

Supporting Information

**Assessment of Antimicrobial Efficacy of Leather
Coating using Chitosan Modified TiO₂-CuO
Nanocomposite**

*Vijay S. Ghodake^{a,b}, Pramod A. Koyale^c, Vikramsinh B. More^d, Kailas D. Sonawane^{a,d}, Sagar
D. Delekar^{a,*}*

^aNanoscience Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur
416 004, Maharashtra, India

^bDepartment of Chemistry, Yashwantrao Chavan Mahavidyalaya, Halkarni, Kolhapur, 416
552, Maharashtra, India

^cSchool of Nanoscience and Biotechnology, Shivaji University, Kolhapur 416 004,
Maharashtra, India

^dDepartment of Microbiology, Shivaji University, Kolhapur 416 004, Maharashtra, India

Email:* Corresponding Author

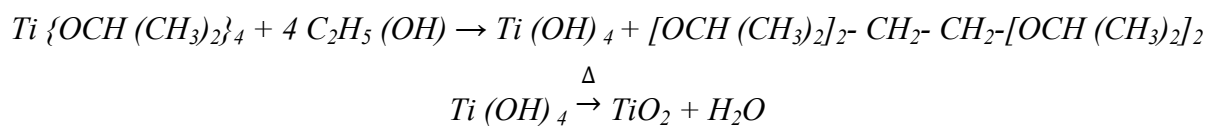
sdd_chem@unishivaji.ac.in (Sagar D. Delekar)

Experimental Section

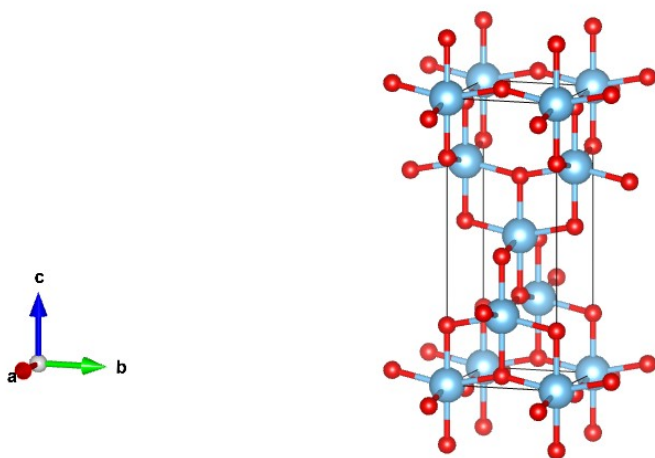
Synthesis of TiO₂ Nanoparticles

TiO₂ nanoparticles (NPs) were prepared by using a simple sol-gel route. In a round bottom flask, the stoichiometric amount of titanium (IV) isopropoxide (Ti {OCH (CH₃)₂}₄) and SDS (Sodium dodecyl sulfate) were dissolved in anhydrous ethanol solution separately and mixed, with constant stirring. The pH of the resulting solution was maintained up to 9.00 ± 0.10 using an aqueous ammonia solution to form the gel. Afterward, the gel solution was stirred at 60 °C for 2 hrs. and then cooled at room temperature. Then, the obtained precipitate was centrifuged at 6000 RPM for 10 minutes, washed thrice with double distilled water (DDW), twice in ethanol to remove formed impurities or by-products during the reaction process, and dried in an electric oven at 80 °C up to dryness. Finally, the dried crude product was calcined (annealed) at 400 °C for 4 hrs.

Reaction:



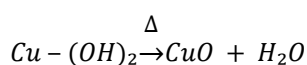
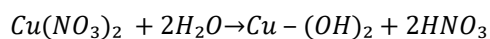
Crystal Structure of TiO₂:



