Synthesis of $Fe_3O_4/ZrO_2/CuO$ magnetic nanohybrid and its applications in reducing chromium(VI) and degrading methylene blue under sunlight

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Materials and Method

Iron(III) chloride ($FeCl_3.6H_2O$), iron(II) chloride ($FeCl_2.4H_2O$), zirconyl chloride ($ZrOCl_2.8H_2O$), copper(II) nitrate ($Cu(NO_3)_2$), sodium hydroxide (NaOH), methylene blue (MB), hydrogen peroxide (H_2O_2), potassium dichromate ($K_2Cr_2O_7$), sodium dithionite ($Na_2S_2O_4$), ethanol (EtOH) and deionized water (DI) used to prepare $Fe_3O_4/ZrO_2/CuO$ nanoparticles were obtained from Merck and Sigma Aldrich Chemical Companies.

Material characterization

Field emission scanning electron microscopy (FE-SEM, FEI-Quanta 450 FEG) and transmission electron microscopy (TEM, Philips EM 208) were used to study the morphology and particle size of $Fe_3O_4/ZrO_2/CuO$. X-ray diffraction (XRD, Philips X'PERT MPD) with an X-ray wavelength of 1.54 Å (Cu Kα radiation source) was used to investigate the crystal phases of the $Fe_3O_4/ZrO_2/CuO$ nanoparticles. A JASCO V-670 UV-Vis spectrophotometer (Japan) was used to record the diffuse reflectance spectra (DRS) in the 200-900 nm range. The absorbance values were used to determine the concentration of the dye solutions. A Jasco Model 460 plus FT-IR spectrophotometer was used to record the Fourier transform infrared spectra (FT-IR). For the determination of Cu content of $Fe_3O_4/ZrO_2/CuO$ nanocomposite, inductively coupled plasma (ICP) analysis (Optima 7300DV ICP-OES, Perkin Elmer) was used. The Surface and valence states were characterized using X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermofisher Scientific). Magnetic properties of $Fe_3O_4/ZrO_2/CuO$ nanocomposite were carried out in a vibrating sample magnetometer (VSM,

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LBKFB) at room temperature. The surface area of the nanocomposite was determined via Barrett-Emmett-Teller (BET) method by BELSORP- mini 2 instrument.

