Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 644–646

Cu-grafted TiO_2 photocatalysts: effect of Cu on action spectrum of composite material

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S1. Materials

Copper (II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) from AO Vekton Inc., Russia and sodium borohydride ($NaBH_4$) from Sigma-Aldrich, USA were employed for the modification of TiO_2 photocatalysts. Acetone (CH_3COCH_3) from AO Reachem Inc., Russia was used as a test compound for oxidation in the photocatalytic experiments. All the chemicals were high purity grade and used as supplied without further purification.

S2. Synthesis

Commercially available TiO_2 photocatalysts (TiO_2-P25, TiO_2-ES, and TiO_2-KC) were modified with copper via the impregnation method using an aqueous solution of $Cu(CH_3COO)_2$ followed by the reduction with $NaBH_4$. Typically, 1 g of TiO_2 were suspended in 10 mL of DI water, and a certain aliquot of copper acetate solution was added. The amount of copper acetate precursor was determined by the required copper content in the catalyst and was as follows: 0.1, 0.4, 0.7, 1, 1.3, 1.6 wt.% for TiO_2-P25; 0.1, 0.4, 0.7, 1, 1.3, 1.6, 1.9 wt.% for TiO_2-ES; 0.1, 0.4, 0.7, 1, 1.3, 1.6, 1.9, and 2.2% for TiO_2-KC. After vigorous stirring, a three-fold molar excess of $NaBH_4$ was added dropwise to the suspension to reduce the copper precursor. After that, the suspension was stirred for 3 h, separated and washed 2 times using the centrifugation, dried in air at 120 °C overnight, gently ground in an agate mortar.

BET analysis of N_2 isotherm measured at 77 K using an ASAP 2400 instrument (Micromeritics, USA). The specific surface area of commercially TiO_2-P25, 0.1%Cu/TiO_2-P25, and 1.6%Cu/TiO_2-P25 is 56 $m^2{\cdot}g^{-1}$, 52.8 $m^2{\cdot}g^{-1}$, and 52.8 $m^2{\cdot}g^{-1}$, respectively. The specific surface area of commercially TiO_2-ES, 0.1%Cu/TiO_2-ES, and 1.9%Cu/TiO_2-ES is 380 $m^2{\cdot}g^{-1}$, 338.1 $m^2{\cdot}g^{-1}$, and 315.1 $m^2{\cdot}g^{-1}$, respectively.

S3. Diffuse-reflectance spectra

All samples were characterized by UV–vis diffuse reflectance spectroscopy. The UV-vis diffuse reflectance spectra were recorded at room temperature 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. A special pre-packed polytetrafluoroethylene (PTFE) from Agilent (USA) was used as a reflectance standard.

S4. Photocatalytic experiments

The pristine and modified TiO_2 photocatalysts were tested in the oxidation of acetone vapor under UV and visible light in a continuous-flow set-up. The photocatalyst was deposited on a round glass plate in the area of 9.1 cm^2 and placed into the photoreactor. The surface density of the photocatalyst on the glass was 1 $mg \cdot cm^{-2}$. In the case of inlet analysis, the gas flows through the IR cell and then through the photoreactor. In the case of outlet analysis, the gas flows through the photoreactor and then through the IR cell. The time interval for the analysis of both the inlet and outlet during the experiments was 10 min. The other experimental parameters were as follows: the reactor temperature is 40 ± 0.1 °C, the relative humidity is 19 ± 1 %, the volume flow rate is 0.065 ± 0.001 L min^{-1}.

Before the evaluation of photocatalytic activity, the adsorption-desorption equilibrium of acetone on the photocatalyst was achieved until no difference in inlet and outlet acetone concentrations was observed. After that, a light source was turned on and the photocatalytic activity was evaluated. A high-power UV-LED with a maximum at 371 nm and Blue-LED with a maximum at 450 nm were used for the photocatalyst irradiation. The total irradiance was 9.7 $mW \cdot cm^{-2}$ for UV-LED and 164 $mW \cdot cm^{-2}$ for Blue-LED. The LED's radiance was measured using an ILT 950 spectroradiometer from International Light Technologies Inc. (USA).

A relative difference in activity (Figure S1) between modified and pristine TiO_2 photocatalysts was calculated for all Cu-grafted photocatalysts as follows:

$$Rel.diff. = \frac{\mathrm{W_{grafted}} - \mathrm{W_{pristine}}}{\mathrm{W_{pristine}}} \times 100\%$$

where $W_{grafted}$ is the activity of grafted photocatalyst ($\mu mol \cdot m^{-1}$), $W_{pristine}$ is the activity of pristine photocatalyst ($\mu mol \cdot m^{-1}$).

The relative difference in activity of X%Cu/TiO_2-ES wasn't calculated due to the pristine TiO_2-ES has no activity under visible light. This means that the denominator would be zero and value of difference would tend to infinity.