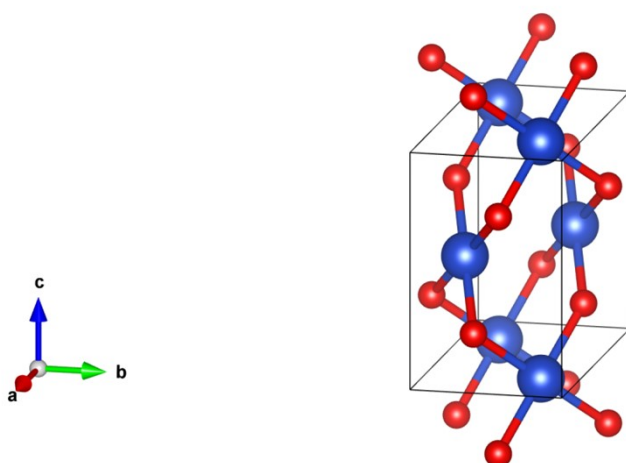
Synthesis of CuO Nanoparticles

CuO nanoparticles (NPs) were prepared by using a simple sol-gel route. The stoichiometric amount of Copper (II) nitrate was mixed with DDW and poly ethylene glycol (PEG) as a capping agent under continuous stirring for 1 hr. Then, the pH of this mixture was adjusted to 9.00 ± 0.10 using diluted ammonia solution, with the formation of gel, and then converted to precipitate. Afterward, the gel solution was stirred at $60\text{ }^{\circ}\text{C}$ for 2 hrs. and then cooled at room temperature. Then obtained precipitate was centrifuged at 6000 RPM for 10 minutes, washed thrice with DDW, and twice in ethanol to remove formed impurities and by-products during the reaction process. After that, it was dried in an electric oven at $80\text{ }^{\circ}\text{C}$ up to dryness. Finally, the dried crude product was calcined (annealed) at $40\text{ }^{\circ}\text{C}$ for 4 hrs.

Reaction:



Crystal Structure of CuO NPs:



Synthesis of TiO₂-CuO Nanocomposites (TC NCs)

TC NCs were prepared using a simple sol-gel route with a different composition of CuO content from 10, 20, 30, and 50 wt. %. The stoichiometric amount of titanium (IV) isopropoxide (Ti {OCH (CH₃)₂}₄) and SDS (Sodium dodecyl sulfate) were dissolved in an anhydrous ethanol solution separately and mixed with constant stirring. The pH of the resulting solution was maintained up to 9.00 ± 0.10 using an aqueous ammonia solution to form a gel. Afterward, the gel solution was stirred at 60 °C for 2 hrs. and cooled at room temperature. Then, the desired amount of CuO NPs was added to the titanium precursor solution. This whole content was stirred at 60 °C for 3 hrs. and then obtained precipitate was centrifuged at 6000 RPM for 10 minutes, washed thrice with DDW, and twice in ethanol to remove formed impurities and by-products during the reaction process. After that, it was dried in an electric oven at 80 °C up to dryness. Finally, the dried crude product was calcined (annealed) at 450 °C for 4 hrs. We obtained the black crystalline powder of TC NCs.

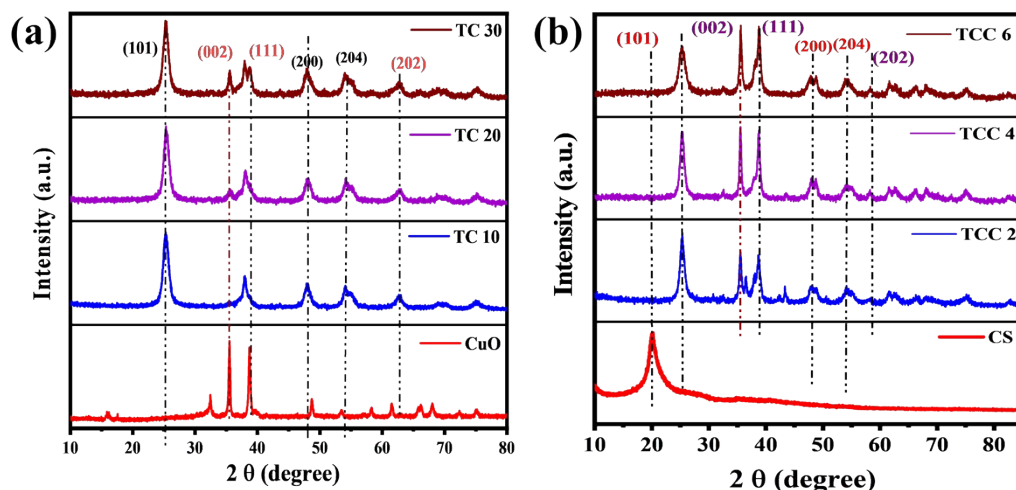


Figure S1. XRD patterns: (a) CuO NPs, TC 10, TC 20, and TC 30 NCs with varying content of CuO (10, 20 and 30 wt. %), (b) CS NPs, TCC 2, TCC 4, and TCC 6 NCs with varying content of CS NPs (2, 4 and 6 wt. %).

