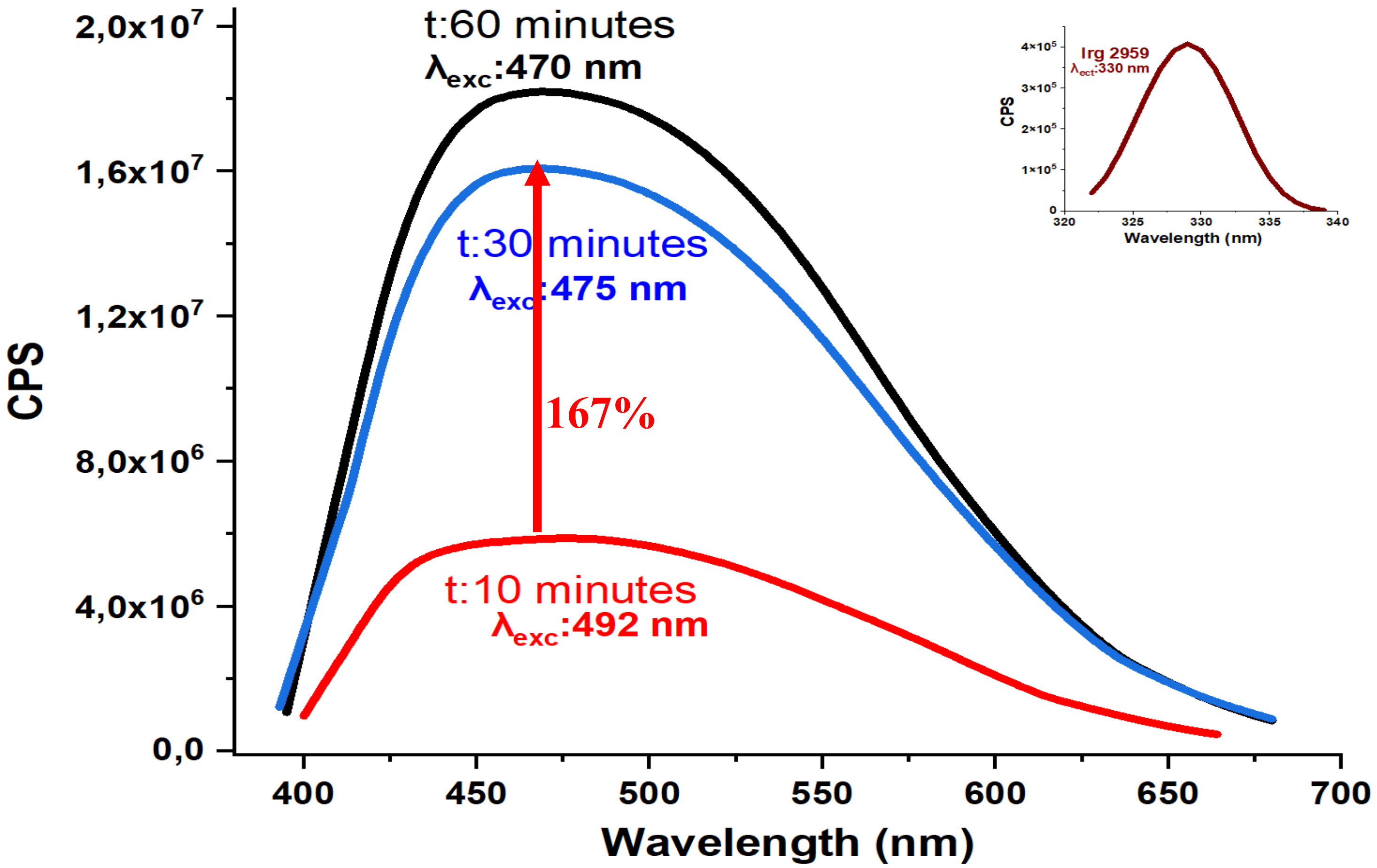
Fluoresence Emission Studies of ZrO_2 NPs

Solution 1:

