

Scientific paper

Photocatalytic Deposition of Gold on Nanocrystalline TiO₂ Films

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Abstract

Nanocrystalline TiO₂ films were prepared on glass supports by the dip coating technique using colloidal solutions consisting of 45 Å TiO₂ particles as a precursor in order to probe the feasibility of exploiting solid state photocatalytic reactions for efficient deposition of gold. The reduction of Au³⁺ ions was maintained by photoirradiation of unmodified TiO₂ films with metal ions being attached directly to the surface of TiO₂. Absorption spectrum as well as atomic force microscopy measurements revealed presence of gold grains in the nanosize regime. Conductivity of deposited gold was measured in the temperature range from 45 to 295 K.

Keywords: TiO₂ films, gold, photocatalytic deposition, conductivity

1. Introduction

Photocatalytic reactions on TiO₂ surfaces are very important in environmental cleanup and remediation, such as oxidation of organic materials^{1–3} and reduction of heavy metal ions^{4–8} in industrial waste streams. We have recently shown that nanocrystalline TiO₂ material differs from the bulk material, having larger surface area and unique surface chemistry due to distortions in surface Ti sites from the octahedral geometry to pentacoordinate square pyramid with one double Ti–O bond.^{9–11} Photoirradiation of TiO₂ nanoparticles, with photon energy larger than the band gap (3.2 eV), creates electron – hole pairs. Following irradiation, the TiO₂ nanoparticles act as either electron or hole donors to reduce or oxidize materials in the surrounding media. However, the photo-induced charge separation in bare TiO₂ nanoparticles has a very short lifetime due to charge recombination. Therefore, it is important to prevent electron – hole recombination before a designated redox reaction occurs.

Recently, the performance improvement of TiO₂ nanocrystals for photocatalytic reduction of heavy metal

ions was achieved by using multifunctional ligands, which bind both particle surface and heavy metal ions.^{6,12} In these studies it was shown that surface modification of 45 Å TiO₂ particles with bidentate and tridentate ligands that have mercapto, carboxyl and amino groups in different positions results in increased adsorption rate of metal ions compared to bare particles, enlarged initial charge separation distances, and overall enhanced photoreduction chemistry. In this work we report efficient reduction of Au³⁺ ions to its metallic form on the surface of dry unmodified nanocrystalline TiO₂ film. Atomic force microscopy (AFM) and absorption spectroscopy were used to confirm the presence of gold grains in the nanosize regime. Conductivity of photocatalytically deposited gold was measured in the temperature range from 45 to 295 K.

2. Experimental

2.1. Synthesis of 45 Å TiO₂ Colloids

The TiO₂ colloids with mean particle diameter of 45 Å were prepared by controlled hydrolysis of titanium (IV)

chloride, as described elsewhere.¹³ The concentration of TiO₂ (0.1–0.6 M) was determined from the concentration of the peroxide complex obtained after dissolving the colloid in 1.44 M H₂SO₄.¹⁴

2. 2. Preparation of Nanocrystalline TiO₂ Films

Nanocrystalline TiO₂ films were prepared on glass supports by the dip coating technique using titania colloidal solutions consisting of 45 Å TiO₂ particles with anatase crystalline structure, as precursor. After dipping the glass slides in 0.12 M TiO₂ colloidal solution, the samples were dried at elevated temperature (150 °C) for 30 min. The nanocrystalline TiO₂ films having different thickness ($d = 240\text{--}560$ nm) were prepared repeating the above-mentioned procedure different number of times (typically, the number of depositions varied from 3 to 7).

The nanocrystalline TiO₂ films were immersed in a solution of 0.013 M AuCl₃ in 0.007 M HCl (pH ~ 2.5–3) and stored in a dark for a week. As-prepared samples were rinsed with distilled water and dried in a stream of argon.

2. 3. Apparatus

A photochemical apparatus UV 17 F Helios Italquartz that consists of the low pressure Hg lamp, ATE 215 M, placed into quartz shielding was employed for steady-state illumination. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. The atomic force microscopy (AFM) studies were performed by using Digital Instruments Dimension 3100 in the tapping mode. The ac electrical measurements were carried out by a four probe technique using a lock-in amplifier and an ac constant current source in a frequency range of 10–6000 Hz. The dc resistance was measured at very low frequencies (57 Hz) in a closed circuit helium cryostat, varying the sample temperature between 45 K and room temperature. Average composition of the sample prepared for transport measurements was determined by microprobe analyses.

