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Tannin-mediated assembly of gold–titanium oxide hybrid nanoparticles for plasmonic photochemical applications

Ho Yeon Son^a, Hwiseok Jun^a, Kyeong Rak Kim^a, Cheol Am Hong^{a,*}, Yoon Sung Nam^{a,b,*}

^a Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

^b KAIST Institute for the NanoCentury, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

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ABSTRACT

Plasmonic nanostructures have received increasing attention for photochemical applications due to high light absorptivity, tunability, sensitivity, and robustness. However, the short lifetime of hot electrons limits their efficient extraction, requiring the well-defined assembly of neighboring functional materials (e.g., electron filters and catalysts) along with the plasmonic nanostructures. Here we report the polyphenol-mediated assembly of gold nanoparticles (AuNPs) and titanium dioxide nanoparticles (TiO₂ NPs) into colloidal plasmonic heterostructures. Tannic acid (TA) is deposited on the surface of TiO₂ NPs through metal–ligand coordination, where TA serves as a reducing agent to synthesize AuNPs on the surface of TiO₂ NPs. The generation and injection of hot carriers from the plasmonic heterostructures exhibit faster electron transfer kinetics under visible light illumination as determined using ferricyanide as a redox agent. Subsequent surface coatings of TiO₂ NPs with phosphate-functionalized polyethylene glycol is shown as an effective means of selective surface passivation to suppress the charge transfer in the semiconductor/electrolyte interface. We expect that the interface control of plasmonic heterostructures for functional assembly and passivation can be utilized for their photochemical applications through integration with catalytic and sensing components.

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Introduction

Solar water splitting has received increasing attention as a carbon-free process for the production of solar fuels (e.g., hydrogen). Water splitting requires multiple charge transfer processes with a theoretically minimum energy of 1.23 eV. In particular, water oxidation is a very complex oxidative half-reaction based on a proton-coupled electron transfer (PCET) process with four-electron transfers [1,2]. In photo-induced water oxidation, a big challenge is the development of efficient light-harvesting systems with a high chemical stability and strong light absorption in the solar spectrum. A few stable wide bandgap oxide semiconductors can be used only in the UV light region [3], while organic photosensitizers and compound semiconductors are not stable enough for long-term uses in aqueous media under harsh conditions of water oxidation [4].

Recently, plasmonic metal nanostructures were suggested as promising light-harvesting materials for water splitting because of their excellent stability and strong light absorption in the visible light region due to localized surface plasmon resonance (LSPR) [5,6]. Highly energetic electrons, known as ‘hot electrons,’ are generated via plasmon decay in metal nanostructures and injected into a semiconductor in contact with the metal nanostructures over the metal–semiconductor Schottky barriers. The injected electrons can be eventually utilized for photocatalytic reactions [7–10]. For efficient plasmonic water splitting, the well-defined assembly of a series of various functional materials, including water oxidation catalysts, plasmonic metal nanostructures, semiconducting materials, and hydrogen evolution catalysts, is critically important to facilitate SPR-mediated electron and hole transfers. Despite several examples for the fabrication of plasmonic nanoparticles/semiconductor heterostructures [11,12], the selective assembly of water oxidation catalysts on metal nanostructures and hydrogen evolution catalysts on the semiconductor is still very challenging.

In this work, we introduce the polyphenol-mediated colloidal assembly of gold nanoparticles (AuNPs) and titanium dioxide nanoparticles (TiO₂ NPs) into a plasmonic heterostructure

* Corresponding authors at: Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea.

E-mail addresses: cahong@kaist.ac.kr (C.A. Hong), yoonsung@kaist.ac.kr (Y.S. Nam).

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photoanode for photochemical applications. Several phenolic compounds (e.g., hydroquinone, tannin, and catechol) can serve as reducing agents for noble metal precursors [13–18]. In particular, tannic acid (TA) can also serve as a reducing agent to reduce Au precursor ions into metallic AuNPs with a redox potential of about 100 mV vs. normal hydrogen electrode at pH 7 [19–21]. In addition, TA can be spontaneously deposited on the surface of various metal oxide nanostructures as a very thin layer through metal-ligand coordination [22,23]. The two functional properties enabled the coatings of colloidal TiO₂ NPs with TA and the *in situ* TA-mediated synthesis of AuNPs on the surface of TiO₂ NPs. Phosphate-functionalized polyethylene glycol (phosphate-PEG) was deposited selectively on the surfaces of TiO₂ NPs other than AuNPs for the passivation of the exposed TiO₂ surfaces. The kinetics of electron transfer in the plasmonic photoanodes was analyzed using Fe(CN)₆^{3-/4-} as a redox couple under visible light illumination.

Experimental

Materials

Titanium (IV) isopropoxide, tetrabutylammonium hydroxide 30-hydrate, gold(III) chloride trihydrate, sodium citrate dihydrate, sodium hexachloroiridate (IV) hexahydrate and TA were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ion-exchange resin Monobed MB-1 was purchased from BDH Chemicals (Poole, UK). Milli-Q water was used as deionized water in all experiments.