3.8×10^{-3} M $ZrCl_4$

2.7×10^{-3} M Irg 2959

in DMF

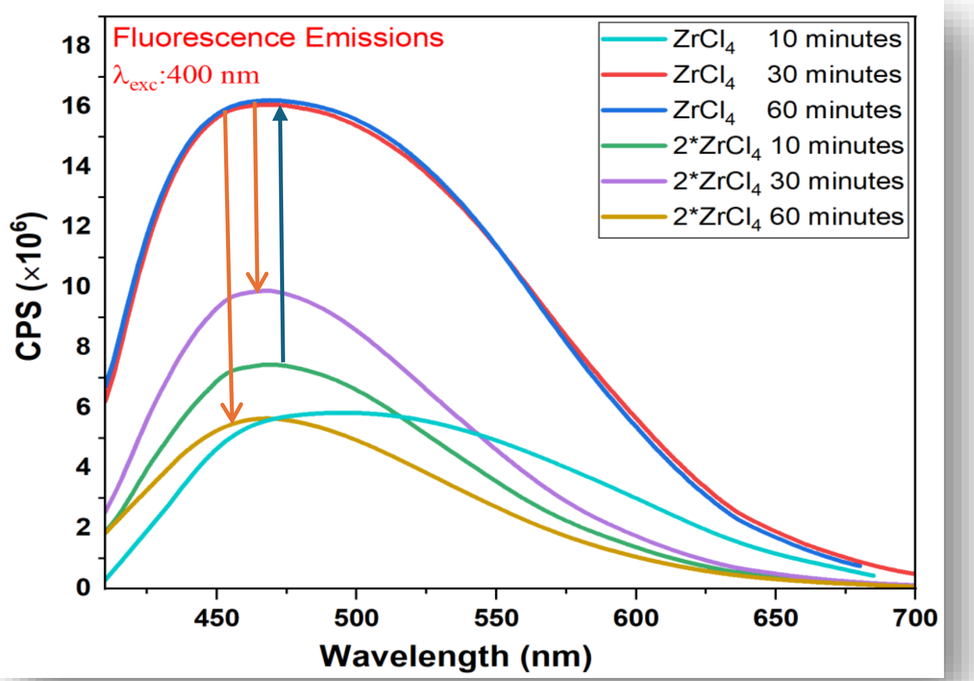


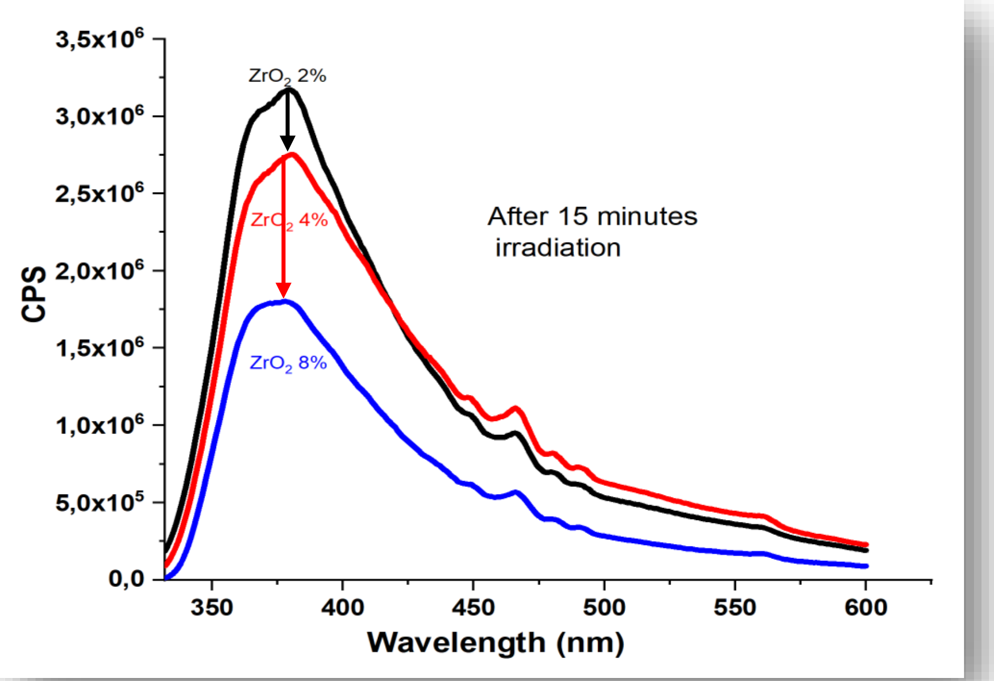
In-situ photochemical synthesis of ZrO_2 nanoparticles from $ZrCl_4$, and the effect of concentration and irradiation time on their fluorescence emission

- Irradiation time & concentration of ZrO_2 NPs
- Increasing emission intensity of ZrO_2 during 15 minutes of irradiation

Solution 1:
3.8×10^{-3} M $ZrCl_4$
2.7×10^{-3} M Irg 2959
in DMF

Solution 2:
7.6×10^{-3} M $ZrCl_4$
2.7×10^{-3} M Irg 2959
in DMF





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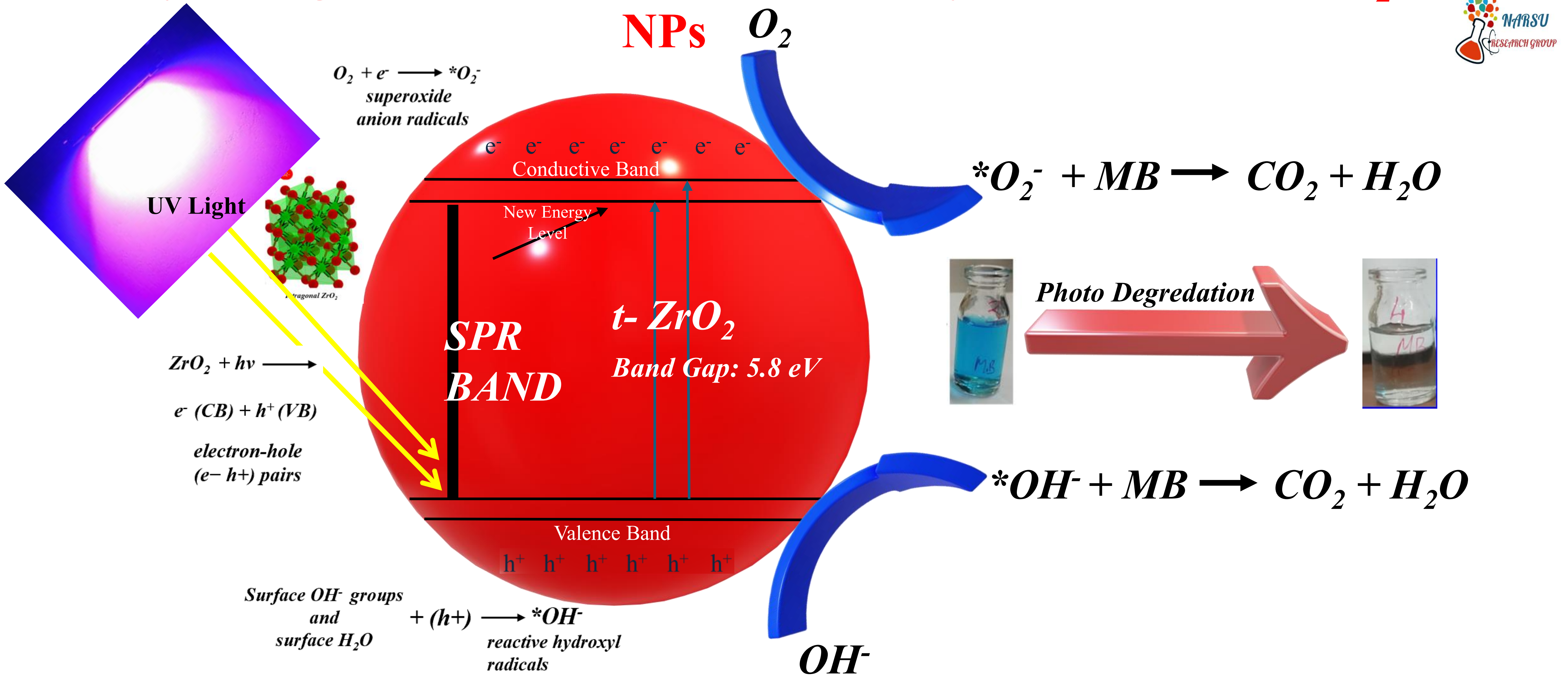
Photocatalytic Degradation Mechanism of Methylene Blue with ZrO_2 NPs



