Influence of Cu dispersion on photocatalytic activity of Cu-doped titania prepared using binary metal alkoxide

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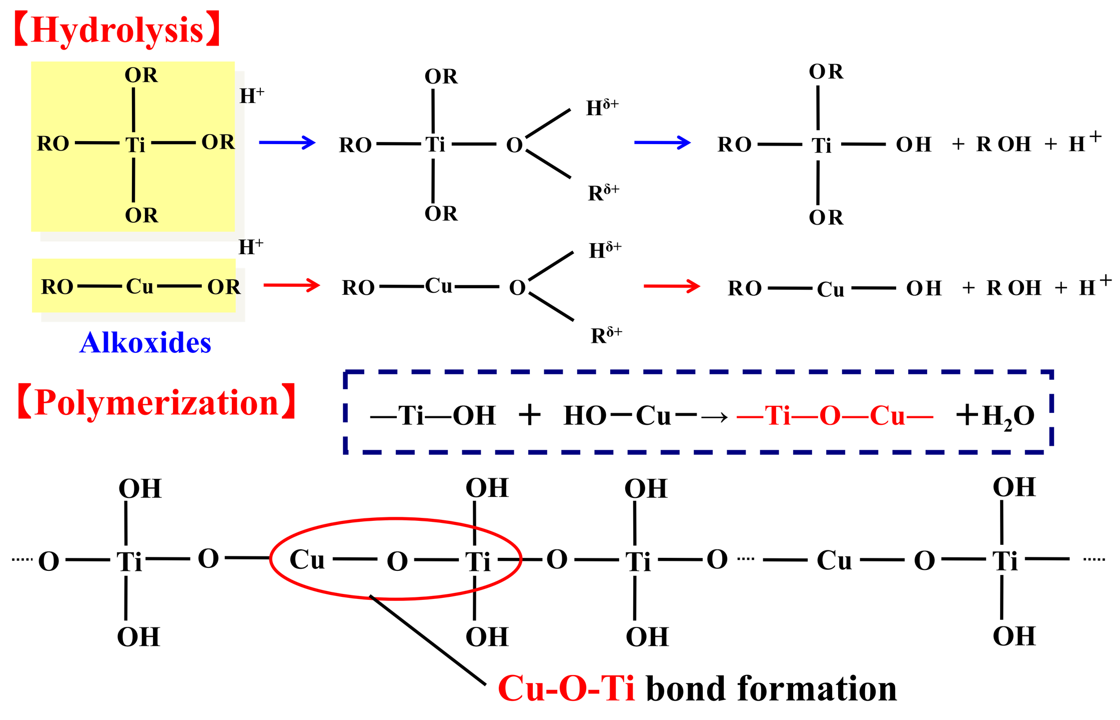
Introduction