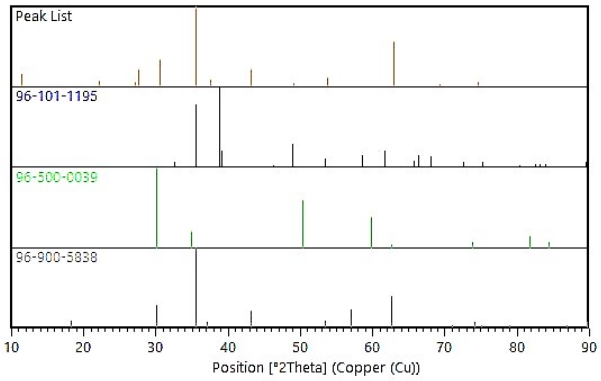

Figure S1. The standard cards of Fe_3O_4, ZrO_2 and CuO

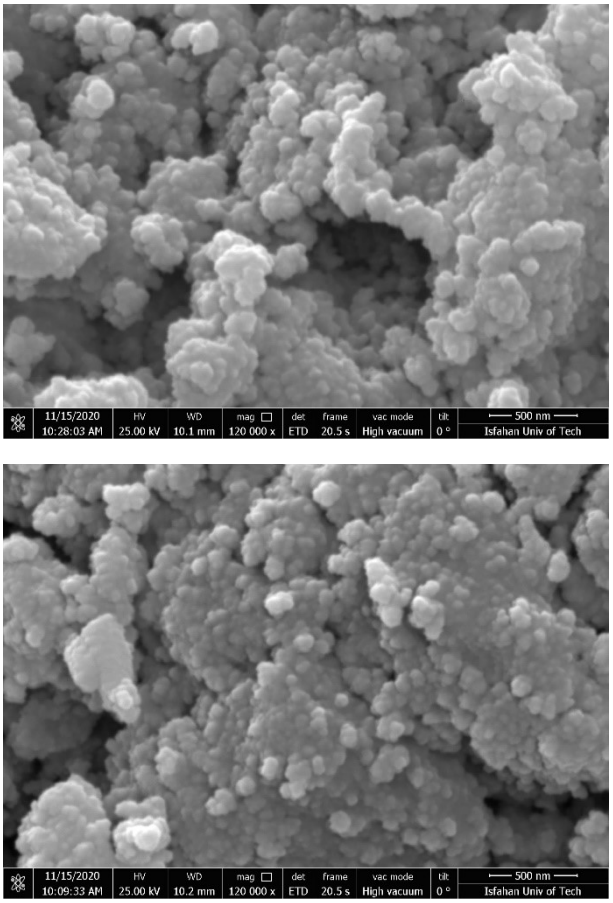

Figure S2. The FE-SEM images of Fe_3O_4 nanoparticles

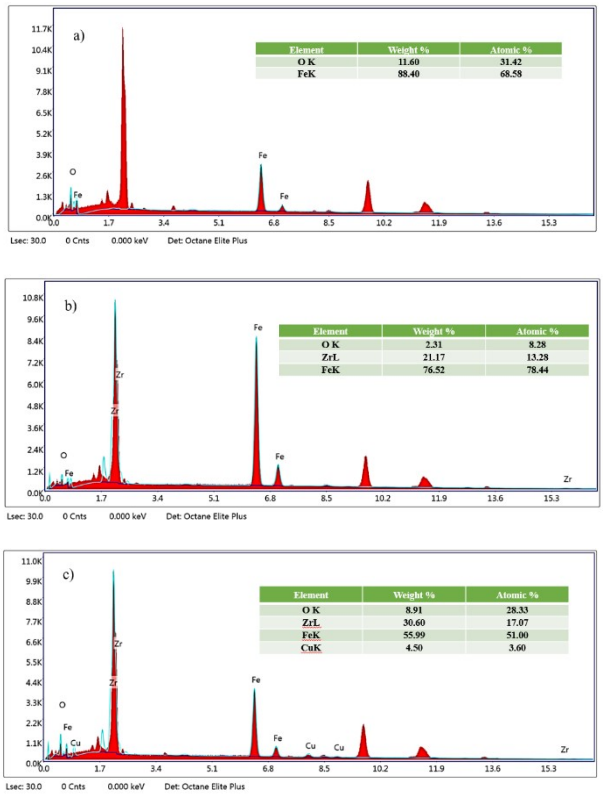

Figure S3. The EDX spectra of a) Fe_3O_4 b) Fe_3O_4/ZrO_2 c) $Fe_3O_4/ZrO_2/CuO$