3. Results and Discussion

The thickness of the nanocrystalline TiO₂ films on the glass slides as a function of number of depositions was followed from the transmission spectra measured in the spectral range of 350–1000 nm (Figure 1). The method proposed by Babu et al.¹⁵ was used to calculate thickness of TiO₂ films from the position of interference fringes in transmission spectra. Briefly, locations of the extrema in the transmission curve are uniquely determined in a first approximation by specifying the product nd , where n is refractive index and d is the thickness of the thin film. In

this approximation, which is applicable for weakly absorbing films, extrema occur at wavelengths specified by

$$\lambda_{\text{ext}} = \left(\frac{m}{4nd} \right)^{-1} \quad m = 1, 2, \dots \quad (1)$$

i. e. the locations of the extrema are uniquely determined by nd . If m' is the order of an extremum from an arbitrary reference extremum (of order m_0), then $m = m' + m_0$ and

$$\frac{1}{\lambda_{\text{ext}}} = \left(\frac{m_0}{4nd} \right) + \left(\frac{m'}{4nd} \right) \quad (2)$$

Hence, for a constant value of nd , a plot of $1/\lambda_{\text{ext}}$ vs. m' will yield a straight line with a slope $1/4nd$ and an intercept $m_0/4nd$.

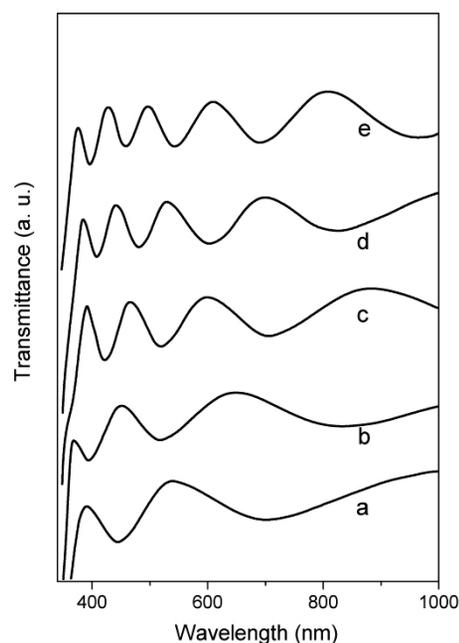


Figure 1: Transmission spectra of nanocrystalline TiO₂ films as a function of number of depositions: (a) 3, (b) 4, (c) 5, (d) 6 and (e) 7

Knowing the value of the refractive index of anatase TiO₂ particles ($n = 2.524$), the thickness of nanocrystalline film was estimated to increase for about 80 nm per each deposition. It should be pointed out that the dip coating technique led to the formation of nanocrystalline TiO₂ films having a fairly uniform thickness across the film.

The illumination of unmodified TiO₂ films where gold ions (Au³⁺) are directly linked to the TiO₂ surface, leads to the formation of metallic form of gold in nanosize regime^{16,17} as confirmed with the appearance of surface plasmon resonance band at 527 nm in absorption spectrum. The absorption spectrum of photocatalytically de-

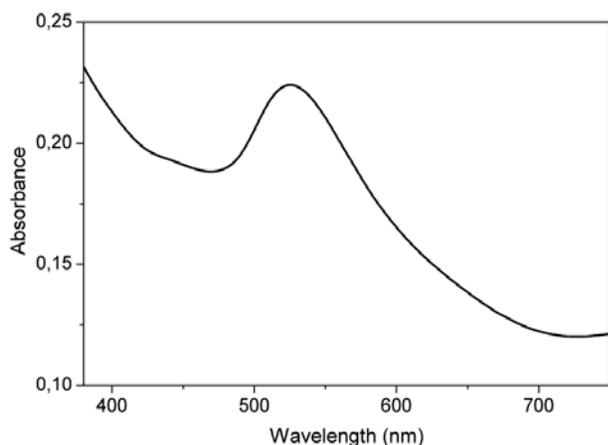


Figure 2: Absorption spectra of photocatalytically deposited metallic gold on the surface of nanocrystalline TiO₂ film.

posited metallic Au on unmodified nanocrystalline TiO₂ film obtained upon illumination is presented in Figure 2.

