Photocatalytic WO$_3$ and TiO$_2$ Films on Brass

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This paper reports on the structure, mechanical, and photocatalytic properties of titanium dioxide (TiO₂) and tungsten oxide (WO₃) films on a brass substrate. TiO₂ and WO₃ films have been successfully deposited on brass by a simple sol-gel dip-coating method and it has been shown that, while both films possess photocatalytic properties, WO₃ films were superior to TiO₂. Higher surface area and rod-like morphology of WO₃ films might have contributed to their higher photocatalytic activity. Nanoindentation results have shown that both films attach well to the substrate and possess good mechanical properties.

Introduction

Over the last few decades, interest in heterogeneous photocatalysis has been growing because of its promising applications in self-cleaning and antibacterial coatings,¹² water and air purification systems,³ solar cells,⁴⁵ and hydrogen production by water dissociation.⁶ Since the discovery of photo-electrochemical splitting of water by titanium dioxide (TiO₂) electrodes under ultraviolet light by Fujishima and Honda in 1972,⁶ TiO₂ has been one of the most studied materials among transition metal oxides because of its unique photoinduced catalytic activity, superhydrophilicity, nontoxicity, physical stability, and chemical inertness. Although TiO₂ is still the gold standard, many other semiconductors, such as WO₃, CdS, SnO₂, SiO₂, ZrO₂, ZnO, Nb₂O₅, Fe₂O₃, SrTiO₃, etc.,⁷ have also been identified as potential photocatalysts. In particular, tungsten oxide (WO₃) is a widely studied material because of its high photoactivity and lower band gap, which, in theory, permits excitation with a lower energy light source (wavelengths outside the UV range).⁸–¹⁰

While standalone photocatalysts are required in some applications, films are often needed to fulfill desired functionalities. However, unlike powder, photocatalytic properties of films can be influenced significantly by the underlying substrate material. For example, the poisoning of TiO₂ films by sodium diffused from glass substrate has been reported.¹¹–¹³ Therefore, film-substrate compatibility is an additional consideration required when selecting photocatalysts for film applications. While glass and ceramic materials are still the most popular of all substrates for photocatalytic films, metals have also attracted some attention, with the majority of research performed on stainless steel.¹⁴¹⁵ Despite being widely used in daily life, copper and its alloys have been rarely investigated as potential substrates for photocatalytic films. For example, brass is a very common decorative material because of its bright gold-like appearance and is widely used on railings, door handles, and other components that are touched by hands and would benefit from anti-bacterial coatings. Decorative panels on constructions would benefit from self-cleaning and protective coatings that would help to maintain the gold-like appearance of polished surfaces for a longer time. This makes brass, copper, and bronze potentially important substrates for photocatalytic films, yet brass has not been investigated for this purpose and it is not known if good adhesion and satisfactory photocatalytic properties can be achieved.

This paper reports, for the first time, on the preparation of sol-gel-derived WO₃ and TiO₂ films on brass substrates. The photocatalytic and mechanical properties of both films were evaluated by the photocatalytic decolorization of aqueous methylene blue and examined by nanoindentor, respectively. Further, the results were compared with each other to study out what semiconductor is more promising as a photocatalytically active film on brass for practical applications.

Experimental Procedure

Both TiO₂ and WO₃ films were deposited from solutions of the respective metal chlorides by sol-gel dip-coating method. A SiO₂ layer, a barrier to prevent the diffusion of elements from the substrate into photocatalytically active film, was deposited similarly from a sol of SiO₂.

TiO₂ sol was prepared as follows: 80 g of ethyl alcohol (200-proof; Electron Microscopy Sciences, Hatfield, PA) and 14 g of TiCl₄ (≥ 99 trace metal basis; Sigma-Aldrich, St. Louis, MO) were mixed and subsequently stirred on a magnetic stirrer for 30 min. Then, 2.3 g of deionized water was added dropwise to the
main solution in molar ratio of H₂O:TiCl₄ = 1:1 and the solution was stirred for 10 min. Then, 6.3 g of acetylacetone (98%, Sigma-Aldrich), in a molar ratio of Acac:TiCl₄ = 1:2, was added to the prepared sol and stirred for 20 min. At the end of the synthesis, 5 g of triethyl o-acetylcitrate (TCI America, Portland, OR) was added in molar ratio to TiCl₄ as 1:2 and stirred for the next 20 min.