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Photocatalytic Degradation of Methylene Blue with ZrO_2 NPs

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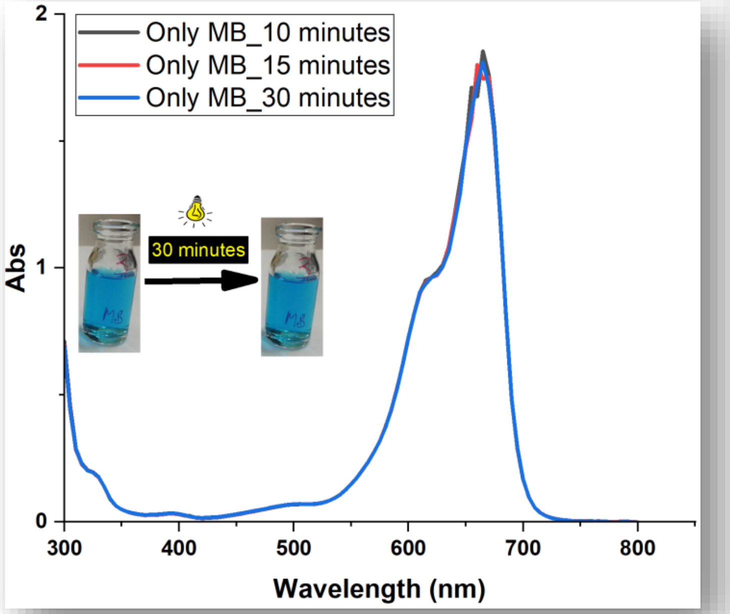
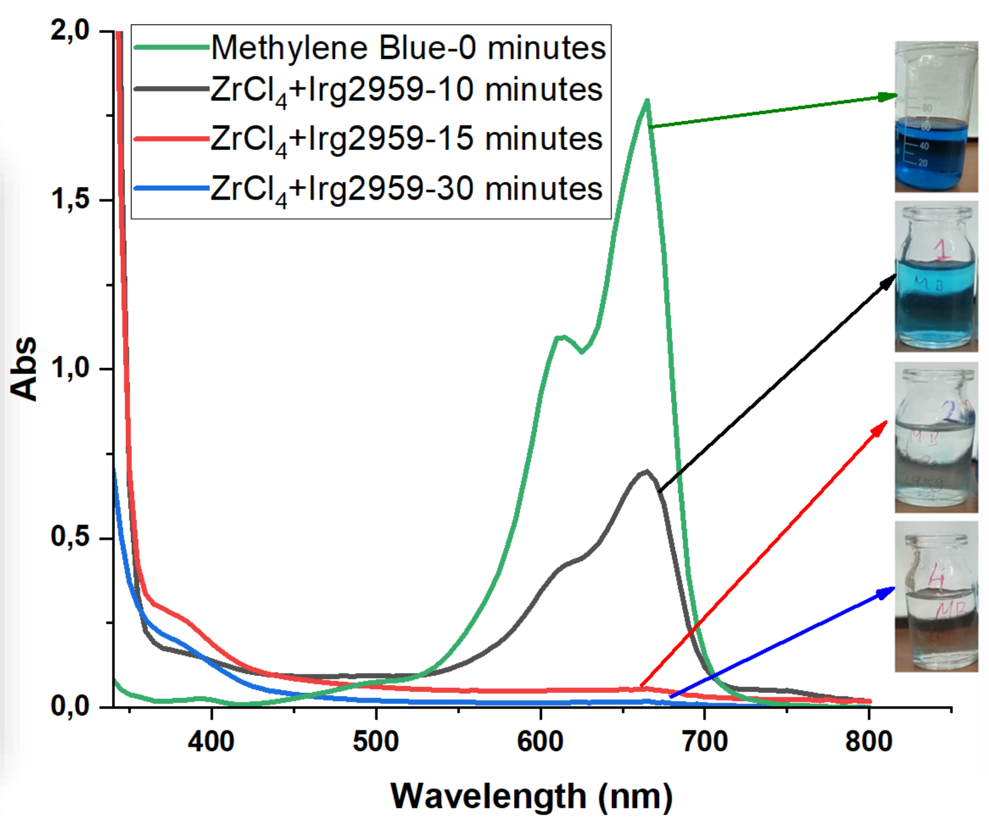
Solution 1:
3.8×10^{-3} M $ZrCl_4$
2.7×10^{-3} M Irg 2959
in DMF