The atomic force microscopy image (Figure 3) shows that a homogeneous gold thin film consisting of well resolved grains is successfully assembled.

Recently, it has been shown that the addition of multifunctional ligands (cysteine, alanine, arginine) leads to the surface modification of TiO₂ colloid particles enhancing their photocatalytic reduction properties. The increase of metal ions adsorption on the surface of modified TiO₂ particles is the consequence of the replacement of TiO₂ surface OH groups upon coordination of surface Ti atoms with carboxylic groups.^{6, 12} In order to extend the investigations of photocatalytic ability of dry nanocrystalline surface modified TiO₂ films with alanine or arginine, we followed the three electron-transfer reduction process of Au³⁺ ions. Contrary to copper or silver¹²

ions which are almost instantaneously reduced to corresponding metals upon illumination of dried modified samples, in the case of gold ions the formation of its metallic form was not noticed.

According to our experimental conditions, before illumination TiO₂ film was immersed in acidic solution (0.007M HCl) of AuCl₃ in order to prevent undesired hydrolysis of the salt. Hence, at pH ~2.5–3 hydroxyl groups on the surface of TiO₂ nanocrystalline film are protonized while Au³⁺ is coordinated with Cl⁻ ions in the form of the halogeno complex [AuCl₄]⁻. Electrostatic interaction between protonized surface hydroxyl groups on TiO₂ and [AuCl₄]⁻ ions could be the explanation for the efficient adsorption and consequent photoreduction of gold ions on the surface of unmodified TiO₂ nanocrystalline film according to redox reaction:



Since the electrochemical potential for the reduction of gold ions is significantly more positive than the position of conduction band of TiO₂, photocatalytic reduction is thermodynamically favorable even upon changing E₀ (AuCl₄⁻/Au⁰) due to interaction with TiO₂ surface. The halogeno complex form of gold ions might be the explanation for unsuccessful reduction of Au³⁺ on the surface of TiO₂ modified with alanine or arginine. In acidic medium (pH ~2.5–3) carboxylate groups of amino acids are negatively charged disabling the approach of halogeno complex form of gold to the surface modified TiO₂ nanocrystals.

With the aim to check the conductivity of photocatalytically deposited layer of gold on the surface of nanocrystalline TiO₂ film we measured the resistivity as a function of temperature. In Figure 4 is presented R vs. T

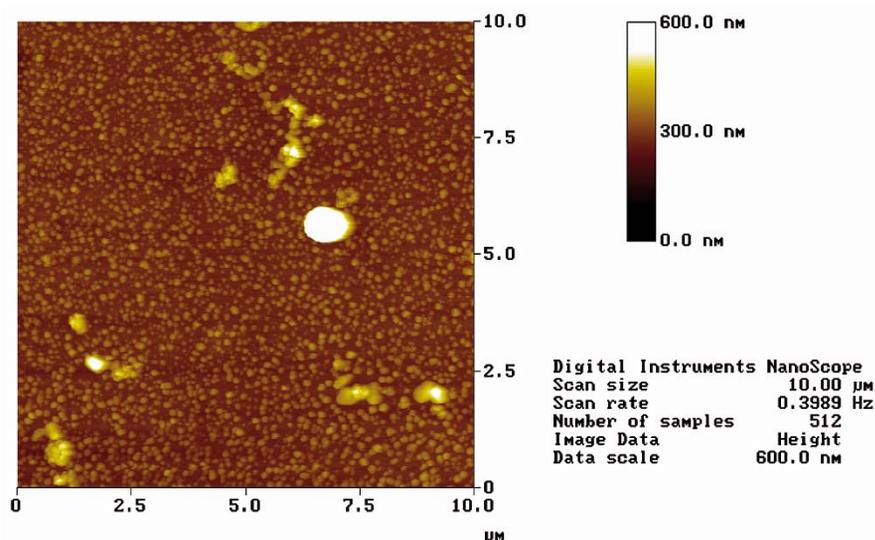


Figure 3: Typical AFM image of gold grains on the surface of nanocrystalline TiO₂ film