WO₃ coatings were prepared using a 10 wt.% solution of tungsten (VI) chloride (WCl₆) (99.6%; Alfa-Aesar, Ward Hill, MA) in N,N-dimethyl formamide (DMF) (anhydrous, 99.8%, Sigma-Aldrich). SiO₂ sol was prepared by mixing 80-g ethyl alcohol, 16-g tetraethyloorthosilicate, 5-g water, and 0.2-g HCl and stirring for 6 h before using.

Films were deposited onto brass substrates by a dip coating process. For this purpose, brass substrates (Cu-35Zn, diameter of 25 mm, thickness of 3 mm) were first dipped into SiO₂ sol, dried at 150°C and dipped into TiO₂ or WO₃ sols, and withdrawn at a constant speed of 100 mm/min by a dip coater (MTI Dip Coater HL-01; MTI, Richmond, CA). Samples were then placed into a tube furnace and calcined at 400°C for 2 h under argon flow. Calcinations were not conducted in air to prevent oxidation of brass substrates. The temperature of 400°C was chosen after prior investigations of temperature influence on films on brass. It was shown that films have low adhesion to the brass substrate at calcinations temperatures of 200°C and 300°C. At the same time, surface oxidation and/or reaction with coatings was observed at 500°C and higher temperatures, leading to darker surface and degradation of the material.

The structure of the films was analyzed by X-ray diffraction (XRD) with a powder diffractometer (Siemens D500; Siemens, Munich, Germany) using Cu Kα radiation, and a step scan of 0.02° and 1 s per step. Raman spectra were recorded using a 514.5 nm Ar ion laser as the excitation source (Renishaw RM1000; Renishaw, Gloucestershire, U.K.). A scanning electron microscope, SEM (Supra 50VP; Zeiss, Oberkochen, Germany), was used to investigate the surface morphology of the films and conduct elemental analysis via energy dispersive X-ray (EDX) spectroscopy (Oxford Inca X-Sight, Oxfordshire, U.K.).

Photocatalytic activities of the films were evaluated by a methylene blue (MB) degradation test. For this, each TiO₂ or WO₃ covered brass sample was placed in a Petri dish containing 15 mL of 2 ppm aqueous MB solution and illuminated with UVA light (16 W, 360 nm) for 3 h. Representative samples (1 mL) were taken every hour from the solutions and the dye concentration was measured using UV-Vis spectrophotometry. Tests were repeated twice producing no more than 5% scatter in the data.

Mechanical properties (hardness and Young’s modulus) of the TiO₂ and WO₃ films on brass were tested by nanoindentation (MTS NanoIndenter XP; MTS Systems, Eden Prairie, MN) using the continuous stiffness measurement mode. Each sample was indented up to 300 nm depths four times with a 5-μm-radius spherical tip. The maximum drift rate and harmonic displacement target were set at 0.1 nm/s and 1.5 nm, respectively.

Results and Discussion

Initially, the TiO₂-coated samples appeared almost transparent but as the number of layers and the annealing temperatures increased it became more opaque and eventually obtained a white matte finish. The WO₃-coated sample had a green appearance before calcination, but after treatment it developed a brown hue owing to the hydrolysis of WCl₆. The thickness of a single layer of TiO₂ or WO₃ on brass was around 350 and 400 nm, respectively.