Table S1. Various parameters of XRD analysis of all samples

Composites	Standard d values (Å)	Observed d values (Å)	(hkl) plane	Cell parameters			Crystallite size (nm)
				a (Å)	c (Å)	V(Å ³)	
TiO ₂ NPs	3.5246	3.5246	(101)	3.2522	5.1830	55.4327	20
CuO NPs	2.6033	2.6014	(002)	3.2532	5.2028	55.0628	23
	2.4759	2.4736	(101)				
	1.6247	1.6266	(110)				
CS	2.6033	2.5914	(002)	3.2408	5.1828	54.4338	25
	2.4759	2.4645	(101)				
	1.6247	1.6204	(110)				
TC 10	2.6033	2.5992	(002)	3.2454	5.1984	54.7527	18
	2.4759	2.4716	(101)				
	1.6247	1.6227	(110)				
TC 20	2.6033	2.6089	(002)	3.2532	5.2178	55.2215	25
	2.4759	2.4816	(101)				
	1.6247	1.6266	(110)				
TC 30	2.6033	2.6089	(002)	3.2518	5.2178	55.1740	26
	2.4759	2.4824	(101)				
	1.6247	1.6259	(110)				
TC 50	2.6033	2.6080	(002)	3.2550	5.2160	55.2636	29
	2.4759	2.4824	(101)				
	1.6247	1.6275	(110)				

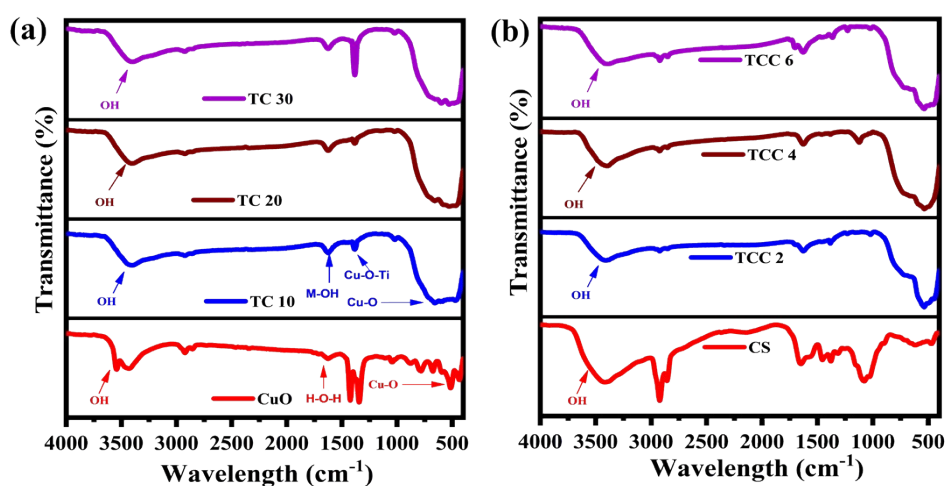


Figure S2. FT-IR patterns: (a) CuO NPs, TC 10, TC 20, and TC 30 NCs with varying content of CuO (10, 20, and 30 wt. %), (b) CS NPs, TCC 2, TCC 4, and TCC 6 NCs with varying content of CS NPs (2, 4, and 6 wt. %).