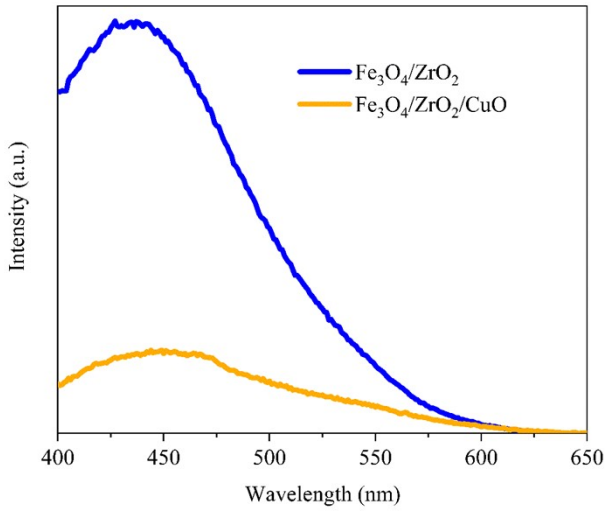

Figure S4. The PL spectra of Fe_3O_4/ZrO_2 and $Fe_3O_4/ZrO_2/CuO$

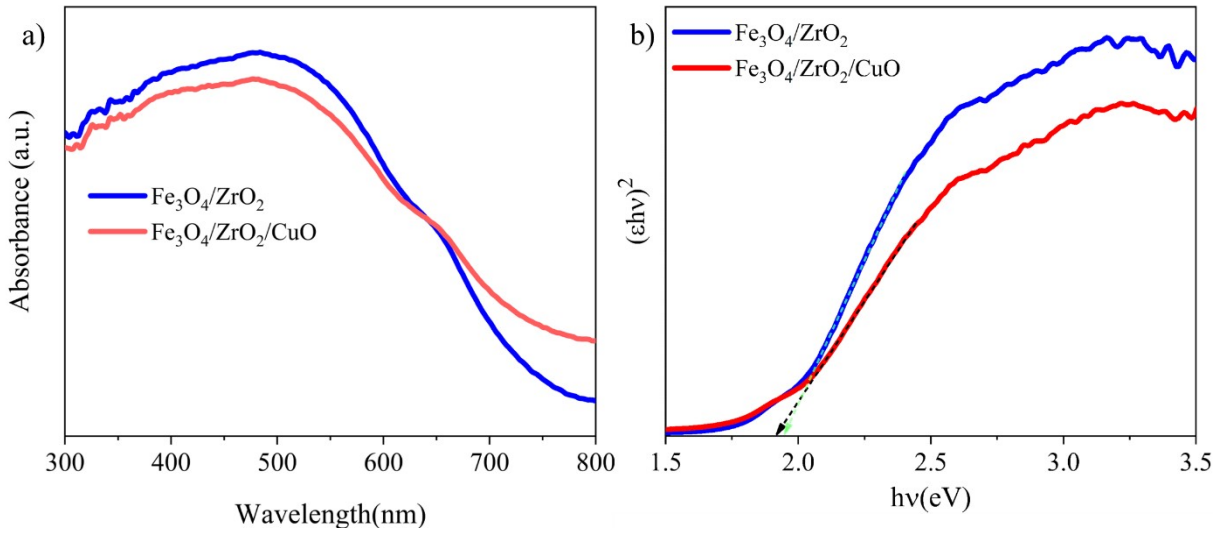

Figure S5. The DRS spectra and Kubelka-Munk plots of Fe_3O_4/ZrO_2 and $Fe_3O_4/ZrO_2/CuO$.

