Photoelectrochemical Responses from Polymer-coated Plasmonic Copper Nanoparticles on TiO$_2$

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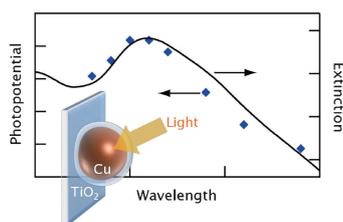
Photoelectrochemical Responses from Polymer-coated Plasmonic Copper Nanoparticles on TiO₂

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Plasmonic Cu nanoparticles photocatalytically deposited on a TiO₂ electrode show photocorrosion under visible light. The electrode protected with poly(vinyl alcohol) exhibits photopotential and photocurrent responses due to localized surface plasmon resonance, suggesting that it could be applied to cost-effective plasmonic devices.

Noble metal nanoparticles (NPs) such as Au, Ag, and Cu absorb and scatter visible light due to localized surface plasmon resonance (LSPR).[1] Since intensity and wavelength of LSPR depend on surrounding dielectric environment, as well as particle size and shape, the NPs are applied to chemical sensing and biosensing.[2] Additionally, since electric fields localize around NPs due to LSPR,[1] NPs are used as light-harvesting antennae for surface-enhanced Raman scattering,[3] fluorescence enhancement,[4] and photocurrent enhancement.[5] We found plasmon-induced charge separation at interfaces between Au or Ag NPs and metal oxides such as TiO₂.[6] The plasmon-induced charge separation has also been studied[7] and used[8–10] by many other research groups. In the case of Au NPs, which are stable during the charge separation process, the system has been exploited for photovoltaic devices[6d–6f,8] and photocatalysis.[6d,9] On the other hand, Ag NPs, which are less stable than Au NPs, are oxidized to Ag⁺ ions as a result of the plasmon-induced charge separation and are re-reduced to Ag NPs by TiO₂ photocatalysis under UV light.[6a,6b,11] These apparently reversible photoelectrochemical reactions have been applied to multicolor[6a,6b] and infrared[6g] photochromism and other photochromic processes[10] and photomorphing hydrogels.[11]

Cu NPs also exhibit LSPR in the visible light region and the work function of Cu (4.65 eV) lies between Ag (4.0 eV) and Au (5.1 eV).[12] For these reasons, plasmon-induced charge separation might also be possible at the Cu NP–TiO₂ interface. Since Cu is much less expensive than Au and Ag, more cost-effective plasmonic devices could be developed by use of Cu NPs. New functionalities could also be expected for Cu NP–TiO₂ systems. However, most of the previous work on Cu–TiO₂ systems has been for antibacterial effects.[13] In addition, it is known that Cu NPs are easily oxidized and lose their plasmon resonance gradually under ambient conditions.[14] For stabilization of Cu NPs, Kominami and co-workers[9b] alloyed them with Au. To stabilize pure Cu NPs, it is effective to protect them with a capping agent.[14,15] However, perfect protection would insulate Cu NPs from the surrounding system and inhibit observation of the charge separation through photoelectrochemical reactions. In the present work, we deposit Cu NPs on TiO₂ by photocatalytic reactions[16] and coat the deposited NPs with poly(vinyl alcohol) (PVA) to mildly protect the NPs from extensive oxidation during photoelectrochemical processes. As a result, photoelectrochemical responses based on LSPR of Cu NPs are observed under visible light.

TiO₂ suspension (75%, STS-21, Ishihara Sangyo) was spin coated at 1500 rpm for 10 s on a cleaned ITO-coated glass substrate (40 × 12.5 × 1 mm³) and sintered (temperature was raised up to 723 K at 1.5 K min⁻¹ and kept at the temperature for 1 h) under atmospheric conditions, followed by irradiation with black light (ca. 1 mW cm⁻²) for >1 day to clean the surface photocatalytically. A 0.1 mol L⁻¹ aqueous solution of Cu(CH₃-COO)₂ (pH 5.4, 0.15 mL) was mixed with ethanol (3 mL), deaerated by N₂ gas and was applied to the prepared anatase TiO₂ film surface (0.15 mL). The film was irradiated with UV light (310 nm, 5 mW cm⁻²) by using a Hg–Xe lamp under humid N₂ gas flow for 5 min. As a result, the initially colorless TiO₂ film turned gray and a broad extinction (= absorption + scattering) peak characteristic of LSPR[16] was observed at around 600 nm in the extinction spectrum (Figure 1a). Actually, particles 20–40 nm in diameter were observed on the TiO₂ film by SEM. Under UV light, electrons in the valence band of TiO₂ are excited to the conduction band (−0.48 V vs. NHE in a pH 5.4 aqueous medium). Cu²⁺ ions are reduced to metallic Cu NPs ($E(Cu^{0/2+}) = +0.34$ V vs. NHE) by the excited electrons and positive holes generated in the valence band are consumed by oxidation of ethanol. The extinction spectrum of a 30 nm Cu NP on TiO₂ (Figure 1c, inset) was simulated on the basis of finite difference time domain (FDTD).[16] The calculated extinction peaks at 620 nm (Figure 1c), supporting that the experimentally observed extinction peak is due to LSPR of Cu NPs. The broader peak of the experimentally observed spectrum than that of the calculated one is explained in terms of dispersion in the particle size.

