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Effect of temperature on the action spectra of pristine and Cu-grafted titania

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1 Materials and catalyst characterization

High purity grade acetone (CH_3COCH_3) was used as received from AO REAHIM Inc. (Russia) without further purification as a test organic substrate in the photocatalytic experiments. $Cu(CH_3COO)_2$ from AO REAHIM Inc. (Russia) and $NaBH_4$ from Acros Organics (USA) were used for the synthesis procedure. Commercially available TiO_2 powder EuroSupport (100% anatase, $a_{s,BET}$ = 380 m^2 g^{-1}) from Euro Support Manufacturing Czechia (Czech Republic) was employed as photocatalysts. The modified TiO_2 photocatalyst was synthesized via the impregnation of basic photocatalyst with an aqueous solution of precursor $Cu(CH_3COO)_2$ followed by chemical reduction with a 3-fold excess of $NaBH_4$, washing in a centrifuge for 5 times, and drying at 110 °C. The amount of precursor was determined by the required metal content (wt.%) in the catalyst. The details of synthesis can be found elsewhere [S1].

The textural properties were investigated by N_2 adsorption at 77 K using an ASAP 2400 instrument (Micromeritics, USA). A specific surface area values were calculated by BET analysis: ca.320 m^2 g^{-1} for the synthesized Cu/ES catalyst and 380 m^2 g^{-1} for pristine ES TiO_2, respectively. The UV-Vis diffuse reflectance spectra were recorded in the range of 250–850 nm with 1 nm of resolution using a Cary 300 UV-Vis spectrophotometer from Agilent (USA) equipped with a DRA-30I diffuse reflectance accessory at room temperature. A pre-packed PTFE from Agilent (USA) was used. The X-ray photoelectron spectra were measured on a SPECS spectrometer with a PHOIBOS-150-MCD-9 analyzer (AlK_α radiation, hν = 1486.6 eV, 150 W). The binding energy (BE) scale was pre-calibrated using the positions of the peaks of $Au4f_{7/2}$ (BE = 84.0 eV) and $Cu2p_{3/2}$ (BE = 932.67 eV) core levels. The samples were loaded onto a conducting double-sided copper scotch. The $Ti2p_{3/2}$ peak at 458.8 eV of the titanium oxide support was used as an internal standard [S2]. The survey spectrum and the narrow spectra were registered at the analyzer pass energy 20 eV.

A Bruker D8 Advance diffractometer with an Anton Paar XRK900 reaction camera (Austria) with CuKα radiation (λ=1.5418 Å) and a focusing geometry θ-θ was used to capture diffraction data in the *in-situ* mode. A one-dimensional LynxEye detector was used to register the signal. The shooting range of 2θ was 20-80° with a step of 0.05° and an accumulation time of 3 seconds at the point. The samples were heated at a rate of 12 °C min^{-1}. The X-ray recording began immediately when the set temperature was reached. The phase composition of the samples was determined using the ICDD PDF-2 database. The structural data is obtained from the ICSD database. For the data obtained, a full-profile analysis was performed by the Rietveld method using the TOPAS V.4.3 software. To describe the instrumental broadening, an external standard was used – a powder of metallic silicon taken under identical conditions. The size of the coherent scattering region (OCR) was calculated from the value of the integral width to obtain the volume-weighted mean column lengths based on integral breadth (LVol-IB). When modeling the diffraction data by the Rietveld method, the lattice parameters and the sizes of the CSR of the phases were refined.

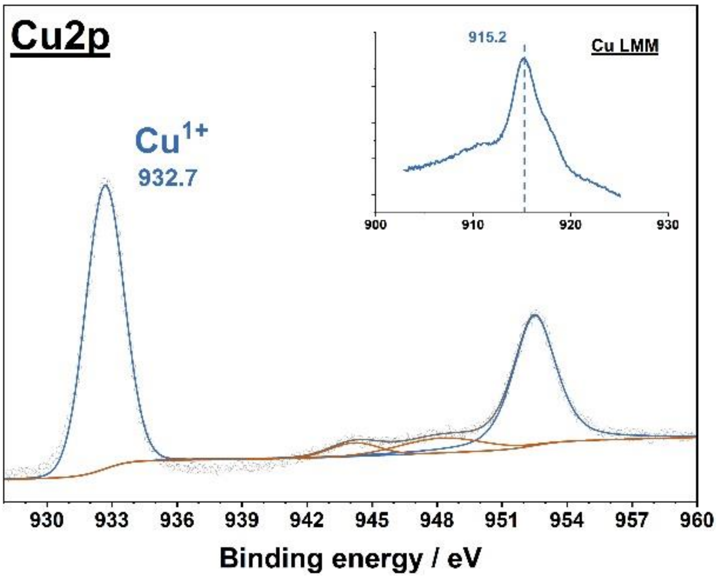

Figure S1 Deconvolution of XPS spectra for Cu/ES sample.

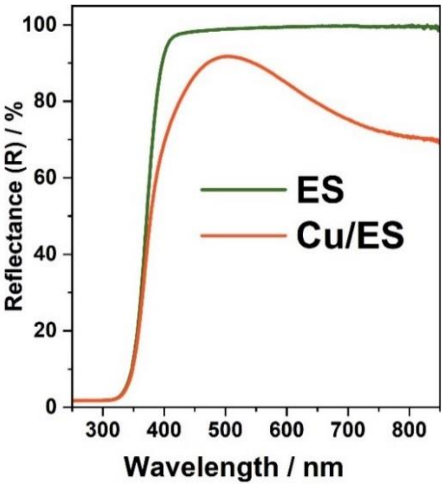

Figure S2 UV-vis diffuse reflectance spectra.

2 Photocatalytic experiments

The photocatalytic experiments were performed in a continuous-flow set-up using the volume flow rate 0.1 ± 0.02 L min^{-1}, the inlet concentration of acetone 38 – 42 µmol L^{-1}, the relative humidity of pre-cleaned inlet air 20±2% at 25 °C. The set-up was connected to Bruker Vector 22 FTIR spectrometer (USA) to monitor periodically the changes in the gas phase. CO_2 generation rate was selected for the measure of activity [S3]. The temperature of the reactor was controlled via a PC-connected thermostatic unit so that the temperature was adjusted in the range of 40-140 °C. Typical methodology of photocatalysts' pretreatment and sampling: catalyst was suspended in deionized water, treated using ultrasound, next suspension was deposited onto a glass plate (ca. 9.1 cm^2) at a surface density of 1 mg cm^{-2}, and dried at 110 °C for 2 h to remove water from the sample. The light source was turned on at 40-min point to ensure the absence of activity without irradiation of the sample. A set of light-emitting diode plates (LEDs) with a special collimating lens were employed for the photocatalyst irradiation during the experiments following the methodology presented elsewhere [S3]. All LEDs were used as adjusted to the photon flux of 1.5 10^{17}photons s^{-1} (i.e., 0.25 µE s$^{-1,}$ or 15 µE min^{-1}). The photonic efficiency during acetone photocatalytic oxidation is calculated as the activity value (CO_2 generation rate, µmol min^{-1}) divided by the total flux of photons incident onto the surface of catalyst per time interval (µE min^{-1}).

References

[S1] N. S. Kovalevskiy, M. N. Lyulyukin, D. V. Kozlov and D.S. Selishchev, *Mendeleev Commun.*, 2021, **31**, 644.

[S2] J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics Division, Perkin-Elmer Corporation, USA, 1992.

[S3] M. Lyulyukin, N. Kovalevskiy, D. Selishchev and D. Kozlov, *J. Photochem. Photobiol., A*, 2021, **405**, 112981.