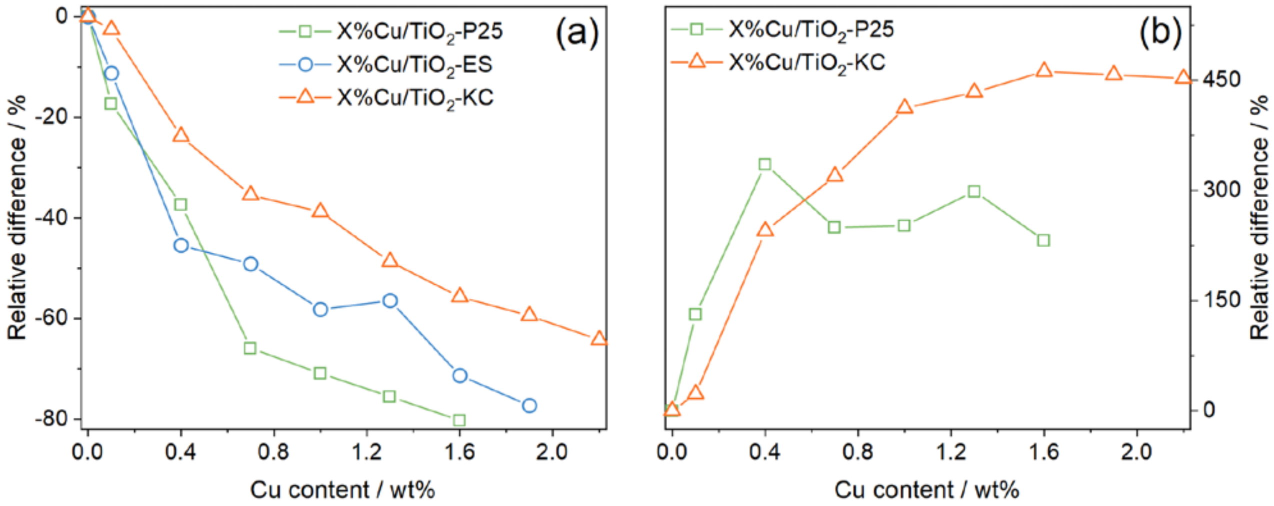

Figure S1 Relative difference in activity between Cu-grafted and pristine TiO_2 photocatalysts under (a) UV and (b) blue light.

S5. Experiments for evaluation of action spectra

Fifteen LEDs were used as radiation sources for irradiation of photocatalysts during the experiment of action spectrum measurement. The photonic efficiency was calculated to evaluate the efficiency for utilization of incident light. The flux of incident photons onto the glass plate for each LEDs was ca. $7{\cdot}10^{17}$ s^{-1}. According to IUPAC recommendations [1], the photonic efficiency of photocatalytic reaction (AQE) can be express as follows:

$$\xi = \frac{W_r}{q_p^0} = \frac{16}{3} \times \frac{W_{CO_2} \times 10^{16}}{7 \cdot 10^{17}} \times 100\%$$

where ξ is the photonic efficiency (%), W_r is the reaction rate (s^{-1}), q_p^0 is the incident photon flux (s^{-1}), W_{CO_2} is the steady-state rate of CO_2 formation measured in the set-up (µmol·min^{-1}), $\frac{16}{3}$ is the conversional factor (Numerator: it requires 16 electrons to decompose the acetone molecule that means 16 acts of electron excitation and requires 16 photons for the excitation; Denominator: 3 molecules of CO_2 are formed from 1 molecule of acetone during 1 act of reaction).

The experimentally obtained data on the dependence of the photonic efficiency on the basic wavelength of used LED for TiO_2-ES and 1.3%Cu/TiO_2-ES samples are shown in Table S1. According to emission spectra, single-peak LEDs used for the evaluation of action spectra are not true monochromatic light sources because they have a distribution of photons on wavelength as compared to the basic wavelength corresponded to the maximum of emission. Therefore, a correction of experimental action spectra is made based on the actual spectral irradiance of certain LED to improve the quality and reliability of the spectra. The details and difference in experimental and corrected action spectra can be found in our recently published papers [2,3].

Table S1 The experimental data of action spectra measurements before and after correction.

LED, nm	TiO_2-ES				1.3%Cu/TiO_2-ES			
	W_{CO_2}, μmol min^{-1}	W_r, s^{-1}	ξ, %	Corrected ξ, %	W_{CO_2}, μmol min^{-1}	W_r, s^{-1}	ξ, %	Corrected ξ, %
380	4.24	4.25×10^{16}	32.6	37.0	1.44	1.44×10^{16}	11.1	12.2
396	1.46	1.47×10^{16}	11.3	8.0	0.68	6.80×10^{15}	5.2	4.7
400	0.94	9.46×10^{15}	7.25	5.0	0.51	5.10×10^{15}	3.9	3.5
403	0.47	4.71×10^{15}	3.6	3.3	0.35	3.46×10^{15}	2.65	2.4
407	0.30	2.99×10^{15}	2.3	1.95	0.28	2.83×10^{15}	2.2	2.1
424	0.048	4.86×10^{14}	0.37	0	0.16	1.56×10^{15}	1.20	1.23
447	0	0	0	0	0.0495	4.95×10^{14}	0.38	0.27
458	0	0	0	0	0.0404	4.04×10^{14}	0.31	0.31
500	0	0	0	0	0.0057	5.75×10^{13}	0.044	0.025
509	0	0	0	0	0.0059	5.95×10^{13}	0.046	0.02
522	0	0	0	0	0	0	0	0
594	0	0	0	0	0	0	0	0
636	0	0	0	0	0	0	0	0
655	0	0	0	0	0	0	0	0
730	0	0	0	0	0	0	0	0

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