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

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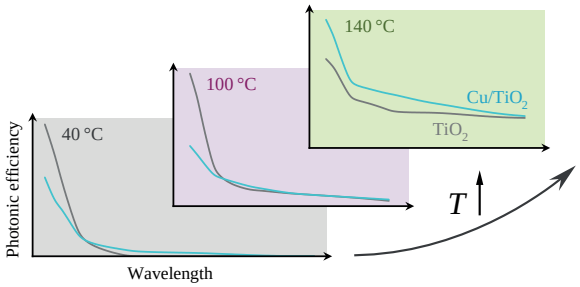
The dependence of action spectra for pristine and Cu-grafted anatase TiO_2 on temperature for photocatalytic acetone vapor oxidation at 40, 100 and 140 °C is described. The results obtained demonstrate the thermal inhibition of activity under UV irradiation for pristine titania at 140 °C, while for TiO_2 grafted with copper species this inhibition is suppressed. Photonic efficiency of visible radiation energy utilization by Cu-grafted titania increases with temperature and exceeds the corresponding value for pure anatase in the investigated temperature range.



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Since titanium dioxide working under UV irradiation is known to be the most common basis for semiconductor photocatalysts, the expansion of its action spectrum into the visible light region appears to be a promising area of scientific research.[1–5] The potential benefit of expanded action spectra is the effective usage of solar radiation.[6] Additionally, this is beneficial for creating modern photocatalytic devices and systems with light-emitting diodes (LED) as light sources instead of mercury lamps.[7–9]

Surface modification by grafting particles (metals, oxides, or other semiconductors) onto the surface of the basic photocatalyst[10] is the simplest and most common approach to affecting the oxidation under UV irradiation[11] and to expanding the action spectra of photocatalysts.[12] Therefore, a lot of effort has been made to develop new methods for creating visible light sensitive TiO_2-based photocatalysts without photocatalytically effective noble metals employed. Currently, modification of TiO_2 surface with copper is of special interest since grafting of Cu particles onto titania leads to the appearance of absorption in the visible light region and activation of the photocatalyst in the photooxidation reaction under visible light irradiation.[13–15] However, the obtained absolute values of photonic efficiency are still low. Raising the reaction temperature is one of the most common strategies for chemical processes acceleration. Meantime, for photocatalytic processes an increase in temperature above a certain value may lead to deceleration of the process.[16] This is partly due to the change in the adsorption capacity of the photocatalyst[17,18] and the hydroxyl groups layer on its surface.[19] Such dependence with a maximum in the region of 80 °C is valid for titania when the process is carried out under UV irradiation, that provides excitation of its structure. But for modified samples light absorption occurs through other processes. Therefore, the thermal inhibition of this absorption is questionable. At the same time, the possibility of obtaining synergy from combining optical and thermal energies suggests researchers to study the phenomenon of thermo-photoactivation[20–22] and the production of materials with photothermal-assisted photocatalytic activity in more detail.[23]

Herein, we explored the wavelength dependence of photocatalytic activity for pristine and Cu-grafted titania at reaction temperatures 40, 100 and 140 °C. The temperature points were selected on the basis of the published data on the temperature effect on the activity of pristine titania under UV irradiation.[16] Namely, 40 °C is the baseline level of photoactivity in the low temperature region, 100 °C is the point of the highest photoactivity of pristine titania. The value 140 °C from the high temperature region was chosen as a relatively safe value for the photoreactor at which a noticeable decrease in activity is observed due to fundamental limitations associated with the adsorption of reagents. Commercially available TiO_2 powder Euro Support (100% anatase, Euro Support Manufacturing Czechia) was employed as photocatalyst and hereafter referred to as ES. The modified TiO_2 photocatalyst was synthesized *via* the impregnation of basic photocatalyst ES with an aqueous solution of precursor $Cu(OAc)_2$ for the calculated copper content of 1.3 wt% and hereafter referred to as Cu/ES. Both samples were characterized by UV-VIS diffuse reflection spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) at the required temperatures, and tested in the photocatalytic oxidation of acetone vapor in a continuous flow setup under the radiation of single-peak LEDs.[24] The actual value of the copper content was selected based on the results of testing a series of Cu-grafted titania as the point of maximum activity under blue irradiation.[15] Additional details of the experiment can be found in the Online Supplementary Materials.