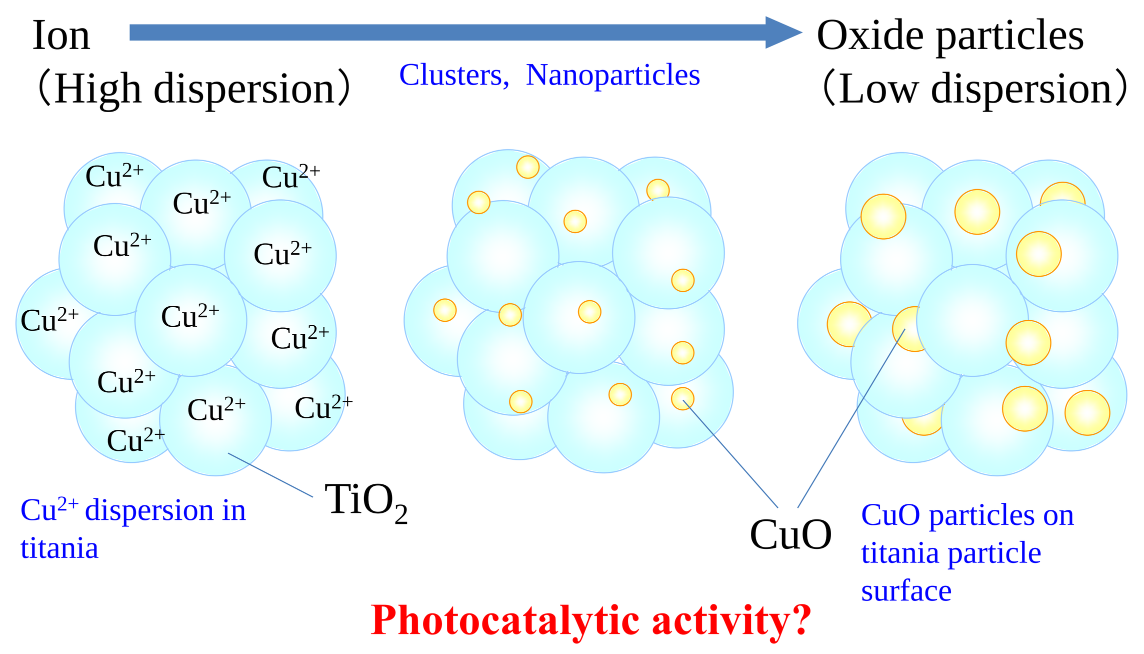
Metal-doped titania can be prepared from a sol-gel precursor solution containing various metal compounds. It is important that the metal species are homogeneously dispersed on the titania surface in order to provide an effective electronic interaction between the titania and the metal.[1,2] One of the transition metals, copper, is a relatively available and effective dopant for trapping the electrons in the conduction band of titania. In this study, we tried to prepare Cu-doped titania from the sols containing titanium tetraisopropoxide (TTIP) and copper(II) isopropoxide (CIP). The Cu dispersion in the titania was controlled by varying the reaction time of TTIP at which CIP was added to the sol. The UV and visible photocatalytic activities of the samples were examined by hydroxyl radical production. The influences of the Cu dispersion in the titania and the electronic interaction between the Ti and Cu on the photocatalytic activity were discussed.

1) R. C. Mehrotra, *J. Non-Cryst. Solids*, **100**, 1 (1998).
2) H. Nishikiori et al., *Res. Chem. Intermed.*, **38**, 595 (2012).