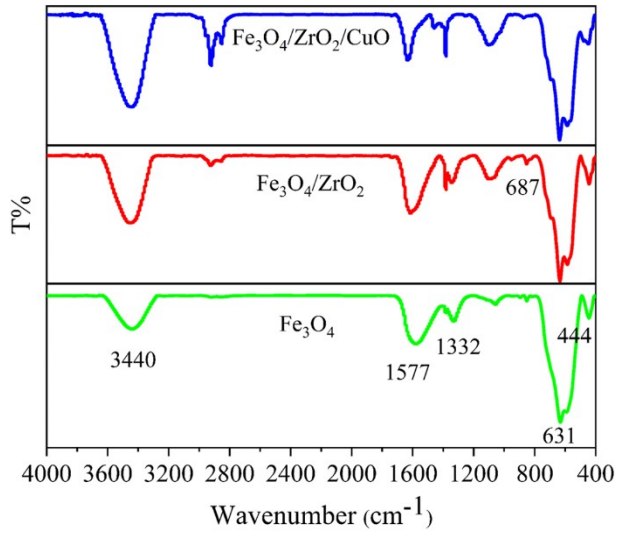

Figure S6. The FT-IR spectra of Fe_3O_4, Fe_3O_4/ZrO_2 and $Fe_3O_4/ZrO_2/CuO$

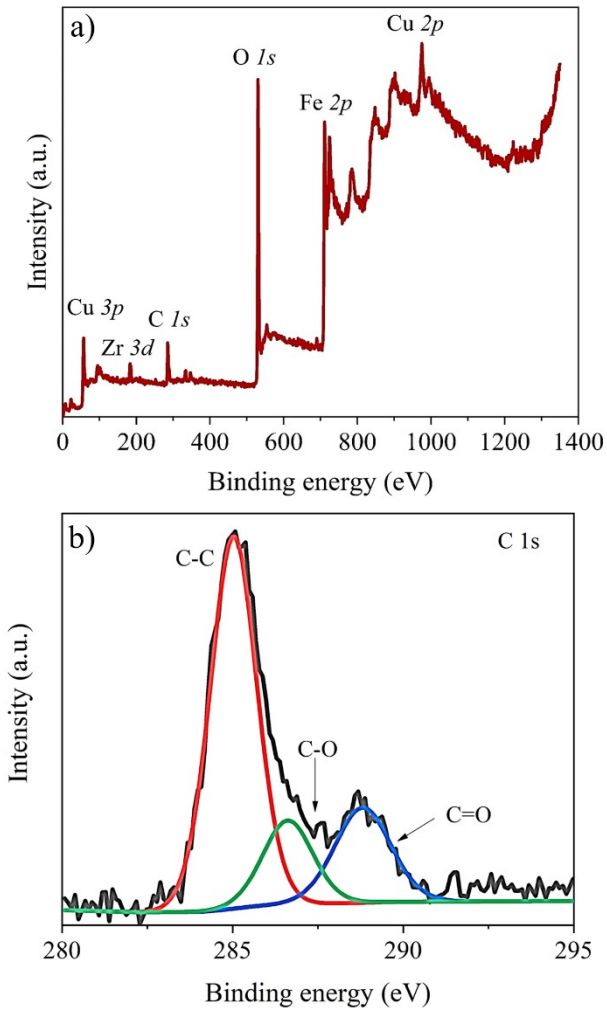

Figure S7. a) The XPS spectrum of O 1s, C 1s, Cu 2p, Zr 3d and Fe 2p. b) high resolution spectra of C*1s*

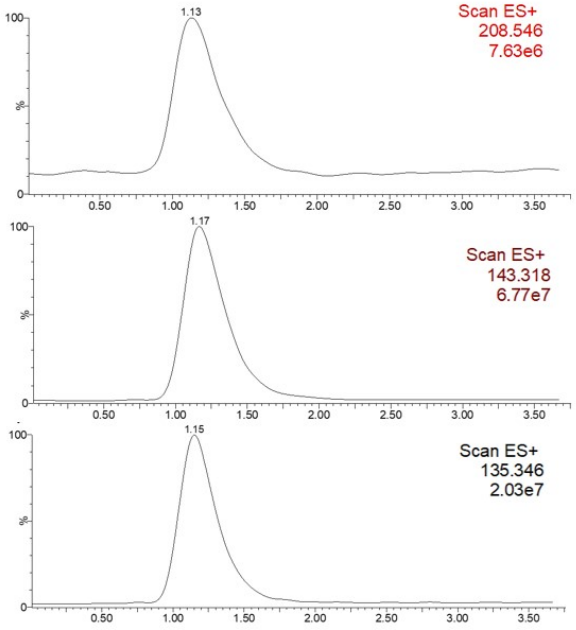

Figure S8. The liquid chromatograms of photodegradation of MB at different retention time.