10 ppm MB- 6 ml





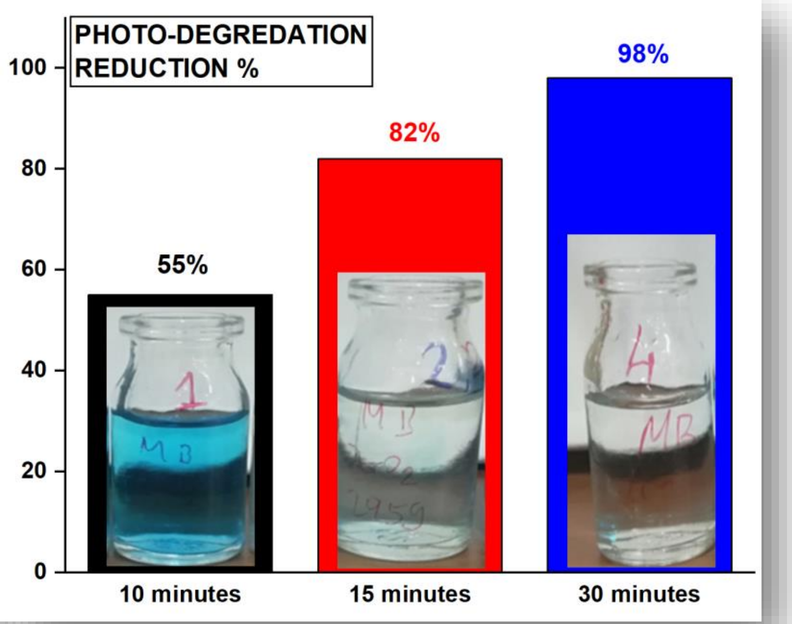
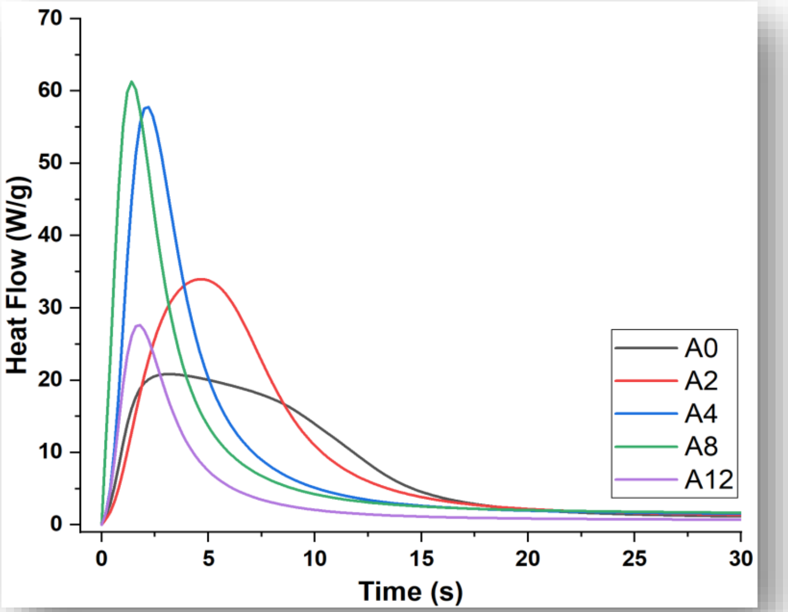
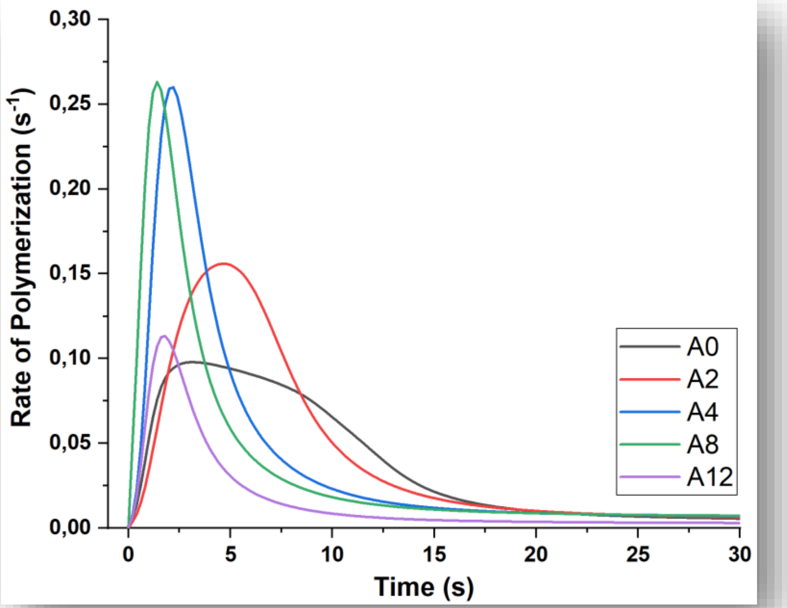
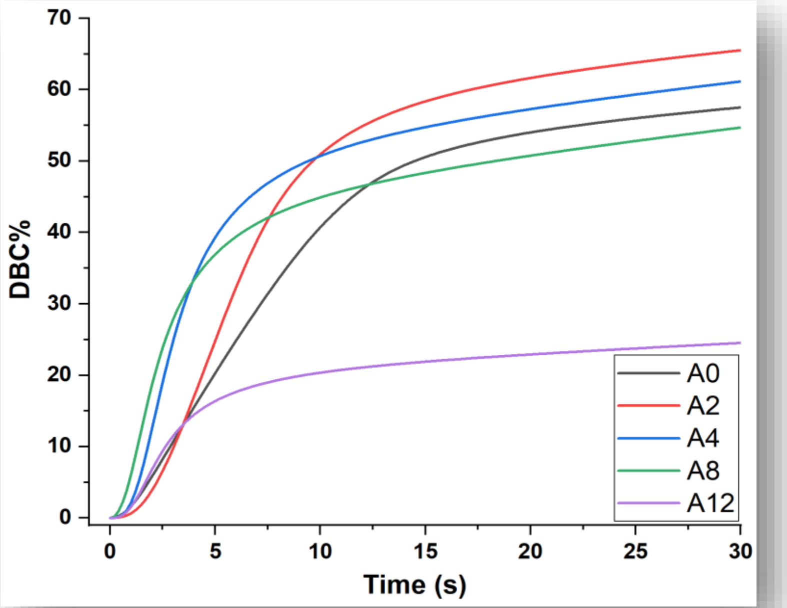