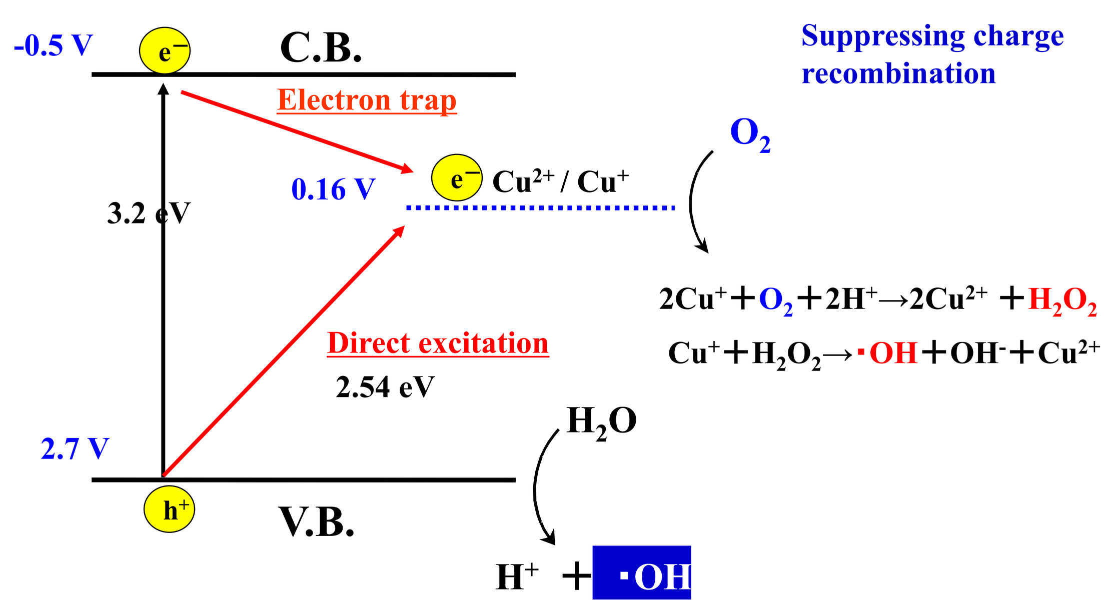
Sol–gel reaction



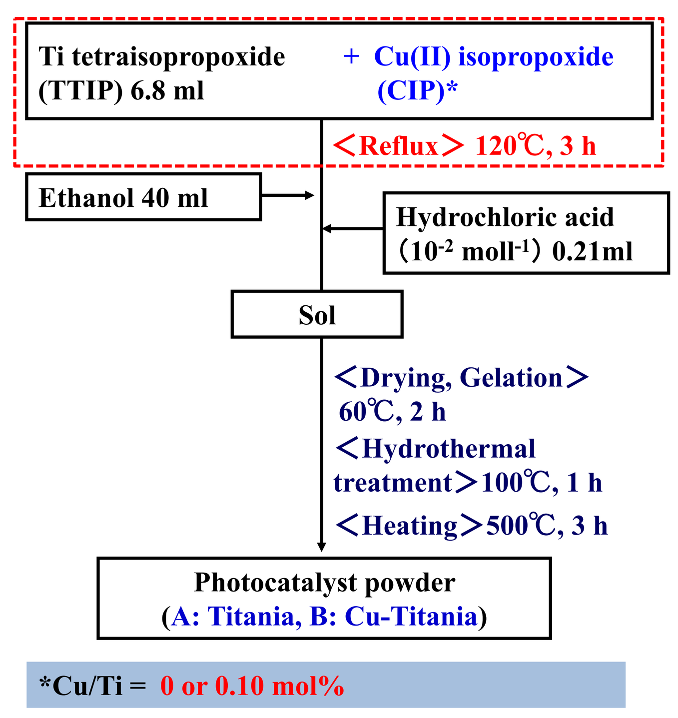
Cu dispersion in titania



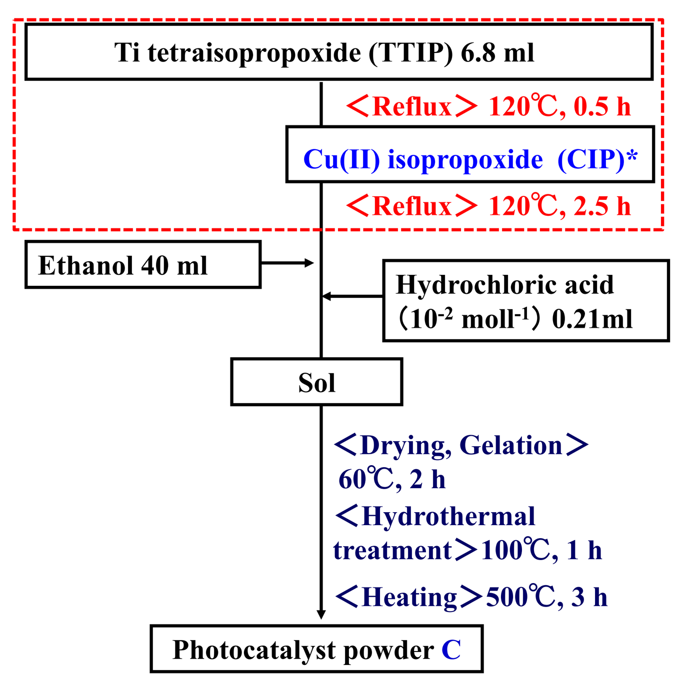
Mechanism of photocatalytic reaction on Cu-doped titania