Figure 1 shows the action spectra curves for ES and Cu/ES photocatalysts, indicating their temperature dependence. The

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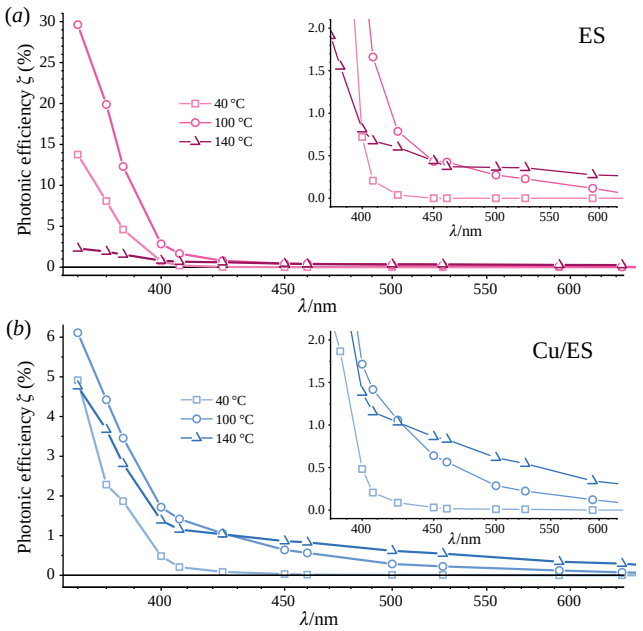

Figure 1 Action spectra of (*a*) ES and (*b*) Cu/ES samples during photocatalytic oxidation of acetone vapor at 40, 100, and 140 °C. Inserts depict enlarged spectral regions with the most noticeable changes.

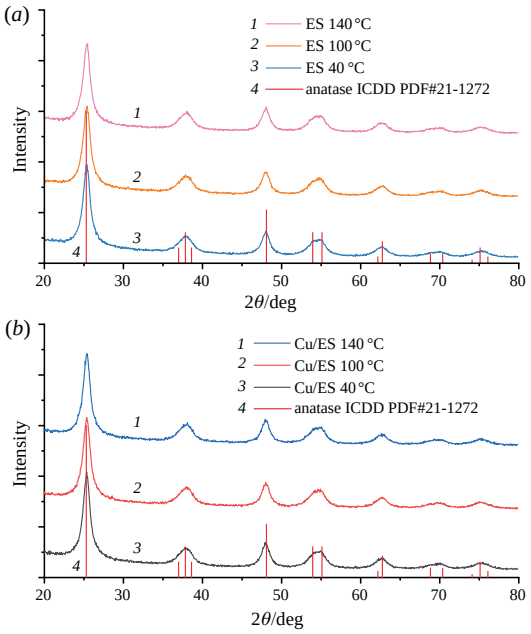

Figure 2 XRD patterns of (*a*) pristine titania ES and (*b*) Cu/ES (1.3 wt% Cu) at various temperatures.

reproducibility error of the photonic efficiency values does not exceed 15%. It is obvious for TiO_2-based photocatalysts that the photonic efficiency of reaction under UV irradiation increases until 100 °C and then decreases for both samples.[16,25] However, shifting to the visible light region reveals some changes. The first one is the existence of photoactivity for ES and Cu/ES under irradiation up to 600 nm at elevated temperatures. As carbon monoxide is a by-product of photocatalytic oxidation,[26] the presence of CO in the reaction products confirms the occurrence of oxidation but not the photodesorption of CO_2. The second one is the gradual increase of activity under visible light irradiation with increasing temperature in contrast to the activity under UV irradiation. According to the obtained data, the overall activity at elevated temperature is always above the dark activity, which means that the samples show photoresponsivity under visible light.

As the thermal change of the crystal lattice may lead to the bandgap change (and shift in the boundary of the photoactivity appearance), a decision was made to investigate a possible change in titania structural characteristics by means of XRD analysis at elevated temperature. The lattice parameters and the mean size of crystallites (in accordance with coherent scattering region size) for the anatase phase at different temperatures are given in Table 1. The anatase phase is observed in both samples. XRD plots of samples at different temperatures are shown in Figure 2. The lattice parameters differ from the typical values for anatase TiO_2 (a = 3.784 Å, c = 9.515 Å), while this difference is obvious for nanosized TiO_2 with size of crystallites about 5 nm.[27–29]

A slight decrease in lattice parameter c is observed only for Cu/ES as temperature increases without visible changes for ES.

Table 1 Structural characteristics of the anatase phase in samples at different temperatures.