Photo-DSC Studies





$$\mathcal{R}p = \frac{Heat\ Flow \times Mw \times Wi}{\Delta H_0}$$

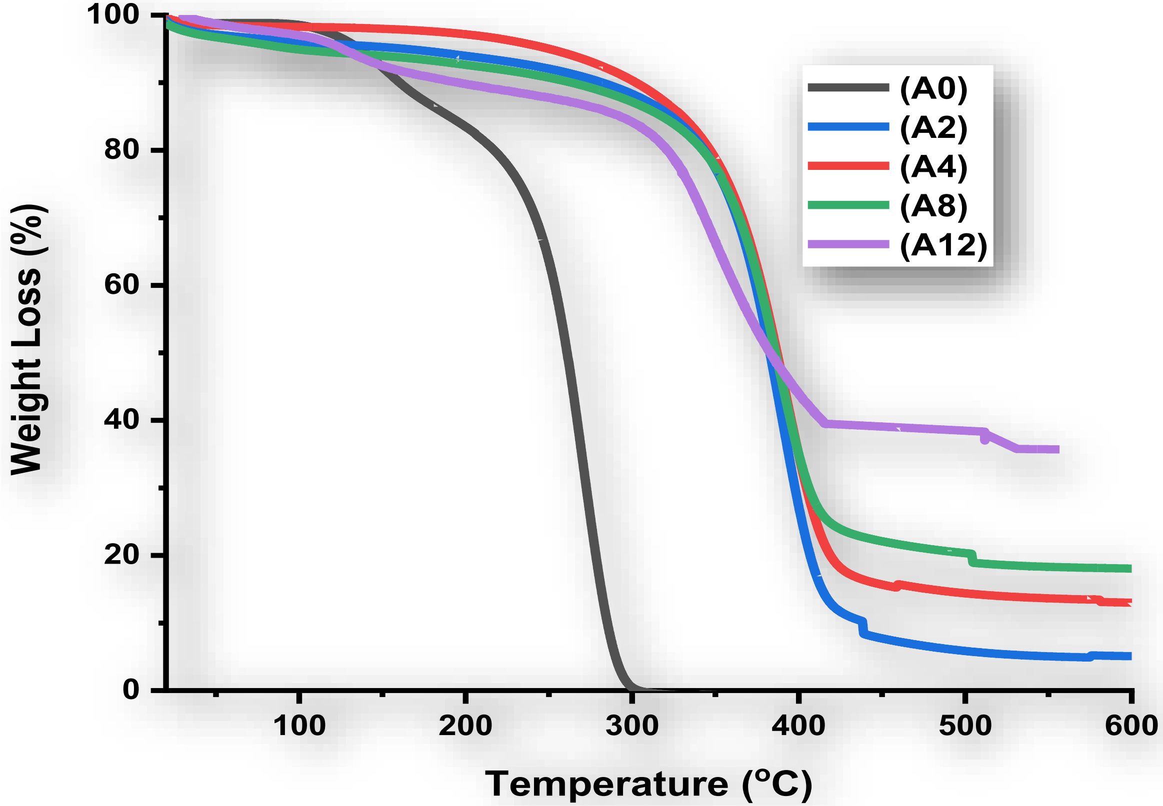


$$DBC\% = \frac{\Delta H_P \times Mw \times Wi}{\Delta H_0}$$

Formulation :

All samples: 0,5% (w/w) Irgacure 2959**,** $ZrCl_4$ (w/w%) **A0:** without $ZrCl_4$, **A2**: 2% $ZrCl_4$ **A4**: 4% $ZrCl_4$, **A8**: 8% $ZrCl_4$ and **A12**: 12% $ZrCl_4$ were prepared in 5 mL DMF solution, EA/TPGDA (80:20 w/w%)