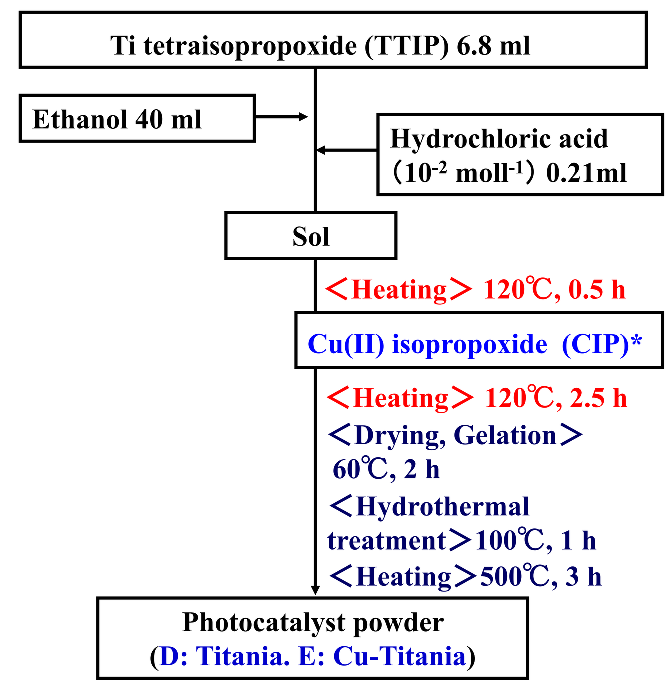


Experimental



Preparation of photocatalyst samples



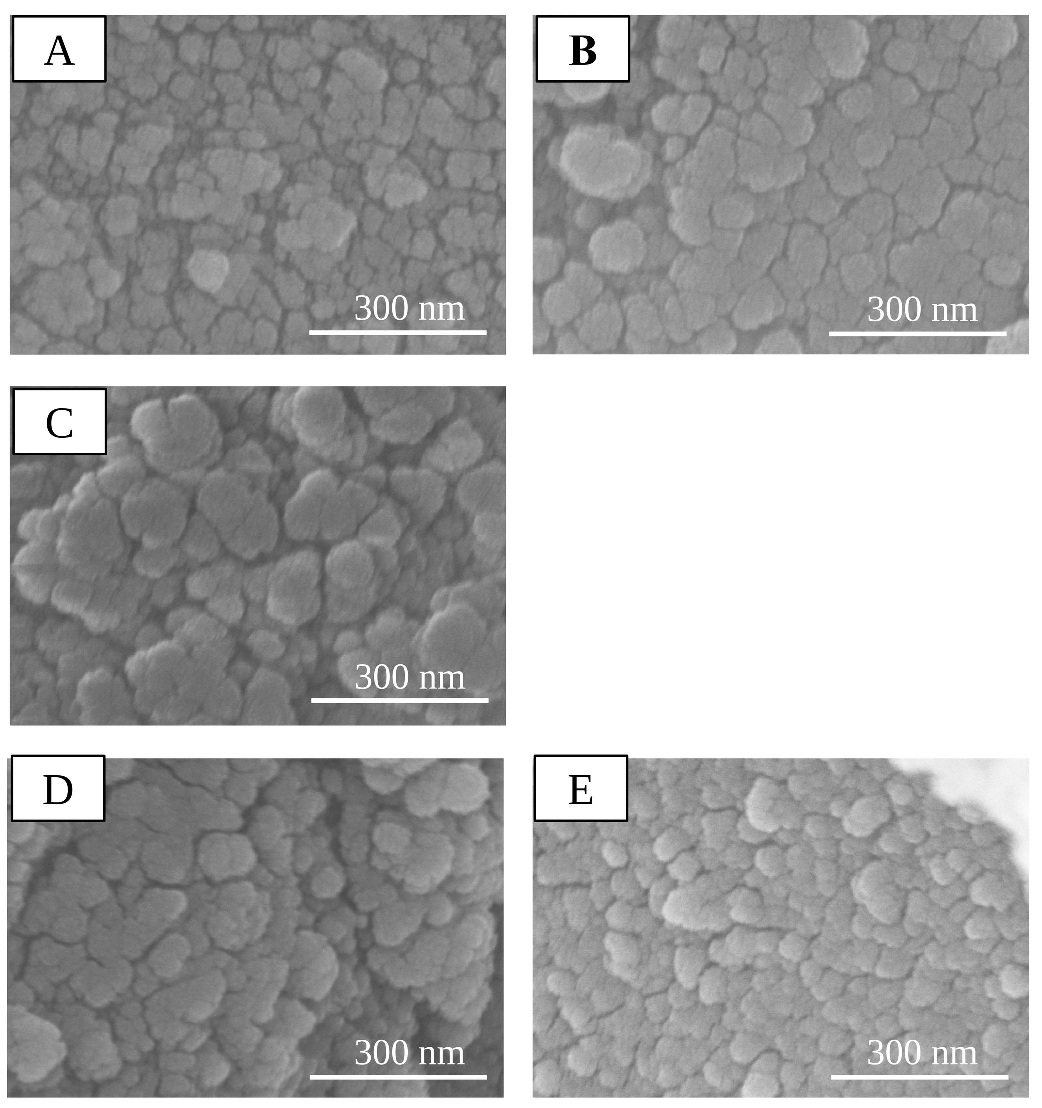


Measurements

<Characterization>
- **SEM observation**
- **XRD analysis**
- **UV-Vis DRS measurement**
- **FT-IR measurement**

<Photocatalytic activity examination>
- **Fluorescence analysis of telephthalic acid (TA) (OH radical detection)**

