Supplementary material

Structural and Optical Characterization of ZnO-ZrO_2 Nanocomposites for Photocatalytic Degradation and Mineralization of Phenol

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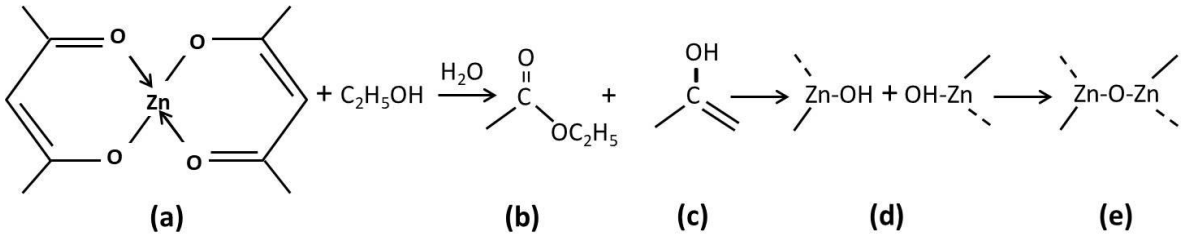

Figure S1. Proposed reactions of ZnO formation. The mechanism shows a nucleophilic attack of ethanol on one of the carbonyl groups of the acetylacetonate ligand (a), hidrolysis leading to the formation of ethyl acetate (b) and acetone in its enolate form (c) from the nucleophilic attack of the water molecule present in the precursor hydrate species. This result in the formation of Zn–OH species (d), which represent the monomeric units for the nucleation of ZnO nanocrystals, which proceeds through the formation of Zn–O–Zn bonds (e) via the condensation reaction [1] [2].

$$Zr(OC_4H_9)_4 + 4H_2O \longrightarrow Zr(OH)_4 + 4C_4H_9OH$$

$$Zr(OH)_4 + 4C_4H_9OH \longrightarrow \equiv Zr\text{-}O\text{-}Zr\equiv + 4H_2O$$

$$Zr(OC_4H_9)_4 + Zr(OH)_4 \longrightarrow \equiv Zr\text{-}O\text{-}Zr\equiv + 4C_4H_9OH$$

Figure S2. Proposed reactions for the formation of ZrO_2 nanoparticles from Zirconium(IV) butoxide by sol-gel process [3].

$$Zr(OH)_4 + Zn\text{-}OH \longrightarrow ZnO\text{-}ZrO_2 + 2H_2O + OH^-$$

Figure S3. Proposed mechanism for the formation of ZnO-ZrO_2 nanocomposites by sol-gel.

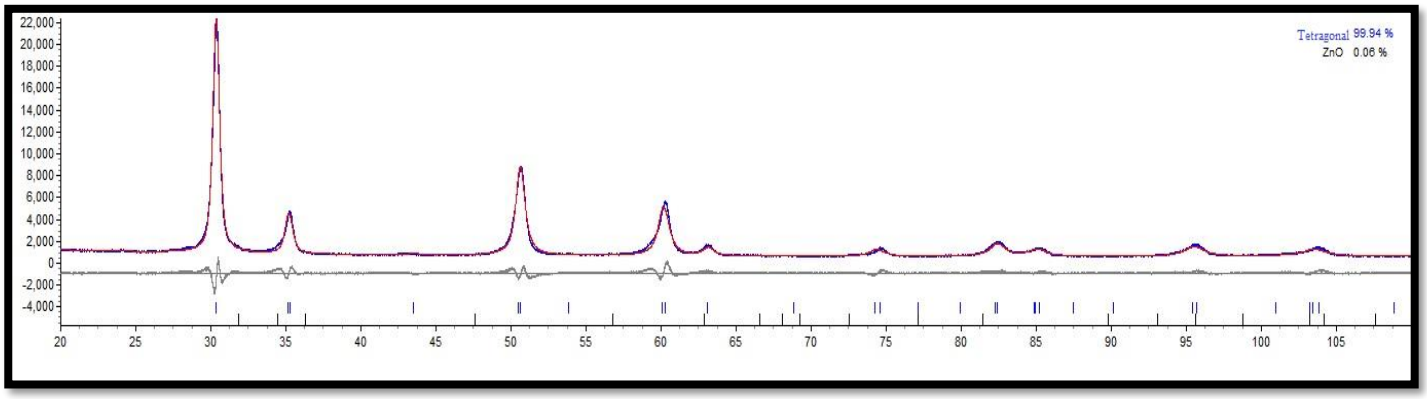

Figure S4. Graphic view of Rietveld refinement of 13ZnO-ZrO_2. Gray line represents the difference between calculated and experimental pattern, red line is the calculated pattern whereas blue line experimental pattern. The sample presents tetragonal phase of ZrO_2 and wurzite of ZnO, whereas cubic and monoclinic phase of ZrO_2 was not detected. No solid solution was formed.

Refinement data:

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Rexp : 2.86     Rwp : 7.75      Rp  : 6.06   GOF : 2.71
Rexp`: 4.75     Rwp`: 12.85     Rp` : 11.14  DW  : 0.27
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Table S1. Lattice parameters of the composites obtained from Rietveld refinement.