TGA Analysis of Nanocomposite Thin Films Containing of ZrO_2 NPs



Weight loss (%)	Temperature (°C)				
	A0	A2	A4	A8	A12
5	136	164	250	97	125
10	160	282	302	263	195
20	217	343	346	342	321
50	260	382	386	386	382
80	278	406	418	503	
84	280	412	444		
Remaind weight % values @600 °C	0	4,5	12	16	35

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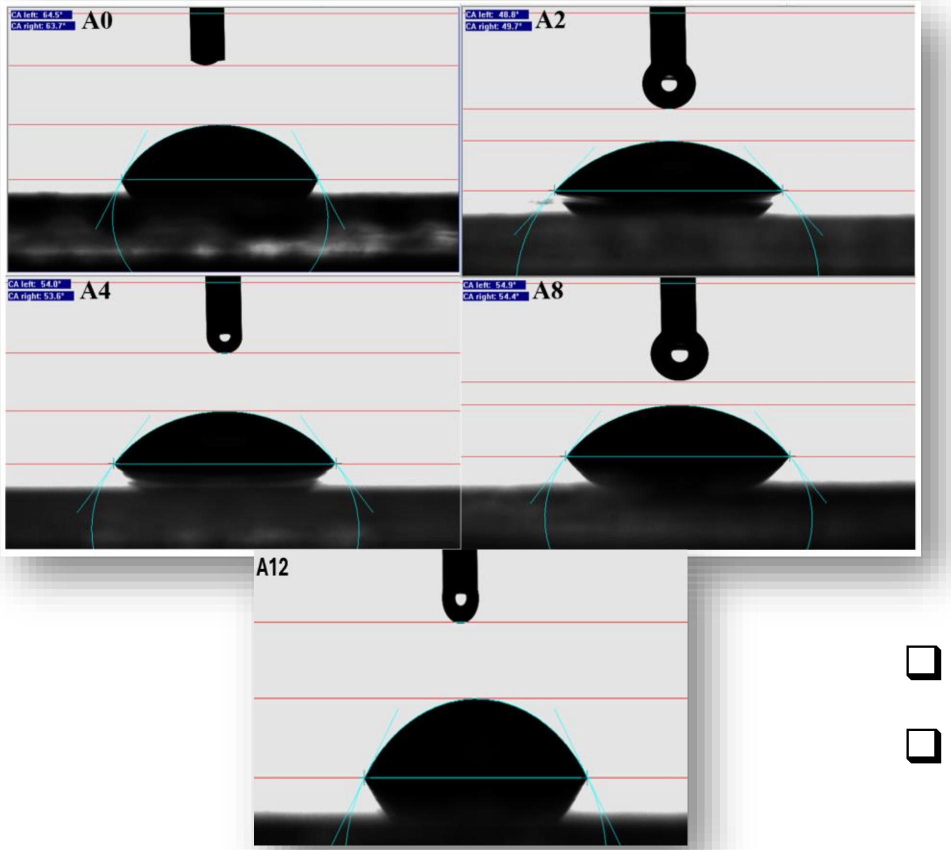
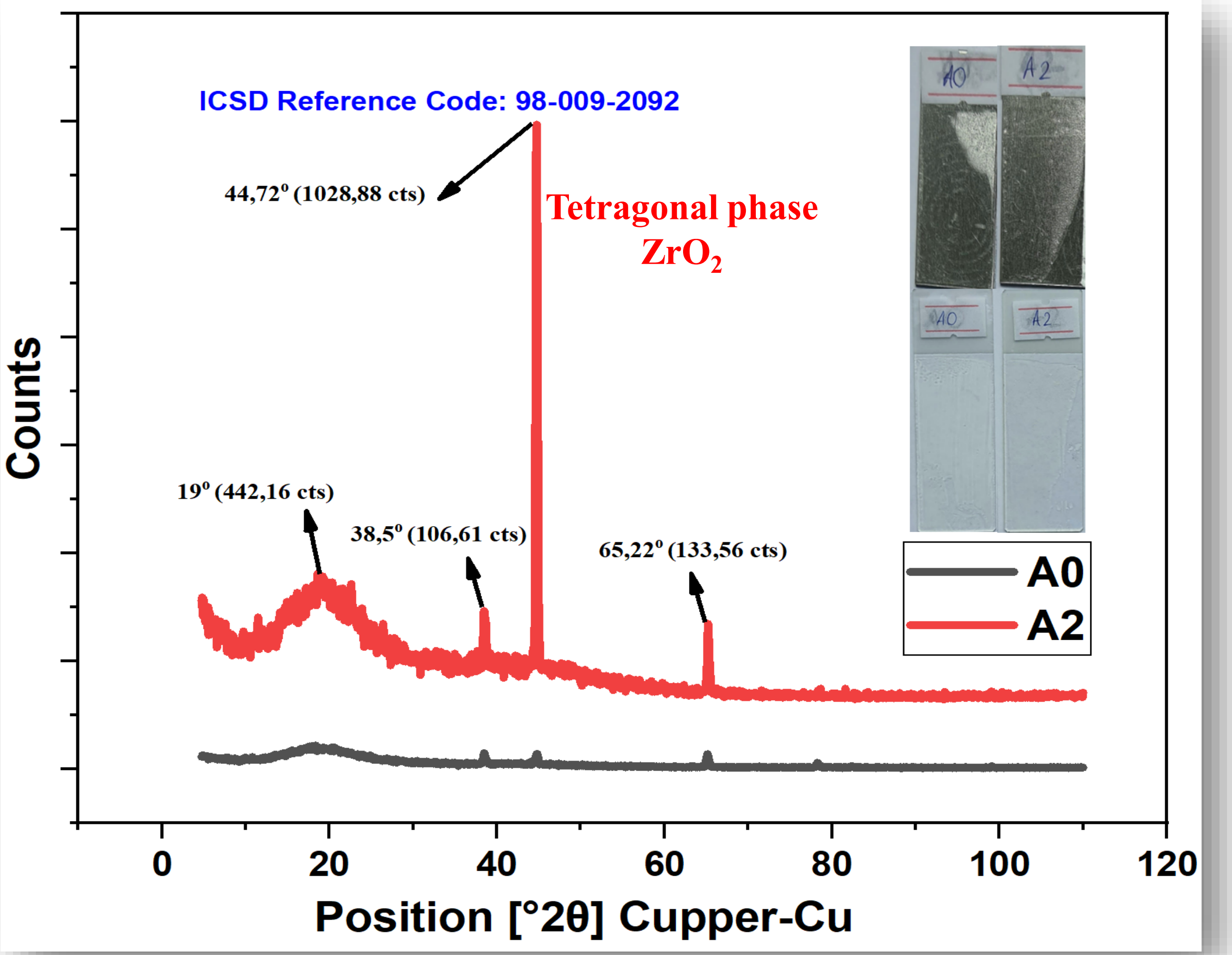
Contact Angle (CA) Measurements