Results and discussion

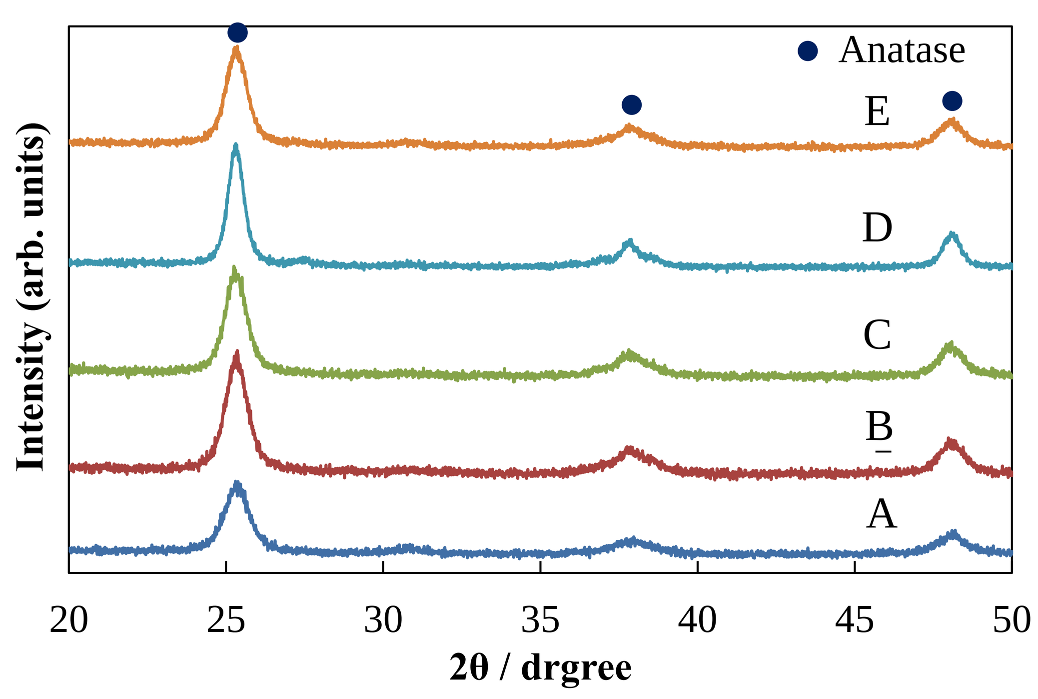


SEM images of the photocatalyst powder samples.

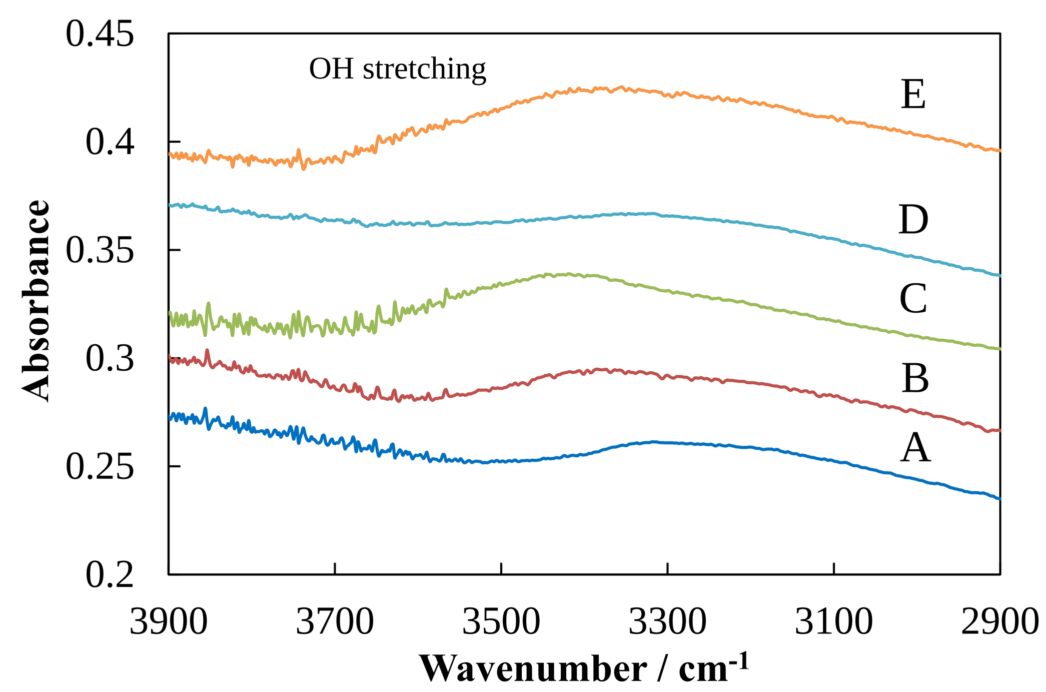
Crystallite sizes of the prepared catalysts estimated by XRD analysis

