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

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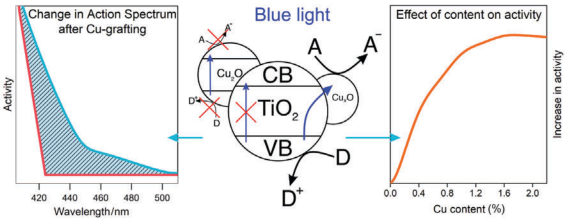
This paper describes a simple technique for the modification of titania with copper to enhance its photocatalytic performance. In addition to the absorption of UV light resulted in band-to-band excitation of electrons, TiO_2 grafted with copper species absorbs radiation in the visible region of spectrum, and it is able to completely oxidize volatile organic pollutants both under UV and visible light. The action spectra of pristine and Cu-grafted TiO_2 photocatalysts are measured and discussed to elucidate the reasons for appearance of the activity under visible light.



Keywords: photocatalytic oxidation, visible light, Cu-grafted TiO_2, action spectrum, interfacial charge transfer.

Anatase TiO_2 is a commonly used photocatalyst for oxidation reactions, which provide the degradation of various contaminants. The decomposition of organic pollutants and dyes,[1–5] the oxidation of harmful volatile compounds,[6,7] the inactivation of bacterial and viral contaminants,[8] and oxygen evolution[9] have been described. Many manufacturers produce low-cost powdered TiO_2 photocatalysts. Typically, commercial powdered TiO_2 photocatalysts have high activity under UV irradiation, but their activity under visible light is extremely low. Currently, there is a growing demand for highly active visible light-responsive photocatalysts due to a new trend toward reducing mercury consumption, especially in light sources, a high cost of UV light-emitting diodes (LEDs) as a Hg-free alternative to mercury lamps, and a low fraction (<5%) of UV radiation in sunlight.

According to Weon *et al.*,[10] the modification of TiO_2 to extend its action spectrum to the visible region still stays the main approach to develop an efficient photocatalyst for utilization of visible light. Surface modification of TiO_2 with copper species is one of the ways to prepare a visible light-active photocatalyst, and this method has a potential for the large-scale production. Many species, such as zerovalent Cu, Cu_xO, and Cu^{2+}, can be detected on TiO_2 surface after the deposition of copper.[11] The reasons for the photocatalytic activity of Cu-modified TiO_2 under visible light can be, first, the surface plasmon resonance of Cu nanoparticles (~580 nm)[12] and, second, the excitation of an electron in Cu_2O followed by electron transfer to the conduction band of TiO_2.[13] Otherwise, the interfacial charge transfer from the valence band of TiO_2 to Cu_xO clusters without excitation of electrons to the conduction band of TiO_2 may also be responsible for the visible light-activity.[14] Therefore, it is difficult to isolate the self-dependent effect of only one Cu species in this multicomponent system to unambiguously establish the origin of activity under visible light. It was our motivation to investigate the action spectrum of Cu-grafted TiO_2 photocatalyst in an attempt to clarify this question. We measured the action spectrum for one of the most active Cu/TiO_2 samples and compared them with the spectrum of pristine TiO_2 that allows us to suggest Cu species responsible for the photocatalytic activity under visible light.

In this study, we show a simple technique for the modification of TiO_2 photocatalysts with copper that results in appearance of light absorption in the visible region of spectrum and provides the photocatalytic activity under visible light. Three commercial photocatalysts, namely, TiO_2-P25, TiO_2-ES and TiO_2-KC were modified with copper via their impregnation with aqueous solution of copper acetate followed by reduction with sodium borohydride.[†] The copper content was varied from 0.1 to 2.2 wt%. All samples were characterized by UV-VIS diffuse reflectance spectroscopy (DRS) and tested in the photocatalytic oxidation of acetone vapor under UV and blue radiations in a continuous-flow set-up.[15] Additionally, the action spectra were measured in the same set-up using 15 single-peak LEDs.[16] The experimental details can be found in Online Supplementary Materials.