Sample	Anatase lattice parameter/Å			Size/nm
	40 °C	100 °C	140 °C	
ES	a = 3.794 c = 9.513	a = 3.795 c = 9.513	a = 3.794 c = 9.513	5.0
Cu/ES	a = 3.795 c = 9.513	a = 3.795 c = 9.508	a = 3.795 c = 9.510	5.0
Published data for typical anatase[30]	(at 47 °C) a = 3.784 c = 9.511	(at 94 °C) a = 3.785 c = 9.515	(at 141 °C) a = 3.786 c = 9.519	~200

Due to the small size of the crystallites, the reflexes of the anatase phase are broadened. Consequently, this leads to a comparatively large error in the refinement of the lattice parameters. Therefore, all differences in the lattice parameters are within the error range. The lattice parameters of the anatase with a particle size of ~200 nm at different temperatures are also given in Table 1.[30] For the large crystal of TiO_2 the increase in the lattice parameters a and c with temperature is observed, which is associated with the lattice thermal expansion. However, such a noticeable change in titania structure is not observed for the nanosized samples. So, the apparent visible light activity is unlikely due to the structure-dependent change in bandgap width. Therefore, the appearance of activity under visible light irradiation and the expansion of the action spectra for both the pristine and modified anatase samples could be associated with other factors, *e.g.* possible ligand-to-metal charge transfer[31] or temperature-related optical changes,[32] which need a special study.

The enlarged plots of action spectra at different temperatures are presented in Figure 3 with dashed lines indicating the activity of samples at certain temperatures without irradiation. Cu/ES sample is more active in acetone vapor oxidation than ES sample for wavelengths above 400 nm. Numerically, the difference in photonic efficiency observed at 450 nm is about 0.03% for 40 °C, 0.21% for 100 °C and 0.42% for 140 °C. Thus, the interfacial charge transfer considered as the most possible reason for the visible light activity of Cu-grafted titania[33,34] does not lead to a decrease in activity at elevated temperatures.

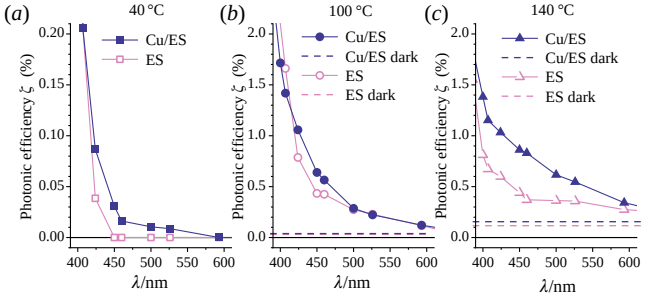

Figure 3 Enlarged region of action spectra for comparison of activity at (*a*) 40 °C, (*b*) 100 °C, (*c*) 140 °C. Dashed lines indicate the observed activity of catalyst with no light irradiation (thermal oxidation activity).

Noteworthy, the difference in activity under green light irradiation (500 and 525 nm) increases with temperature from 40 to 140 °C, but no difference in activity is observed at 100 °C. This effect can be explained by the different optimal temperature conditions for the functioning of titania structure and grafted Cu_xO particles. The temperature of maximum photonic efficiency of pristine titania (ES) is 100 °C and the major contribution to activity of Cu/ES under visible light irradiation at this temperature comes from titania. Effect of interfacial charge transfer between titania and copper is slightly noticeable at 100 °C, which leads to a negligible difference in visible light photonic efficiency between pristine and Cu-grafted titania and to a noticeable prevalence of ES under UV irradiation. On the contrary, ES has a low photonic efficiency at elevated temperature (140 °C), but copper-related activity is not inhibited by the temperature increase. Therefore, in total, this gives a noticeable difference between the activities of Cu/ES and ES at 140 °C.

In conclusion, we have found that the thermal activation of the photocatalytic oxidation process using titania-based catalysts may affect the actual action spectra of the photocatalyst. Surface modification of TiO_2 with copper suppressed its photocatalytic activity under UV irradiation, but the absolute values of the UV activity under thermal activation are relatively stable in contrast to pristine titania. The activity of both pristine and modified titania under visible light irradiation with wavelengths up to 634 nm is above the 'dark' activity for elevated temperatures. Photonic efficiency of the oxidation reaction over of Cu-grafted sample under visible light increases with temperature. The observed increase in photonic efficiency shows a great advantage of using copper-modified titanium dioxide as photocatalyst at both normal and elevated temperatures.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.042.

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