Sample	A	B	C	D	E
Crystallite size / nm	21.3±1.3	20.6±2.9	22.7±1.8	22.7±2.4	19.5±1.8

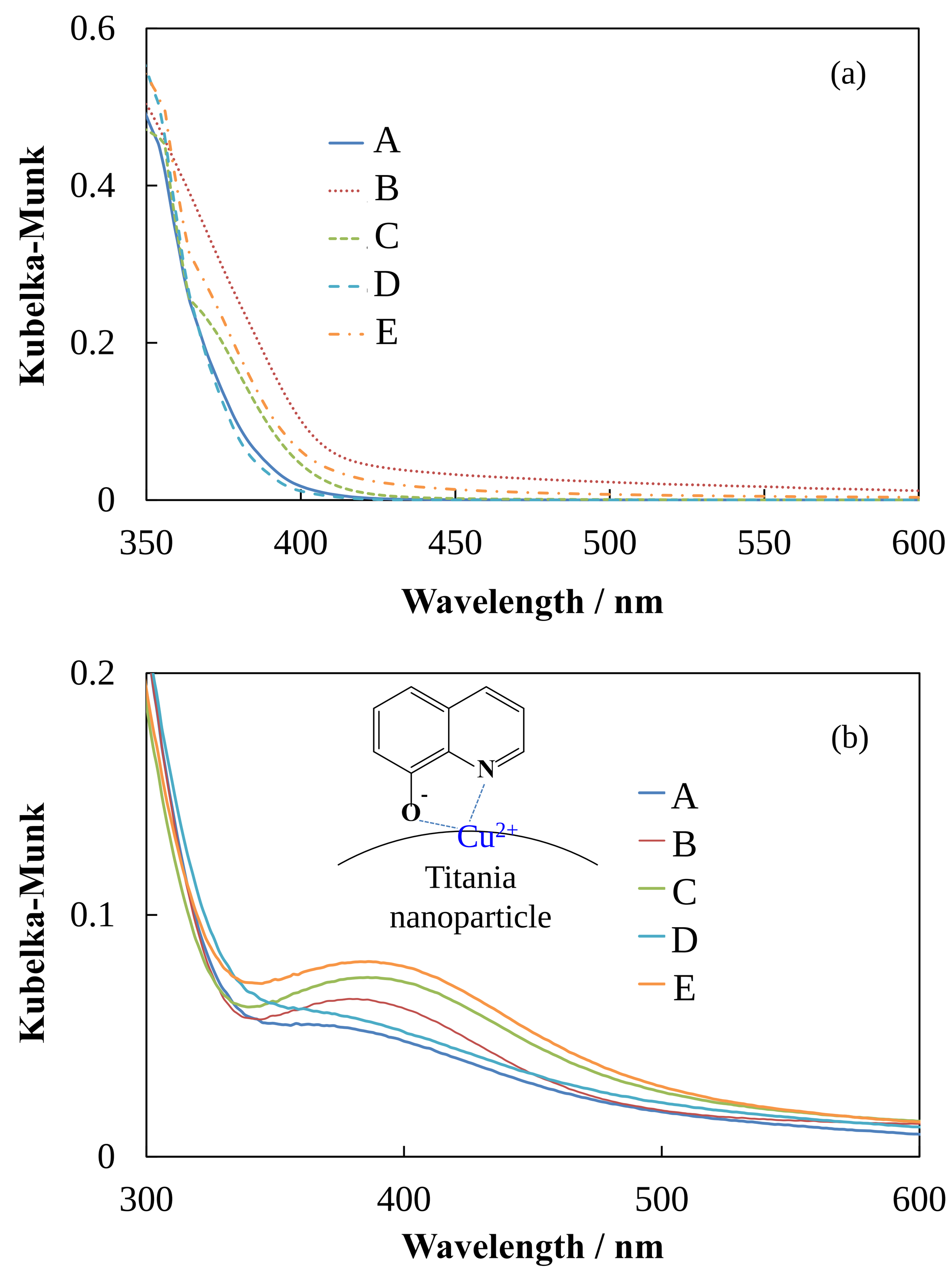
Characterization



XRD patterns of the photocatalyst powder samples.