Figure 1 shows the UV-VIS spectra of the synthesized photocatalysts and initial TiO_2 supports. The supports are crystalline TiO_2, which absorbed UV light. Only TiO_2-KC absorbed visible light due to the presence of an aromatic compound, which plays the role of a sensitizer.[17]

Surface modification of TiO_2 with copper resulted in a color change due to absorption in the visible and near-IR regions. For all TiO_2 supports, light absorption increases as the Cu content increases [Figure 1(*d*)–(*f*)]. The absorption band in a range of 350–500 nm can be attributed to interfacial charge transfer from the valence band of TiO_2 to Cu_xO clusters.[11] The absorption of

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[†] TiO_2-P25 (Aeroxide P25, 80% anatase and 20% rutile, 55 $m^2\ g^{-1}$, Evonik Ind. AG, Germany), TiO_2-ES (anatase powder, 100% anatase, 380 $m^2\ g^{-1}$, EuroSupport, Czech Republic), TiO_2-KC (KRONOClean 7000, >87.5% anatase, >270 $m^2\ g^{-1}$, Kronos Worldwide Inc., USA), $Cu(CH_3COO)_2{\cdot}H_2O$ (AO Vekton Inc., Russia) and $NaBH_4$ (Sigma-Aldrich, USA) were used.

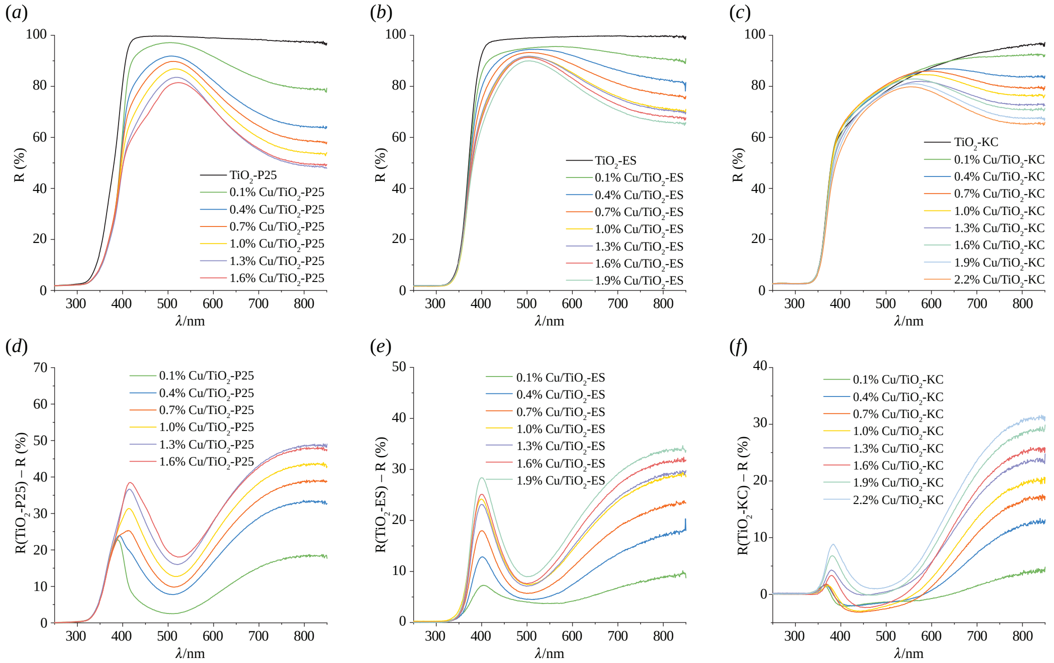

Figure 1 UV-VIS spectra of the Cu-grafted photocatalysts based on (*a*) TiO_2-P25, (*b*) TiO_2-ES, and (*c*) TiO_2-KC. Plots in (*d*)–(*f*) show a relative increase in light absorption compared to corresponding TiO_2.

the samples based on TiO_2-KC in this range was not clearly observed due to the shielding of TiO_2 surfaces with Cu species and a decrease in the light absorption by TiO_2-KC itself.

All Cu-grafted samples also have a broad absorption band at >500 nm, which can be attributed to light absorption by Cu_2O (up to 600 nm),[13] intrinsic exciton in CuO, and/or *d*–*d* transitions in Cu^{2+} species (600–800 nm).[11] Therefore, UV-VIS spectroscopy confirms the presence of many types of Cu species on the TiO_2 surface after copper deposition using copper acetate as a precursor.

All synthesized photocatalysts are able to oxidize acetone vapor to CO_2 and water both under UV (365 nm, 9.7 mW cm^{-2}) and blue (450 nm, 164 mW cm^{-2}) radiations. The steady-state rate of CO_2 formation in acetone oxidation was used as a value of photocatalytic activity. Figure 2 shows the effect of Cu content on the activity of Cu/TiO_2 photocatalysts under irradiation.

