Photochemical synthesis, characterization, photoinduced electron transfer, charging and discharging in copper-titania colloid

Mihir Mehta, Sean Taylor, Alexander Samokhvalov*

Chemistry Department, Rutgers University, 315 Penn St, Camden, NJ 08102, USA

ABSTRACT

One of major goals in photocatalysis and photochemistry is to understand photoinduced charge transfer. Colloidal solutions serve as convenient model systems for mechanistic studies of charge transfer. For the first time, colloid $Cu(0)$-V_O-TiO_2 was prepared by the "one-pot" photochemical synthesis from copper nitrate and titanium isopropoxide precursors in ethanol under UV–vis light. The $Cu(0)$-V_O-TiO_2 colloid shows the surface plasmon resonance (SPR) absorption band of metallic copper and contains oxygen vacancy V_O. Kinetics of the synthesis of $Cu(0)$-V_O-TiO_2 colloid follows the zeroth-order kinetic rate law, while synthesis of Cu_2O colloid under the same conditions follows the first order rate law. Under UV–vis light, $Cu(0)$-V_O-TiO_2 colloid undergoes repeated accumulation of negative charge on metallic copper after photoexcitation of TiO_2, and discharge of electrons from metallic copper occurs in the dark.

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1. Introduction

Titanium dioxide TiO_2 remains a benchmark photocatalyst [1]; coinage metals gold [2], silver [3], and copper [4] serve as photocatalytic promoters which increase the rate of photocatalytic reactions. Minimization of undesirable electron-hole recombination in metal-promoted TiO_2 photocatalysts is achieved by using alcohols, e.g. ethanol [4] and glycerol [5,6] as sacrificial electron donors. The efficiency of photocatalysis significantly depends upon the direction and rate of the photoexcitation induced electron transfer between the semiconductor and metal promoter.

Mechanisms of photoinduced electron transfer have been reported in the series of excellent papers: by Oldfield et al. for gold on nanoparticles (NPs) on tin dioxide [7] and for silver, copper and gold on zinc oxide [8], and by Kamat for silver and gold on titania [9,10]. In these mechanistic studies of photoinduced charge transfer, colloidal solutions of nanoparticles serve as convenient model photocatalytic systems. In addition, colloids find a *direct* use in photocatalytic reforming of alcohols to hydrogen using metal-promoted titania [11,12] and other metal oxides, e.g. [13]. To our knowledge, the *in-situ* mechanistic study of the photoexcitation induced interfacial electron transfer in copper-titania colloid was not reported.

Recently, we reported the preparation, characterization and photocatalytic reforming of glycerol in water to hydrogen by the binary promoted N-M-TiO_2 photocatalysts (N = nitrogen, M = none, Cr, Co, Ni, Cu), under the near-UV and visible light [14], and Cu promoter has demonstrated the highest activity. We also reported the *in-situ* photoreduction of the *as-prepared* Cu(II) site in the "pre-photocatalyst" to the photocatalytically active Cu site [14]. Herein, we report the "one-pot" photochemical synthesis of $Cu(0)$-V_O-TiO_2 model photocatalytic colloid (where V_O is oxygen vacancy) from Cu(II) and Ti(IV) precursors in solution, its characterization by the complementary *in-situ* spectroscopic methods, the *in-situ* measurements of kinetics of formation of this $Cu(0)$-V_O-TiO_2 colloid, and mechanistic study on the direction and dynamics of repeated photoinduced charge transfer in this colloid under the UV and visible light.

2. Materials and methods

2.1. Chemicals

Titanium (IV) isopropoxide $Ti(iPrO)_4$, copper nitrate $Cu(NO_3)_2$, absolute ethanol, and glycerol were from Sigma, and P25 TiO_2 Evonik (Degussa) was from Acros Organics.

2.2. Photosynthesis of colloids

In the 3.5 cc quartz cuvette, 3.0 mL of absolute ethanol was mixed with 0.1 mL of 0.033 M solution of copper nitrate $Cu(NO_3)_2$ in water, and then 0.33 mL of 0.01 M solution of titanium isopropoxide $Ti(iPrO)_4$ in absolute ethanol was added to achieve atomic ratio Cu/Ti = 1. Thus, in this precursor solution, initial

concentrations of precursors were $[Cu(NO_3)_2]_0 = [Ti(iPrO)_4]_0 = 9.6 \times 10^{-4}$ M. Magnetic micro stir bar has been added to the cuvette, this precursor solution was purged with the UHP argon for 5 min to remove dissolved oxygen, and the cuvette was sealed to protect its content from air. For the photo-synthesis of colloids under continuous stirring, we used the 450 W medium pressure mercury lamp from Ace Glass. The light emitted by the Hg lamp was passed through a 1 cm thick 4×4 cm quartz cuvette filled with DI water, in order to eliminate the infrared emission of Hg lamp and to maintain precursor solution at room temperature. To prepare TiO_2 colloid in ethanol, 0.1 mL of DI water was used instead of $Cu(NO_3)_2$ solution in water; to prepare Cu_2O colloid in ethanol, 0.33 mL of absolute ethanol was used instead of solution of $Ti(iPrO)_4$ precursor in absolute ethanol; the other experimental conditions were the same.

2.3. The in-situ UV–vis spectroscopy

The *in-situ* UV–vis spectra of colloid solutions were obtained using Cary 50 spectrophotometer. For kinetic experiments, the precursor solution was exposed to the light of Hg lamp for 90 s, and the UV–vis absorption spectrum was immediately collected for 20 s. The sequence of exposure to the light and acquisition of absorption spectrum was repeated several times. Numeric processing of the UV–vis spectra was performed with Microcal Origin Pro 9.1 software.

