Mechanistic in-situ Study of Photoinduced Interfacial Electron Transfer, Charging and Discharging of One-Pot Prepared Cu-TiO₂

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Introduction
Hydrogen is an ideal fuel that can be obtained from sustainable plant biomass and water. One of major goals in photocatalysis and catalysis is to understand the mechanism of charge transfer across semiconductor/metal junction. Interfacial charge transfer in metal/semiconductor photocatalysts containing noble metals, e.g. [1] has been studied extensively. On the other hand, charge transfer in composite photocatalysts with reduced forms of earth-abundant metal promoters such as Cu reported by us [2] requires special attention, and mechanistic studies need to be performed under the in-situ conditions. We report the "one-pot" synthesis of model photocatalytic colloid Cu(0)-TiO₂ from Cu(II) and Ti(IV) precursors in alcohol, and the in-situ study of repeated photoexcitation induced electron transfer.

Materials and Methods
Titanium isopropoxide, Cu nitrate and absolute ethanol were from Sigma, and P25 TiO₂ Evonik (Degussa) was from Acros Organic. In the 3.5 mL quartz cuvette, absolute ethanol was mixed with water solution of Cu nitrate and with Ti isopropoxide. Precursor solution was purged with argon, and the cuvette was sealed. Light source was a 450 Watt medium pressure Hg lamp. To prepare colloid solution of TiO₂, 0.1 mL of DI water was added instead of Cu nitrate solution; to prepare colloid solution of Cu₂O, absolute ethanol was added instead of Ti isopropoxide. The in-situ UV-Vis spectra were collected using Cary 50 spectrophotometer. The precursor solution was repeatedly exposed to the light of Hg lamp, and UV-Vis spectrum was acquired. Numeric fitting of the spectra was conducted with Microcal Origin. The in-situ photoluminescence (PL) spectra were recorded using Cary Eclipse fluorescence spectrometer equipped with angular fluorescence accessory.

Results and Discussion
When the solution of Ti isopropoxide precursor in ethanol was illuminated, optical absorbance at 200-800 nm progressively increased due to scattering from the in-situ photochemically formed TiO₂ colloid. When precursor solution of Cu nitrate was illuminated in the absence of Ti precursor, the new UV-Vis bands at 300-500 nm and 550-800 nm appeared that were assigned to Cu₂O nanocolloid of ca. 2 nm in size. Integration of absorption band at 550-800 nm as a function of illumination time yields a (quasi)first order rate law A = A₀ * (1 – exp( - k * t)), where A is the integrated absorbance and t is the time of illumination. The kinetic constant is k = 0.204 ± 0.020 min⁻¹ and coefficient of determination is R² = 0.997. In the dark, no spectral changes have occurred. Under the in-situ photoassisted reaction of solution of Ti and Cu precursors, a new peak at 550-650 nm appeared due to absorption by the surface plasmon resonance (SPR) of Cu metal nanoparticles (NPs) [3]. Kinetics of in-situ formation of plasmonic Cu(0) NPs follows the zero order rate law. The in-situ PL spectroscopy showed the presence of oxygen vacancy V(O) formed simultaneously with Cu(0) NPs, and both Cu(0) and V(O) were oxidized by air under ambient conditions. Without Ti precursor or Cu precursor, V(O) was not observed. The structure of “one-pot” prepared photocatalytic colloid is Cu(0)-V(O)-TiO₂, and illumination causes photoexcitation of TiO₂ rather than Cu(0) plasmonic NPs. The repeated illumination and keeping colloid in the dark (Figure 1) causes the repeated blue and red shifts [4] of the maximum of absorbance of the SPR, due to repeated electron transfer from photoexcited TiO₂ to Cu(0) and discharge of supported Cu(0).

Significance
For the first time, a repeated photoinduced charge transfer across semiconductor → metal interface was in-situ demonstrated in Cu(0)-V(O)-TiO₂ model nanocolloid for photoreforming alcohols. Proposed novel multi-spectroscopic in-situ approach is useful to study chemical composition and charge transfer in model heterogeneous photocatalysts and catalysts.

Figure 1. A) Blue shift of absorption maximum due to the SPR of Cu(0) in Cu(0)-V(O)-TiO₂ after the illumination was turned on. B) Red shift of this peak after the illumination was turned off. C) The following blue and red shifts after the illumination was turned on and off.

References