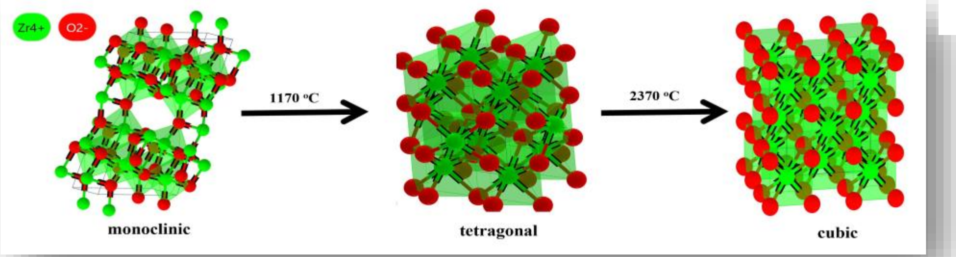


Sample	CA Left	CA Right
A0	64,5	63,7
A2	48,8	49,7
A4	54	53,6
A8	54,9	54,4
A12	56,2	56,4

- increased hydrophilicity can enhance antifouling properties
- promote better dispersion of water-based systems in functional coatings.

XRD Analysis





- The in-situ photopolymerization method successfully induces the crystallization of **ZrO_2 into its tetragonal form at room temperature**, a phenomenon typically requiring high-temperature conditions **(>1100°C)**[(4-6)].
- Exiting oportunities devoloping **optical coatings, nanocomposites films and advanced ceramics under ambient conditions**
- The average crystallite size of the A2 sample calculated using the **Scherrer equation**, changing the crystallite size diameters of ZrO_2 **NPs between 23.19 nm and 89.5 nm.**

[4] J. Musil, Hard nanocomposite coatings: Thermal stability, oxidation resistance and toughness, Surf. Coat. Technol. 207 (2012), 50-65, https://doi.org/10.1016/j.surfcoat.2012.06.089.

[6] S. Li, J. Liu, X. Li, Zirconia nanomaterials: recent developments and perspectives, Nanoscale 12 (2020), 12606-12636, https://doi.org/10.1039/D0NR03074G.

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SEM Images of Nanocomposite Thin Films Containing ZrO_2 NPs