2.4. The in-situ PL spectroscopy

The *in-situ* photoluminescence (PL) spectra of colloid solutions were recorded using Cary Eclipse fluorescence spectrometer. To minimize primary and secondary absorption of light [15] in colloid solution, fluorescence spectrometer was equipped with the angular fluorescence accessory from Quantum Northwest Inc. as was reported in our earlier papers [16,17]. The 3.5 cc quartz fluorescence cuvette with colloid solution was placed so that the excitation beam was at 20 degrees to the normal to the front face of the cuvette. To improve the monochromaticity of the excitation light, fluorescence spectrometer was equipped with the narrow bandpass (5 nm or 10 nm) optical filters at 468, 580 and 605 nm. Excitation and emission slits were set at optical bandwidth of 5 nm or 10 nm.

2.5. The in-situ high-resolution PL spectroscopy

The high resolution *in-situ* PL spectra were collected using a Fluorolog-3 model FL3-22 fluorescence spectrometer from Horiba Scientific. This fluorescence spectrometer is equipped with a dual monochromator grating on both the excitation and emission optical pathways to exclude stray excitation light from emission spectra. Further, to minimize primary and secondary absorption of light [15] in colloid solution, the standard front face (FF) geometry has been used, with the emission collected at 20 degrees to the normal to the front face of the cuvette. In the *in-situ* PL emission experiments, the excitation and emission slits were set at 3 nm. In the *in-situ* PL excitation experiment, the emission slit was set at a 5 nm bandwidth, and the excitation slit at 3 nm.

2.6. Preparation of colloidal solution of P25 TiO_2

Colloidal solution of P25 TiO_2 in water was prepared by magnetic stirring 1.0 g P25 TiO_2 with 100 mL DI water at room temperature, followed by centrifugation at 3800 rpm for 1 h. Then, a supernatant was collected, centrifuged for an additional 1 h, and a clear supernatant was collected again. The obtained colloidal

solution of TiO_2 was diluted with DI water to achieve absorbance $A = 1$ at $\lambda = 365$ nm.

3. Results and discussion

3.1. Characterization of colloids by the in-situ UV–vis spectroscopy

Colloidal solution of TiO_2 in ethanol was reported to be formed by hydrolysis of titanium isopropoxide precursor with small amounts of water [9] in the absence of exposure to the light. We decided to determine experimental conditions of the *in-situ* photochemical synthesis of TiO_2 colloidal solution from titanium isopropoxide $Ti(iPrO)_4$ precursor under illumination with the UV–vis light source. Fig. S1 shows the emission spectrum of medium pressure Hg lamp used as light source in our experiments. Fig. 1 shows the progression of the *in-situ* UV–vis absorption spectra of Ti$(iPrO)_4$ precursor solution in ethanol at variable exposure time to emission of Hg lamp. No change of the *in-situ* UV–vis spectrum of $Ti(iPrO)_4$ precursor in ethanol was observed without illumination; dashed line in Fig. 1 indicates the UV–vis spectrum of $Ti(iPrO)_4$ precursor in ethanol at the zero time of illumination.

When the total accumulated time of exposure to the light increases up to 15×90 s, optical absorbance progressively increases. The featureless broad spectrum in Fig. 1 is representative of absorption and scattering of the UV–vis light [9] by colloidal solution of TiO_2 reaction product formed from $Ti(iPrO)_4$ precursor.

Next, we decided to determine the kinetics of formation of the products of photochemical reaction of $Cu(NO_3)_2$ precursor in ethanol in the *absence* of titanium precursor $Ti(iPrO)_4$. Fig. 2A shows the time-dependent *in-situ* UV–vis absorption spectra of Cu$(NO_3)_2$ precursor solution in ethanol (see Section 2) at the variable time of exposure to the Hg lamp.

No change of the UV–vis spectrum was observed without illumination with Hg lamp. The time of each illumination was 2 min, and the time to measure the spectrum after each illumination was 20 s. At the total exposure to the light of Hg lamp exceeding 8 min, destruction of the colloid solution occurred with precipitation of brown powder.

When the total time of illumination increased, absorbance due to spectral bands in the ranges at ca. 300–500 nm and 550–800 nm increased, see Fig. 2A and Inset therein. The observed spectral change is due to photochemical reduction of Cu(II) precursor in ethanol to either Cu(I) or Cu(0) product in colloidal solution. For the Cu(0) colloid, the typical absorption band would be present

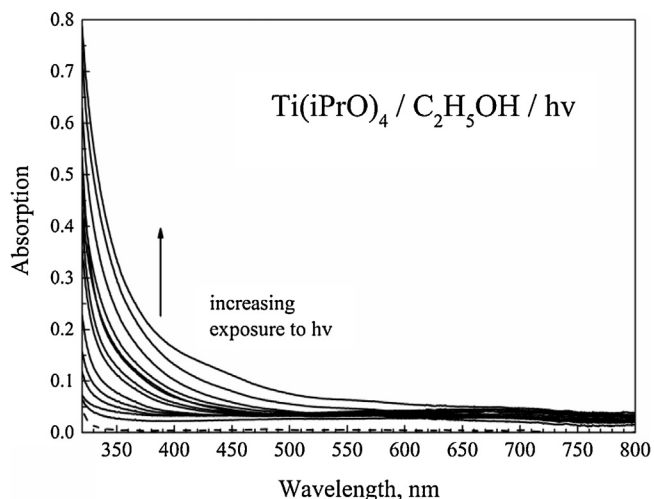**Fig. 1.** The *in-situ* time-dependent UV–vis spectra of precursor $Ti(iPrO)_4$ in ethanol under illumination. Dashed line denotes the spectrum at a zero time of illumination.