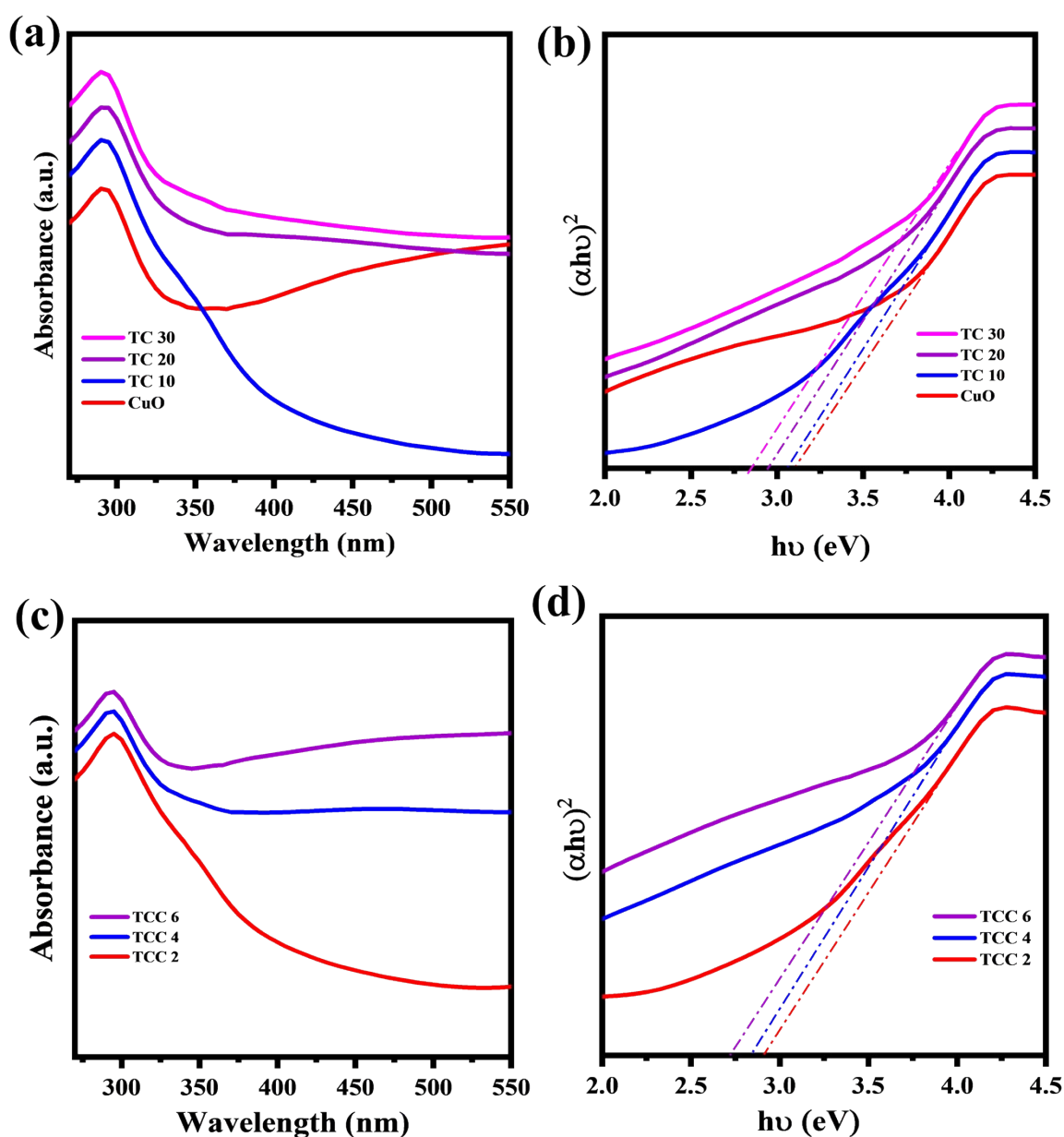


Figure S3. UV-DRS spectra and Tauc Plot: (a-b) CuO NPs, TC 10, TC 20, and TC 30 NCs with varying content of CuO (10, 20, and 30 wt. %), (c-d) TCC 2, TCC 4, and TCC 6 NCs with varying content of CS NPs (2, 4, and 6 wt. %).

Table S2. Absorbance and optical band gap (eV) values of bare TiO₂ NPs, TC 50 NCs, and TCC 8 NCs

Sr. No.	Samples	Band edge (nm)	Optical band gap (eV)
1	TiO ₂ NPs	391.16	3.17
2	CuO NPs	407.89	3.10
3	TC 10 NCs	427.58	3.06
4	TC 20 NCs	441.28	2.93
5	TC 30 NCs	464.41	2.86