FTIR spectra of the photocatalyst powder samples.

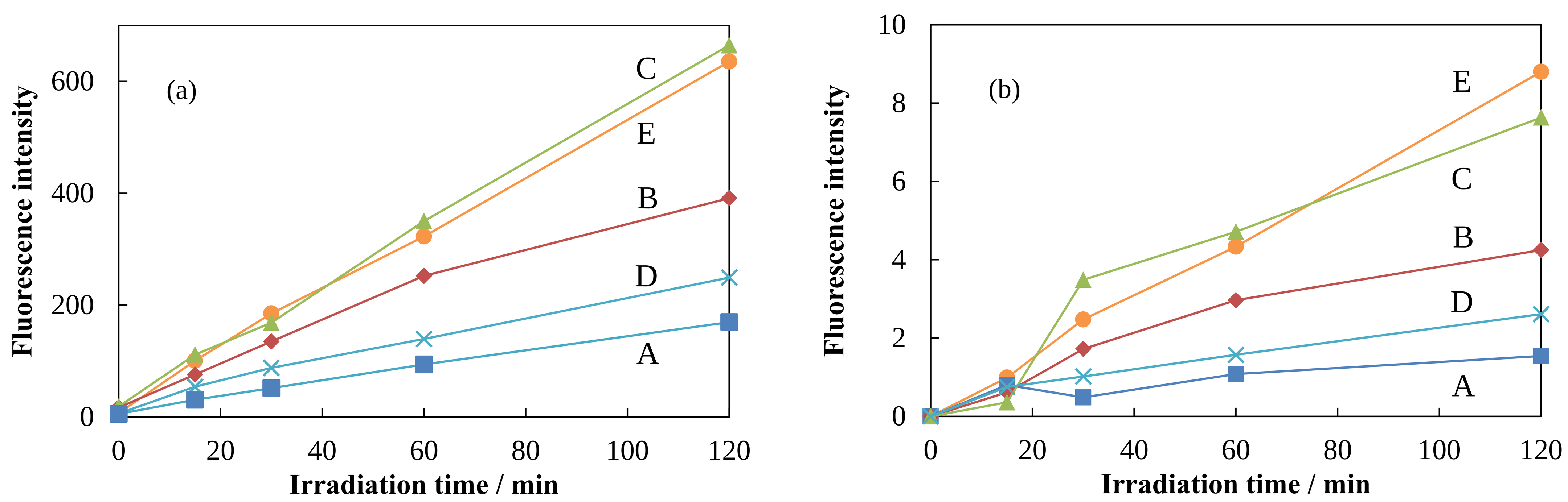


DRS spectra of the photocatalyst powder samples (a) as prepared and (b) adsorbing 8-hydroxyquinoline (HQ).

Pore characteristics of the prepared catalysts estimated by BET and BJH methods from the adsorption isotherms of nitrogen gas measured by the volumetric gas adsorption method

Sample	A	B	C	D	E
Specific surface area / m^2g^{-1}	96	94	90	85	83
Average pore size / nm	6.7	6.1	6.0	6.5	6.1
Total pore volume / cm^3g^{-1}	0.14	0.14	0.13	0.12	0.13

Photocatalytic activity



Time course of the fluorescence intensity of 2-hydroxy terephthalic acid in order to detect hydroxyl radicals produced during (a) UV and (b) visible light irradiations using the photocatalyst powder samples

Conclusions

- The Cu distribution in the titania was controlled by varying the reaction time of TTIP at which CIP was added to the sol.
- A higher distribution of the Cu on the titania surface was achieved in the sample prepared by adding CIP after the longer TTIP reaction time.
- The high distribution of Cu on the titania surface enhanced the electronic interaction between the Ti and Cu and the photocatalytic activity.
- The impurity states of Cu^{2+} on the titania surface effectively trapped the electrons in the conduction band of the titania and received the electrons in the valence band upon photoexcitation, and consequently, suppressed charge recombination of the electrons and holes.
- In the sample, the high Cu distribution on only the titania surface rather than inside the titania bulk led to its high photocatalytic activity due to its accessibility from the surroundings.