Sample	Lattice parameters	Rwp
13ZnO-ZrO_2	ZrO_2-Tetragonal phase: a (Å)=3.6109 c (Å)=5.0845 ZnO-Wurzite structure: a (Å)= 3.2419 c (Å)= 5.2070	Rexp: 2.86 Rwp: 7.75 Rp: 6.06 GOF: 2.71 Rexp`: 4.75 Rwp: 12.85 Rp: 11.14 DW: 0.27

Table S2. Band gap values of ZnO, ZrO_2 and ZnO-ZrO_2 composites. A direct transition for ZnO and indirect transition for ZrO_2 and ZnO-ZrO_2 were used, because of the highly accurate results obtained.

Sample	Eg (eV)	R^2	Eg (eV)	R^2

ZnO	3.26	0.99257	-	-
ZrO_2	4.53	0.99907	5.06	0.99703
13ZnO-ZrO_2	4.73	0.99953	3.07	0.98750
25ZnO-ZrO_2	4.35	0.99825	3.10	0.97904
50ZnO-ZrO_2	3.76	0.99678	3.15	0.99103
75ZnO-ZrO_2	4.16	0.99914	3.16	0.97762

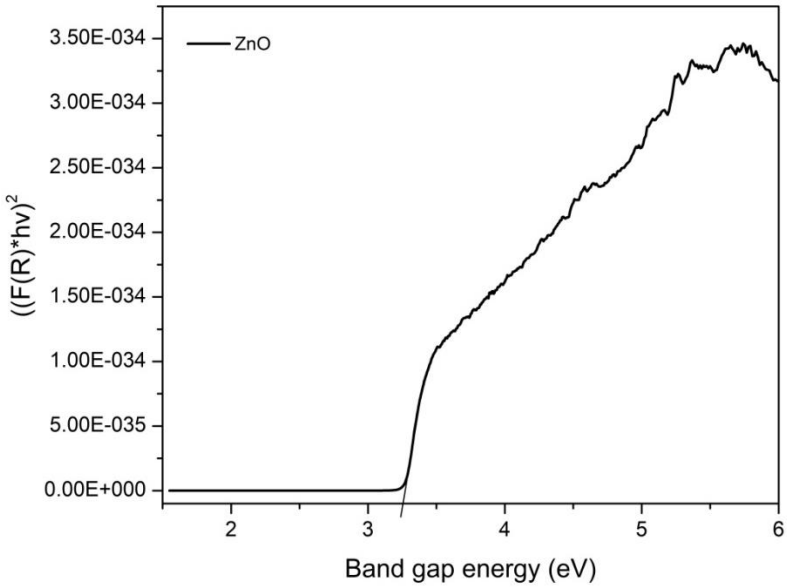

Figure S5. Plot of Kubelka-Munk function vs energy to obtain the band gap enegy of ZnO.

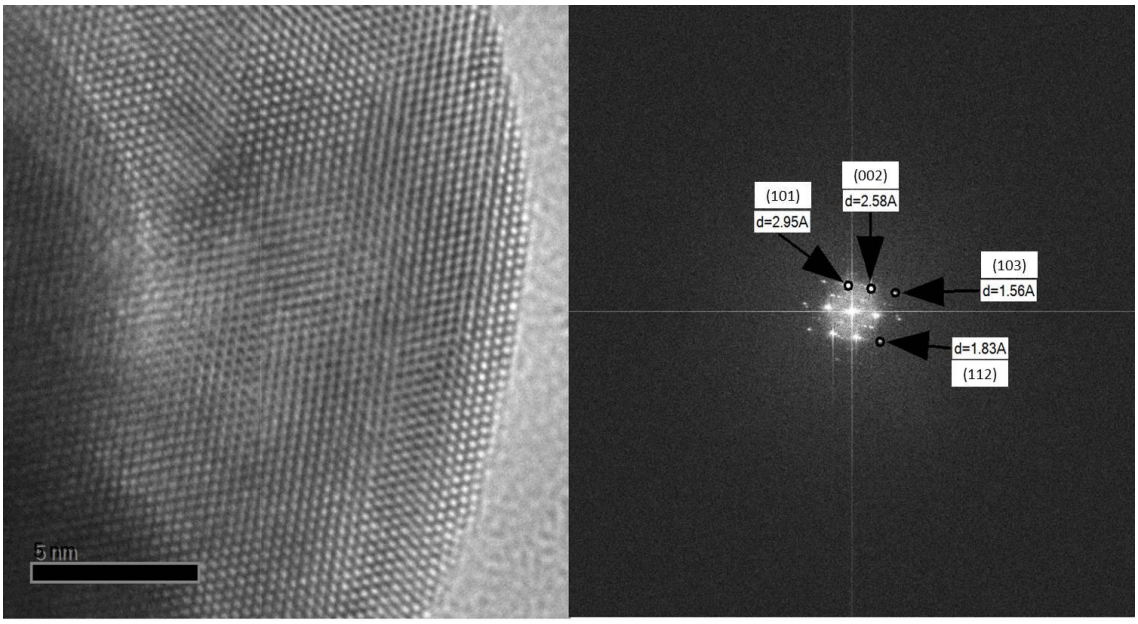

Figure S 6. TEM micrograph of tetragonal phase of ZrO_2 in the 13ZnO-ZrO_2 sample.

REFERENCES

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