When the Cu NP–TiO₂ sample was left in air under dark conditions, the extinction peak gradually deteriorated as shown in Figure 1a. The sample left for 60 min was subjected to X-ray photoelectron spectroscopy (XPS) and satellite peaks specific to CuO and a Cu LMM Auger signal ascribed to Cu⁺ were observed as well as peaks ascribed to Cu⁰, whereas only the peaks for Cu⁰ were observed for as-deposited NPs. We therefore conclude that the Cu NPs were partially oxidized by ambient oxygen to Cu oxides such as CuO and Cu₂O and the LSPR signal deteriorated.

Thus we spin-coated as-deposited Cu NPs with 3.4 wt% aqueous poly(vinyl alcohol) (PVA, Mw: 2000) followed by drying in air at 393 K for 5 min to protect the NPs from oxidation. The coating red-shifted the extinction peak of Cu NPs by 25 nm due to an increased refractive index (ca. 1.5) around the NPs (Figure 1b). The PVA-coated sample exhibited no significant change in the spectrum for at least 60 min in air under dark conditions, indicating that the Cu NPs were protected by PVA from oxidation in this period of time. Coating with poly(vinylpyrrolidone) (PVP) also protected Cu NPs from oxidation. PVA and PVP adsorb on the Cu surface by van der Waals interaction.[14d]

The PVA-coated Cu NPs were repeatedly irradiated with visible light (480–700 nm, 15.5 mW cm⁻²) in air. As a result,
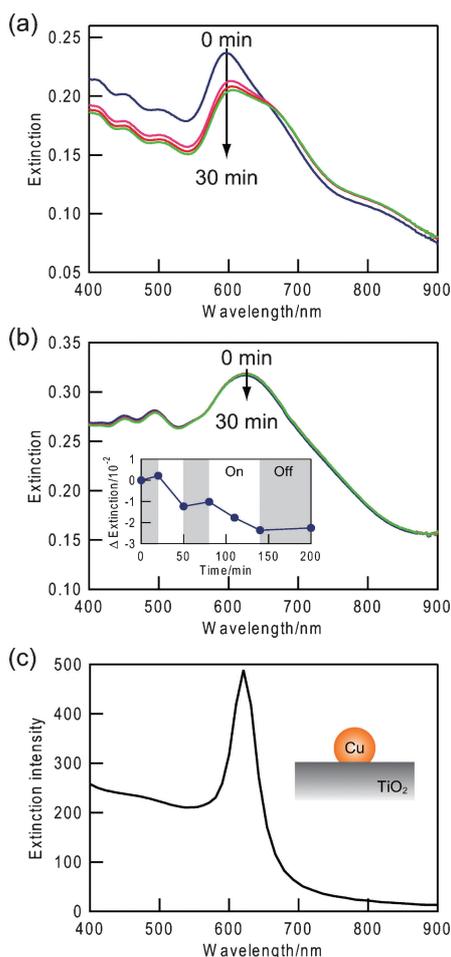
Figure 1. (a, b) Changes in the extinction spectra in air under dark conditions of (a) bare and (b) the PVA-coated Cu NPs deposited on TiO$_2$, respectively. (b inset) Changes in the peak extinction under repeated irradiation with visible light (480–700 nm, 15.5 mW cm^{-2}). (c) Simulated spectrum of a single Cu NP on TiO$_2$ (30 nm diameter).

Figure 2. (a) Photopotential and (b) photocurrent action spectra (latter: in the presence of 0.1 mol L^{-1} triethanolamine) of the PVA-coated Cu NP–TiO$_2$ electrode. Extinction spectra of the electrode are also shown.

the extinction peak height decreased during the irradiation (Figure 1b, inset) likely due to the plasmon-induced charge separation. In the case of Ag NPs on TiO$_2$, the charge separation results in oxidation of Ag to Ag$^+$ ions and reduction of ambient O$_2$.[6a,11,17] Similar redox reactions possibly take place for the present system with Cu NPs.

Therefore the possible plasmon-induced charge separation for the present system was examined by photoelectrochemical means. In the case of TiO$_2$-coated ITO electrodes with Au NPs or Ag NPs, negative shifts of open-circuit potential and short-circuit anodic currents are observed under visible light.[6c,6d,8,17] If the charge separation occurs also at the Cu NP–TiO$_2$ interface, similar photoelectrochemical responses should be obtained.