6	TC 50 NCs	488.18	2.74
7	TCC 2 NCs	494.02	2.92
8	TCC 4 NCs	510.28	2.85
9	TCC 6 NCs	527.65	2.74
10	TCC 8 NCs	529.91	2.61

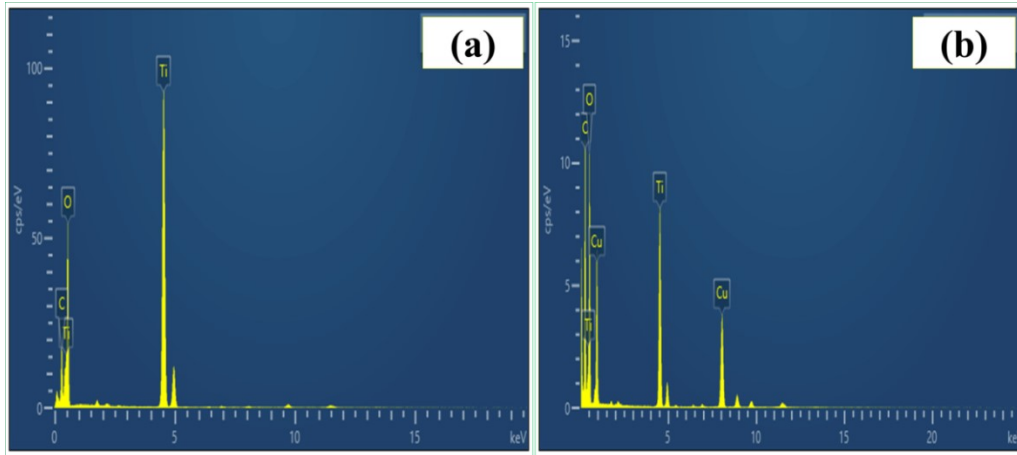


Figure S4. EDS spectrum of (a) TiO₂ NPs, and (b) TC 50 NCs.

The morphological behavior and elemental mapping of TiO₂ NPs and TC 50 NCs were done by using SEM as shown in **Figure S5**. **Figure S5(a-b)** shows SEM images of bare TiO₂ NPs and TC 50 NCs. **Figure S5(a)** clearly shows the irregular shape morphology, while TC 50 NCs show aggregated nanoparticles associated with irregular shapes, as shown in **Figure S5(b)**.

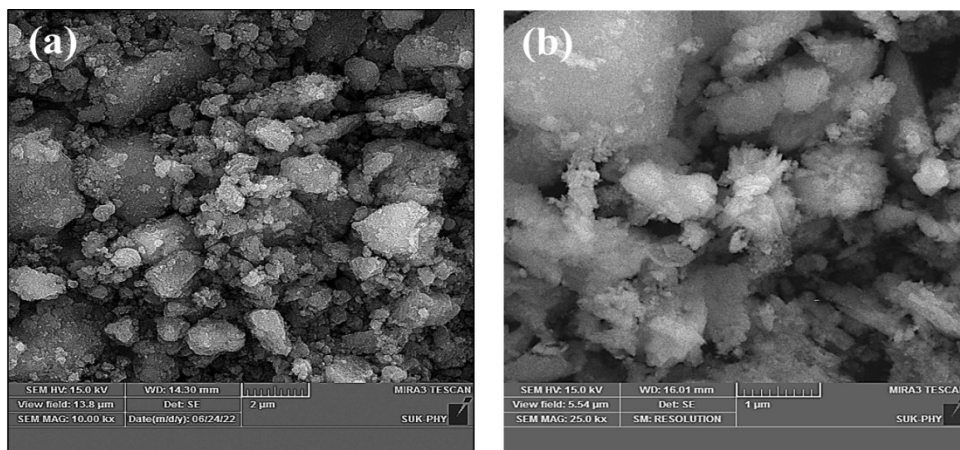


Figure S5. SEM images of (a) TiO₂ NPs, and (b) TC 50 NCs.