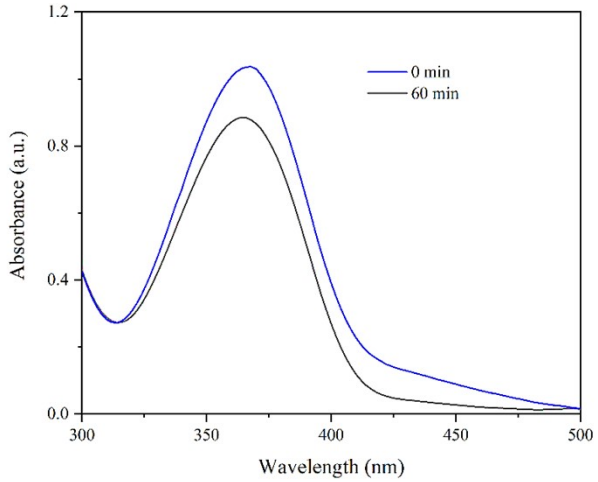

Figure S9. adsorption of Cr(VI) by $Fe_3O_4/ZrO_2/CuO$

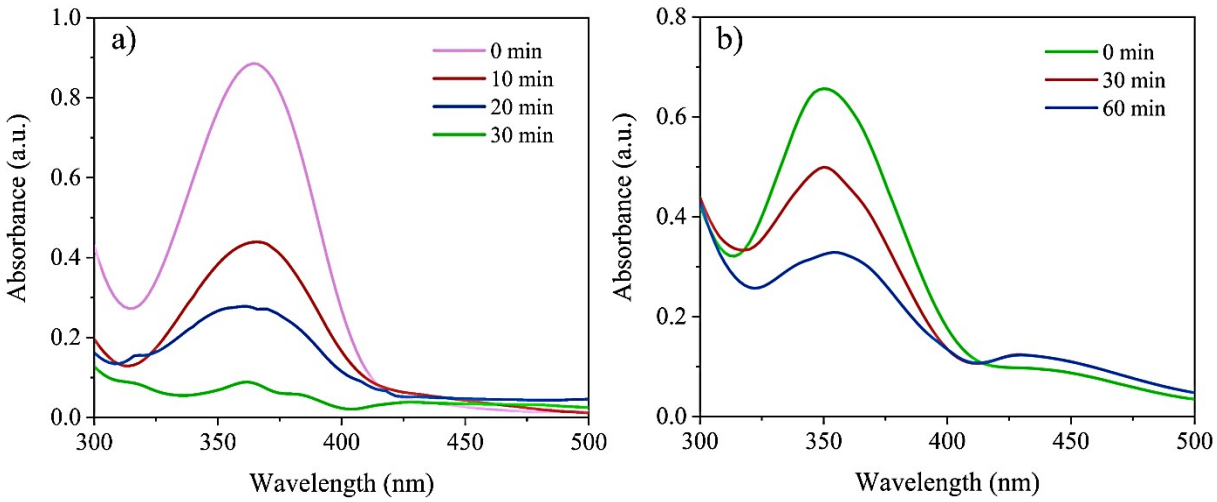

Figure S10. UV- Vis spectroscopy of Cr(VI) reduction (pH = 6), a) in presence of reducer agent b) in absence of reducing

Figure S11. Reusability of photoreduction of Cr(VI) with $Fe_3O_4/ZrO_2/CuO$

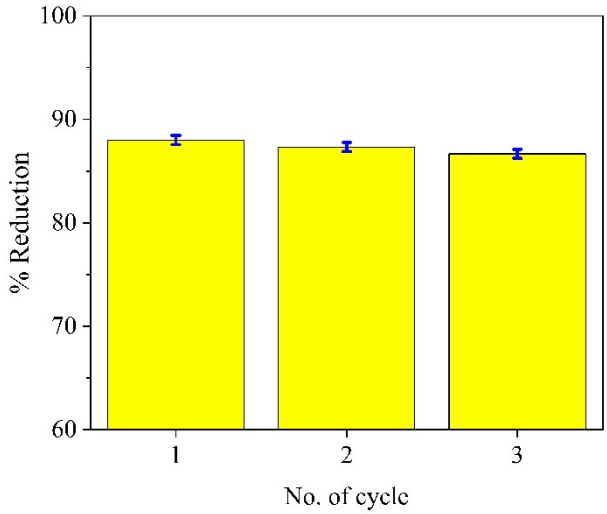

Table S1. The amount of Ms, Mr, and Hc for Fe_3O_4, Fe_3O_4/ZrO_2 and $Fe_3O_4/ZrO_2/CuO$

Magnetic compound	Ms	Mr	Hc
Fe_3O_4	49.30	1.23	12.23
Fe_3O_4/ZrO_2	39.55	0.23	-2.05
$Fe_3O_4/ZrO_2/CuO$	36.02	0.21	-2.2

Table.S2 Determined of photocatalyst dosage

mg of catalyst	1	3	5
Time (min)	25	23	19