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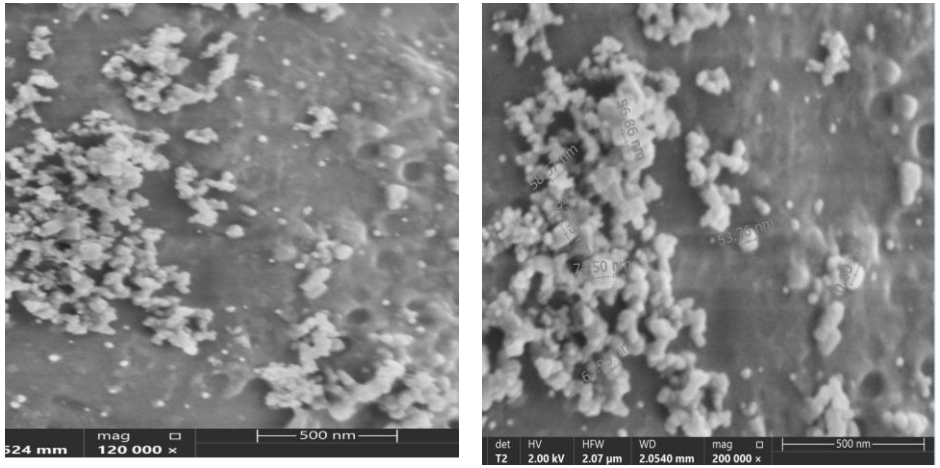
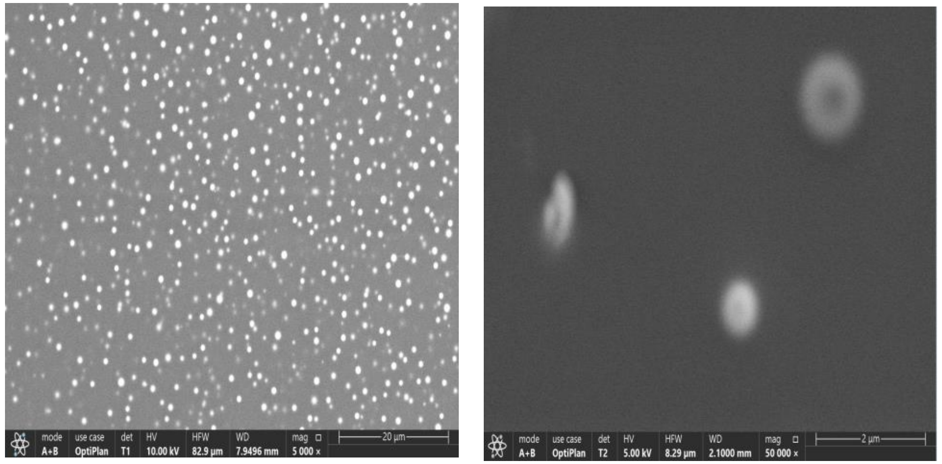
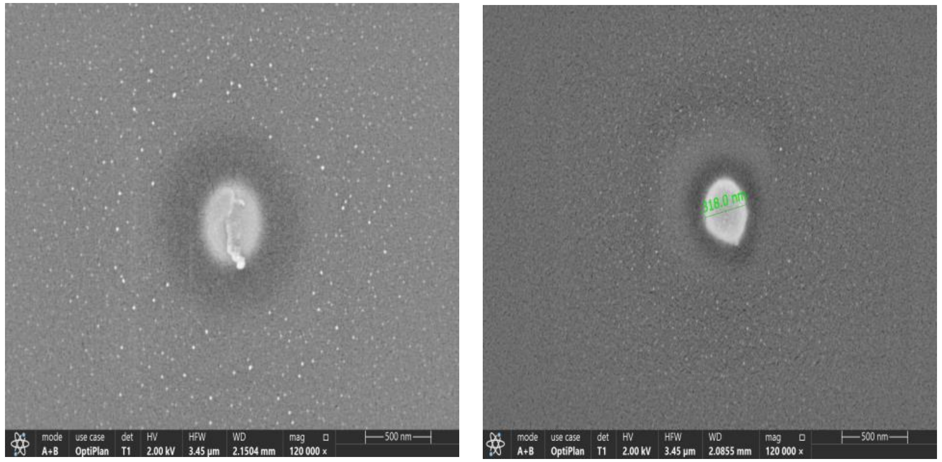
A2



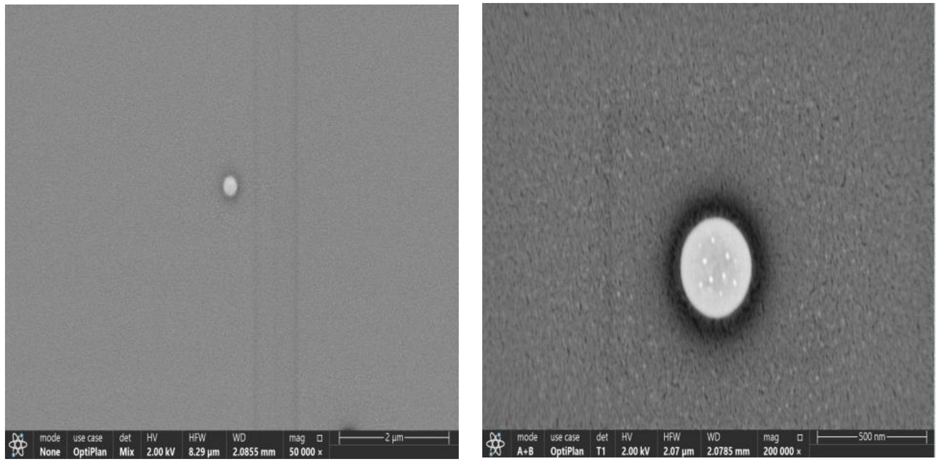
A4



A8



A12



As Conclusion

Potential Industrial Applications of ZrO_2-Based Coatings

1. **UV-Curable Protective Topcoats**
   Thanks to their enhanced **thermal stability** and **photocatalytic properties**, ZrO_2-containing formulations can be used in **clear or pigmented UV-curable topcoats**, especially for surfaces requiring **scratch resistance**, **UV protection**, or **self-cleaning** effects.

2. **Anti-fouling and Hydrophilic Coatings**
   The observed improvement in hydrophilicity suggests potential use in **marine coatings**, **bathroom/kitchen surfaces**, or **glass surfaces** where **anti-fouling** or **fog-resistant** behavior is desired.

3. **High-Durability Epoxy Primers or Barrier Layers**
   ZrO_2-enhanced films may serve as high-performance **intermediate layers** in multi-coat epoxy systems offering **thermal resistance**, **chemical durability**, and **corrosion barrier properties** on metal, concrete, or composite substrates.

4. **Photocatalytic Indoor Coatings (Air-Purifying Paints)**
   Due to the **photo-degradation of organic dyes** like methylene blue, such coatings may also contribute to **VOC reduction** or **air-purifying functions** under indoor UV/LED exposure.

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