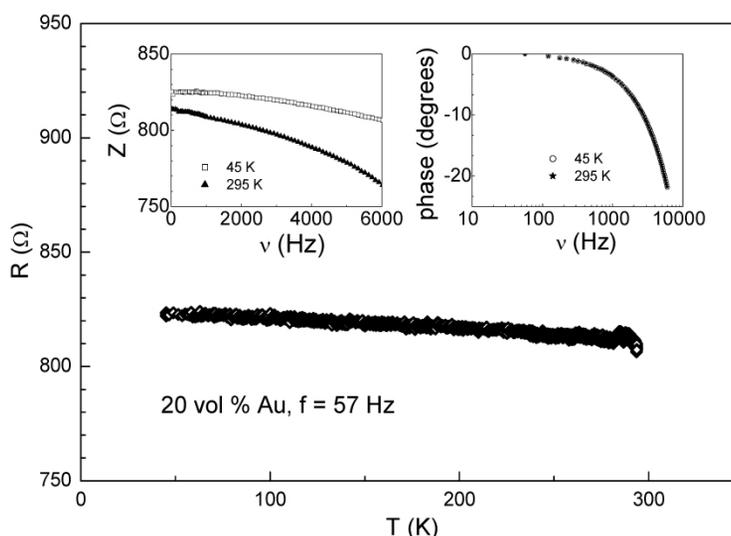


Figure 4: Temperature dependence of the resistivity of Au–TiO₂ film on glass support. Insets: Modulus of the impedance $|Z|$ (left) and voltage phase drop ϕ (right) vs. frequency

dependence obtained for Au–TiO₂ film which contains 20 vol. % of Au⁰ (or 55.19 wt. %) determined by microprobe analyses. Very slight changes of the resistivity with temperature indicate that the sample is near the percolation threshold. The modulus of the impedance $|Z|$ decreases with frequency at all temperatures indicating the presence of capacitive conduction (see $T = 45$ K and $T = 295$ K in left inset of Fig. 4). This is even more clear from the huge frequency dependence of the voltage phase drop ϕ (right inset of Fig. 4).¹⁸ At frequencies close to dc limit, ϕ is roughly zero, corresponding to the dc current circulation essentially between small closely packed particles. By increasing frequency, curves display a phase drop as the electron current, due to the capacitive effect between particles, becomes more and more important. As the dc current is only slightly dependent on T and the capacitive current between distantly separated particles is T -independent, the phase drop appears to be essentially the same for all temperatures (see $T = 45$ K and $T = 295$ K in right inset of Fig. 4). The negative value of the temperature coefficient of the resistivity indicates the sample containing nonelectrically connected nanoparticles *i. e.* samples situated in the dielectric region.¹⁹

4. Conclusions

Layer of gold grains photocatalytically deposited on the surface of nanocrystalline TiO₂ film was prepared. It was found that the gold ions directly attached on the surface of unmodified TiO₂ nanocrystalline film are reduced via multielectron transfer process from TiO₂ conduction band. The position of the surface plasmon absorption band reveals presence of gold grains in the nanosize regime. Conductivity measurements show that sample con-

tains nonelectrically connected metallic particles near percolation threshold.

5. Acknowledgments

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Povzetek

Preverjali smo možnost izkoriščanja trdnih fotokatalizatorjev za učinkovito depozicijo zlata. Nanokristalinične tanke sloje TiO_2 smo pripravili na steklenih nosilcih s tehniko pomakanja v koloidno raztopino delcev TiO_2 velikosti 45 Å, kot prekursorjev. Redukcijo Au^{3+} smo dosegli z obsevanjem tankih slojev TiO_2 z adsorbiranim zlatom na površini. Meritve absorpcijskih spektrov in mikroskopija na atomsko silo so potrdile prisotnost nanodelcev zlata. Električno prevodnost zlata, nanešenega po opisanem postopku, smo izmerili v območju 45 do 295 K.