Synthesis of TiO₂ NPs

TiO₂ NPs were synthesized according to the previous report [20]. Tetrabutylammonium hydroxide 30-hydrate (Bu₄NOH, 1 g, 1.25 mmol) was dissolved in propanol (46 mL) at an ambient temperature, and titanium(IV) isopropoxide (1 mL, 3.38 mmol) was dissolved in propanol (10 mL). The molar ratio of titanium

isopropoxide to Bu₄NOH varied from 2.7 to 8.1 with the different amount of Bu₄NOH (0.5 g, 0.625 mmol) and titanium (IV) isopropoxide (1.5 mL, 5.07 mmol) to control the morphology of the TiO₂ NPs. The titanium isopropoxide solution was slowly added to the Bu₄NOH solution, and then boiled Milli-Q water (232 mL) was slowly added to the mixture with magnetic stirring at 500 rpm at an ambient temperature. The mixture was transferred to a 100 °C oil bath, and then magnetically stirred with reflux for 2 days. The synthesized TiO₂ NP dispersion (100 mL) were purified by dialysis (MWCO = 1 kDa, SpectraPor) against Milli-Q water (6 L) for 2 days.

Synthesis of AuNPs on TiO₂ NPs

One milliliter of TA in deionized water (2 mg mL⁻¹) was added to 1 mL of the pristine TiO₂ NP (1 mg mL⁻¹) suspension, and then the solution was mixed by sonication for 5 min. TA-coated TiO₂ NPs were collected by centrifugation at 9391 × g for 5 min, rinsed with 1 mL deionized water, and then re-dispersed in 1 mL of deionized water. The TA-coated TiO₂ NP solution was mixed with 1 mL of 0.4 mM gold(III) chloride trihydrate by sonication for 5 min, followed by magnetic stirring in an oil bath at 100 °C for 10 min. The synthesized AuNP-deposited TiO₂ NPs were collected by centrifugation at 9391 × g for 5 min, rinsed with 1 mL deionized water, and then re-dispersed in 1 mL of deionized water.

Characterization

The TiO₂ NPs and Au/TiO₂ NPs were observed using TEM (Tecnai G2 F30 S-Twin, FEI company) at an acceleration voltage of 300 kV. X-ray diffraction patterns of TiO₂ NPs were examined using a X-ray diffractometer at 40 kV and 300 mA (D/MAX-2500, Rigaku). The TiO₂ NPs and TA-coated TiO₂ NPs were analyzed using UV–visible absorption spectrophotometry (UV-1800, Shimadzu Corp., Kyoto, Japan) and multipurpose XP spectroscopy (Sigma Probe, Thermo VG Scientific).

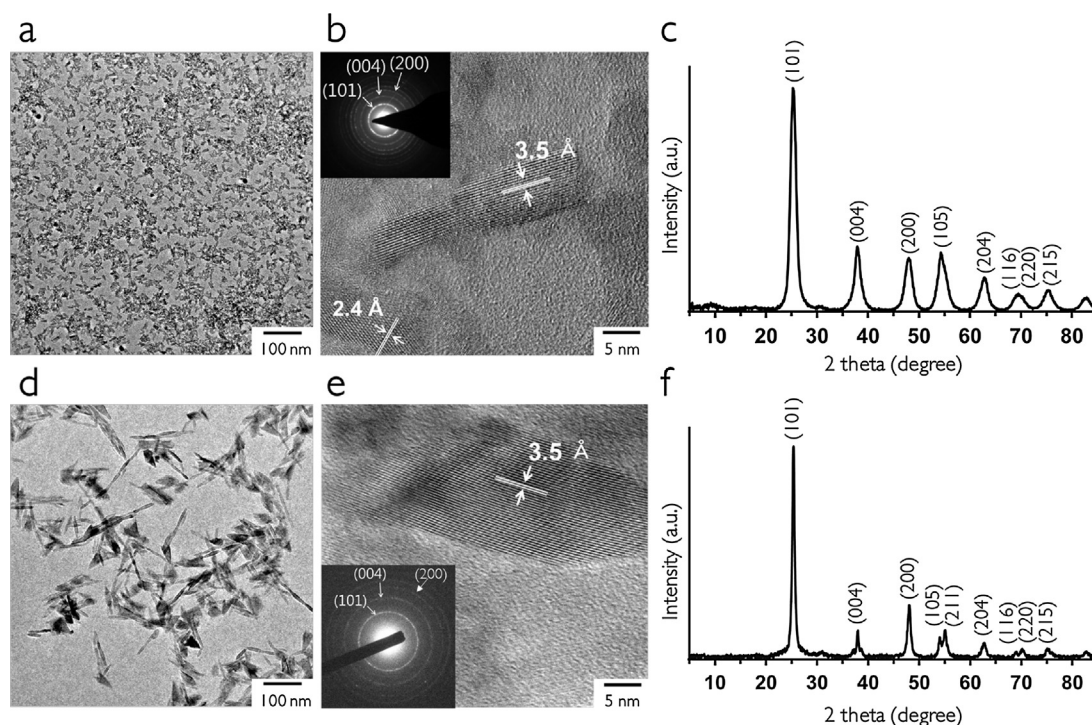


Fig. 1. TEM images and XRD patterns of TiO₂ NPs synthesized at different molar ratios of titanium isopropoxide to Bu₄NOH: 8.1 (a–c) and 2.7 (d–f).

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