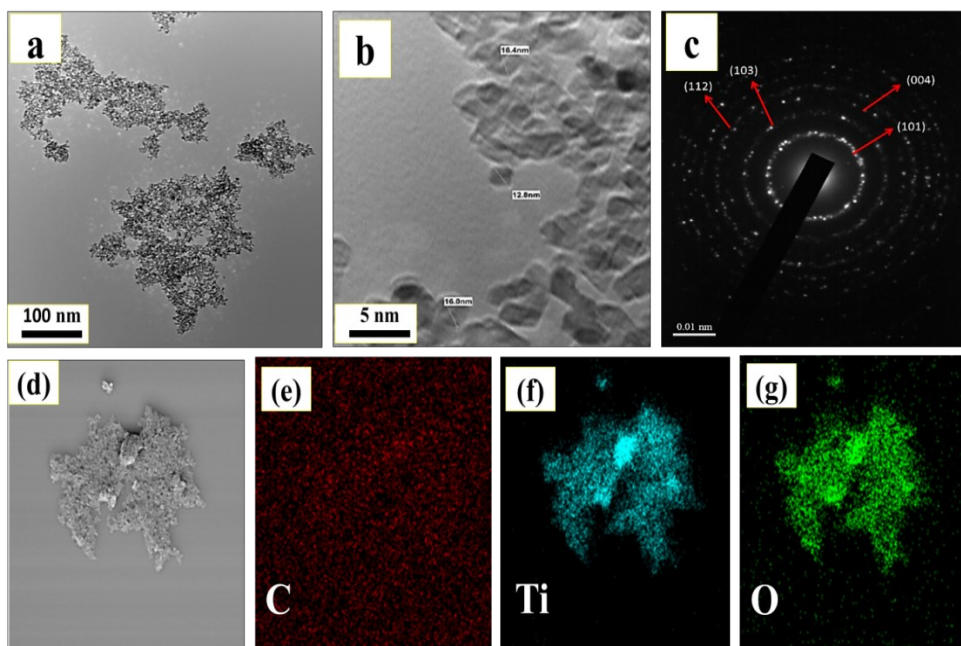


Figure S6. TEM images of (a-b) TiO₂ NPs; SAED pattern of (c) TiO₂ NPs, elemental mapping images of (d - g) TiO₂ NPs representing elements C (e), Ti (f), and O (g).

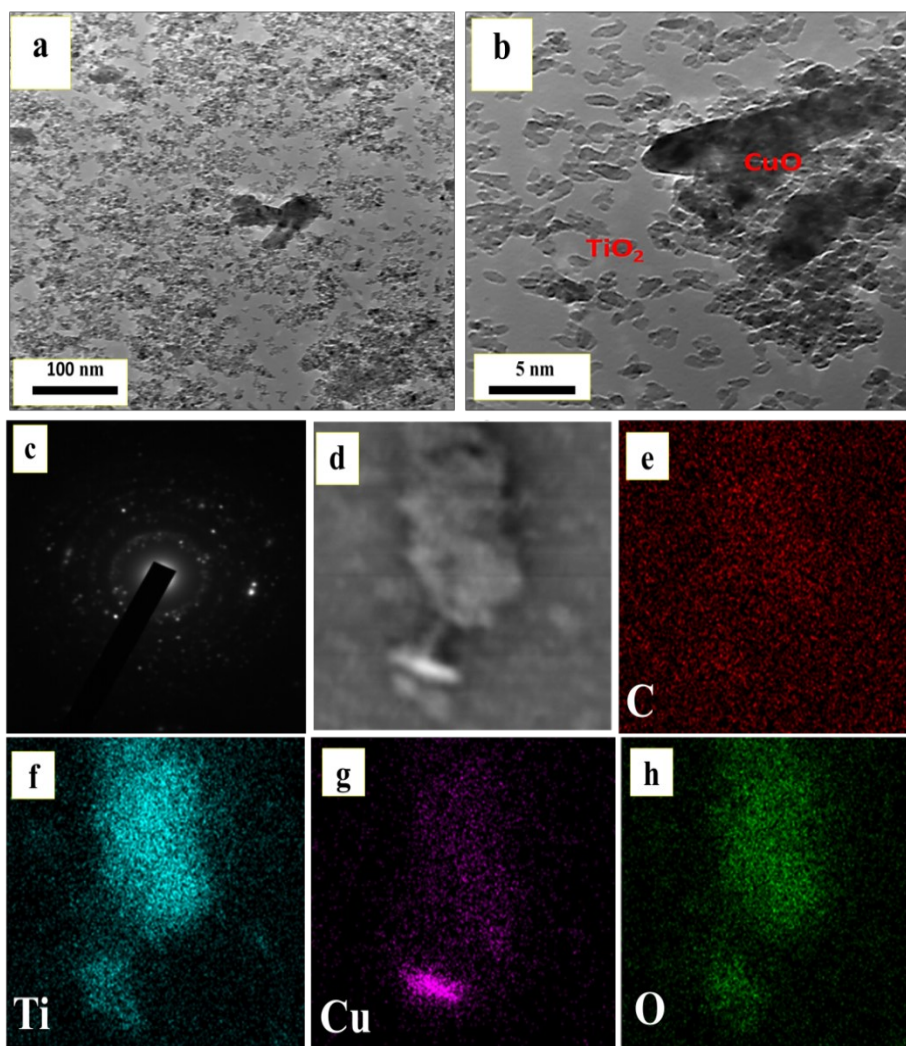


Figure S7. TEM images of (a-b) TC 50 NCs; SAED pattern of (c) TC 50 NCs, elemental mapping images of (d - h) TC 50 NCs representing elements C (e), Ti (f), Cu (g), and O (h).

Table S3. Specific surface, and pore size from BET analysis of bare TiO₂ NPs, TC 50 NCs, and TCC 8 NCs

Sample	Specific surface area (m ² g ⁻¹)	Pore size (nm)
TiO ₂ NPs	235.107	2.435
TC 50 NCs	273.774	3.168
TCC 8 NCs	328.972	3.606