The deposition of copper species on TiO_2 negatively affected its activity under UV radiation. The values of activity monotonically decrease for all TiO_2 supports as the Cu content increases in whole studied range [Figure 2(*a*)]. This fact can be explained by a shielding effect mentioned above and by an enhanced recombination of charge carriers on Cu sites. The second effect is due to pristine TiO_2 photocatalysts have a high photonic efficiency under UV. Impurity sites on the TiO_2 surface led to the localization of electrons and holes on these sites followed by their recombination, which reduces the efficiency of light utilization in target process.

In contrast to UV, the photocatalytic activity of Cu/TiO_2 samples under blue light increases as the Cu content increases. At higher values of Cu content, which depend on the type of TiO_2 support, activity reaches a constant value [Figure 2(*b*)]. These results confirm that the visible-light activity of Cu-grafted samples was due to Cu species on the TiO_2 surface. The action spectrum may help to discover the origin of photocatalytic activity under visible light. If the interfacial charge transfer from TiO_2 to Cu_xO clusters is the main reason for the visible-light activity, the edge of action spectrum will be at ~500 nm and Cu-grafted photocatalysts will not have the activity under green and red radiations. Otherwise, if the surface plasmon resonance of Cu nanoparticles or photoexcitation of electrons in Cu_2O nanocrystallites is the main reason, the edge of action spectrum will be at ~600 nm or longer.

One of the most active samples based on TiO_2-ES [1.3% Cu/TiO_2-ES, Figure 2(*b*)] was selected for investigating the action spectrum because TiO_2-ES is pure anatase without a rutile phase or an organic admixture, and it does not absorb visible light [Figure 1(*b*)]. Figure 3 shows the action spectra of the initial and Cu-grafted TiO_2 samples. As expected, the pristine TiO_2-ES exhibited activity only in a range up to 424 nm. On the contrary, the Cu-grafted TiO_2-ES sample manifested activity under visible light up to ~500 nm, and no activity was observed under red radiation. These results allowed us to conclude that the interfacial charge transfer from TiO_2 to Cu_xO clusters is the major pathway resulting in

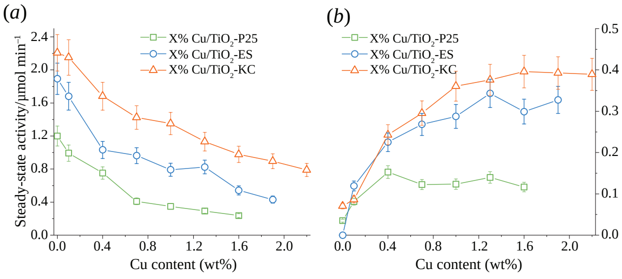

Figure 2 Effect of Cu content on the photocatalytic activity of composites under illumination with (*a*) UV and (*b*) blue light.

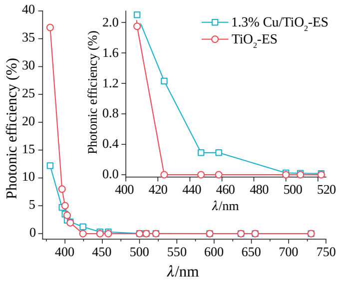

Figure 3 Action spectra of 1.3% Cu/TiO_2-ES and TiO_2-ES photocatalysts. Inset: the action spectra in a range of 400–520 nm.

the photocatalytic activity of the Cu-grafted TiO_2 samples under visible light.

In conclusion, using three commercial TiO_2 photocatalysts, we found that the surface modification of TiO_2 with copper suppressed its photocatalytic activity under UV radiation. The activity of Cu-grafted samples in this region monotonically decreases as the Cu content increases. On the contrary, the photocatalytic activity of Cu/TiO_2 under blue light increases as the Cu content increases until reaching a constant value at 0.4–1 wt% Cu on different TiO_2 supports. According to the action spectrum, the Cu-grafted TiO_2 is photocatalytically active under radiation with wavelengths up to ~500 nm that may indicate the interfacial charge transfer from TiO_2 to Cu_xO clusters as the major pathway for the photoactivation in the visible region.

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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.2021.09.017.

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