Cu NPs were deposited on a TiO$_2$-coated ITO electrode, and coated with PVA and dried to obtain a PVA-coated Cu NP–TiO$_2$ electrode. This electrode as the working electrode and a Pt counter electrode were immersed in acetonitrile containing 0.01 mol L^{-1} tetrabutylammonium perchlorate (12 mL) as an electrolyte. No significant change in the spectrum was observed,

indicating that the PVA coating was thicker than the penetration length of the localized electric field. Although the working electrode was illuminated repeatedly (480–700 nm, 15.5 mW cm^{-2}), no significant changes in the open-circuit potential (vs. counter electrode) were observed. This may be explained in terms of poor permeability of the dried PVA film to electrolyte ions. Similar behavior is observed for a hydrophilic conducting polymer-coated electrode, which exhibits electrochemical responses in an organic medium only after addition of a certain amount of water, which swells the polymer film.[18] We therefore added 0.8 mL of water to the electrolyte, and observed shifts in the potential (ca. −35 mV) during the light irradiation.

A TiO$_2$-coated ITO electrode without Cu NPs was coated further with PVA and was subjected to control experiments. However, no changes in the potential were observed under illumination. Next we examined photopotential action spectrum of the PVA-coated Cu NP–TiO$_2$ electrode under monochromatic light irradiation (full width at half-maximum: 10 nm, 5 × 10^{15} photons cm^{-2} s^{-1}) (Figure 2a). The action spectrum is roughly in agreement with the extinction spectrum of the electrode. These results indicate that Cu NPs and their plasmon resonance are essential for the photopotential responses.

We also examined photocurrents from the PVA-coated Cu NP–TiO$_2$ electrode in the electrolyte containing 0.1 mol L^{-1} triethanolamine as an electron donor under monochromatic light. As a result, anodic photocurrents were observed (Figure 2b). Since no significant photocurrents were observed for the electrode without Cu NPs, we ascribe the photocurrents to the plasmon resonance of the Cu NPs. The peak wavelength of the action spectrum is shorter than that of the extinction spectrum by ≥20 nm. These results suggest that Cu NPs of which peak wavelengths are short contribute largely to the photocurrents. Since the resonance peak of Cu NPs red shifts by PVA coating, the resonance at the shorter wavelength may be attributed to Cu NPs with a thin PVA coating or a much swollen

PVA coating, of which dielectric constant is close to that of water, rather than that of dried PVA. The thin or swollen coating may facilitate supply of the electron donor (i.e., triethanolamine) from the bulk electrolyte to Cu NPs, and removal of the oxidized donor to the bulk electrolyte.

Although the peak of the photopotential action spectrum also blue-shifted from that of the extinction spectrum, the shift (≤ 20 nm) was smaller than that for the photocurrent action spectrum. This is reasonable because the photopotential response does not need electron donors, unlike the photocurrent response. Therefore, the PVA coating does not interfere with the photopotential responses, unless the NPs are completely insulated.

In the case of Au and Ag NPs, ITO/TiO$_2$/NP electrodes exhibit negative photopotential shifts and anodic photocurrents as described above,[6c,6d,17a] while ITO/NP/TiO$_2$ electrodes exhibit positive photopotential shifts and cathodic photocurrents.[6e,17b] The polarity inversion of photoresponses under visible light, which is not observed when TiO$_2$ is excited by UV light, strongly supports electron injection from resonant NPs to TiO$_2$, whereas the inversion cannot be explained in terms of plasmonic enhancement of excitation of electrons from TiO$_2$ surface states to conduction band. The plasmon-based photoresponses of the present system may also be due to similar electron injection from Cu NPs to TiO$_2$. If an n-type semiconductor is in contact with a metal of which work function is greater than electron affinity of the semiconductor, a Schottky barrier forms at the junction. This holds for junctions of anatase TiO$_2$ (ca. 3.9 eV[19]) with Au, Ag, and Cu (5.1, 4.0, and 4.65 eV, respectively[12]). The barrier may contribute to the charge separation by preventing the separated charges from recombination.

Thus we found for the first time that pure Cu NPs deposited on TiO$_2$ exhibit photopotential and photocurrent responses. The low response (incident photon to current conversion efficiency: ca. 0.01%) is likely due to PVA, which improves stability at the expense of efficiency. Since the plasmon-induced charge separation is enhanced at the sites at which oscillating electric field is strongly localized,[20] employment of NPs with such fields (e.g., NPs with sharp tips) would improve the efficiency. On the other hand, we have demonstrated that Ag NPs can be protected by coating the NPs with TiO$_2$.[17b] A similar strategy would give more stable and practical photoelectrodes with Cu NPs without undue deterioration in the efficiency. The photoelectrochemical corrosion in the absence of the polymer coating could also be exploited for photofunctionalities. Ag NPs, of which resonance wavelength largely varies as the particle size changes on TiO$_2$, can be applied to multicolor photochromism.[6a,6b] Since resonance wavelength of Cu NPs is less sensitive than that of Ag NPs to changes in the particle size,[16] monochromatic photochromism may be a potential application of Cu NPs.

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