Figure 1 shows the Raman spectra of titanium- and tungsten oxide–coated brass samples. Raman spec-

![Fig. 1. Raman spectra of (i) titanium dioxide and (ii) tungsten oxide films on brass covered with silica layer.](image-url)
trum of the TiO$_2$-coated brass shows peaks at 149, 199, 400, 515, and 627/cm, in a good agreement with the reported values for anatase. Thus, bands at 149, 199, and 627/cm (Fig. 1) correspond to the E$_g$ modes, 400/cm corresponds to the B$_{1g}$ mode, and 515/cm is the superposition of B$_{1g}$ and A$_{1g}$ modes of anatase. Raman spectrum of tungsten oxide film shows prominent peaks at 806 and 716/cm corresponding to O-W-O stretching vibrations and at 273/cm corresponding to O-W-O deformation vibrations. These peaks are characteristic of crystalline WO$_3$. Low-frequency bands at 133 and 184/cm can be assigned to lattice modes. Deposition of TiO$_2$ and WO$_3$ films on brass was also confirmed by EDX analysis. The spectra taken in the range 0–5 keV showed peaks at 4.51 and 1.77 keV, which correspond to the photon energy of the Ti K$_\alpha$ and W M lines emission, respectively.

X-ray diffraction analysis of the samples gave less clear results, with no indication of any crystal phases of TiO$_2$ or WO$_3$ (Fig. 2). We believe this is related to the small thickness and nanocrystalline structure of the films, where a sufficient thickness of the film material is needed to obtain a good signal-to-noise ratio for nanocrystals. Micro-Raman spectroscopy is a powerful tool for analysis of oxide films on metals, as reported previously, as WO$_3$ and TiO$_2$ have pronounced bands in the Raman spectra and metals are not Raman active. However, XRD patterns show peaks from [111] and [200] peaks of Cu$_{0.64}$Zn$_{0.36}$ at around 42 and 49° 20 and [321] and [421] peaks of Cu$_2$Zn$_8$ at around 38 and 43° 20, respectively) as well as ZnO and Cu$_2$O owing to partial oxidation of brass.

Figure 3 shows SEM images of the surface morphology of the films. Both films were porous. TiO$_2$ films show rounded structures with sizes around 180 nm (Fig. 3a, b). WO$_3$ films show rod-like morphology (Fig. 3c, d). Formation of WO$_3$ rods by various methods such as PVD, hydrothermal method, heating tungsten under controlled atmosphere, and formation of W$_{18}$O$_{49}$ rods from heating tungsten foil under Ar in the presence of SiO$_2$ was previously reported.

Results of the photocatalytic degradation of methylene blue are summarized in Fig. 4. The rate of MB photodegradation $k$ is proportional to the concentration of dye in the solution at low concentrations and follows a first-order reaction given by:

$$k = \frac{\ln(C_0/C)}{t},$$

where $C$ and $C_0$ are the concentration at time $t$ and the initial concentration of solution of MB, respectively.

While both TiO$_2$- and WO$_3$-coated brass samples show photocatalytic activity (Fig. 4a), performance of the TiO$_2$-coated brass was surprisingly poor. This may be related to the poisoning of TiO$_2$ catalyst by Cu$_2$O. It is known that doping can strongly affect the photocatalytic activity of titania films and diffusion from the substrate should be taken into account. Cu$_2$O is a strong reducing agent and can, in theory, directly inject an electron to the TiO$_2$ or, alternatively, regenerate oxidized methylene blue, which in turn decreases the photocatalytic activity. WO$_3$ conduction band lies well below TiO$_2$ conduction band and thus can directly compete with methylene blue to capture electrons from Cu$_2$O, and hence prevent MB regeneration. To understand the underlying cause of its poor performance, a photocatalytic activity test was repeated on a TiO$_2$-coated brass substrate without a precoated SiO$_2$ layer (Fig. 4b). Although SiO$_2$ precoating has a positive effect on the photocatalytic activity, the effect is not dramatic. Assuming that the SiO$_2$ layer can block the direct interaction between the substrate and TiO$_2$ film, it is likely that the low photocatalytic activity is related to an indirect process (i.e., regeneration of MB by Cu$_2$O in other parts of the brass sample — parts that are not covered by TiO$_2$) rather than a direct poison-

Fig. 2. Diffraction patterns of (i) titanium dioxide and (ii) tungsten oxide on brass covered with silica layer.
ing. Another explanation of the higher photocatalytic activity of WO₃ is its somewhat higher surface area (i.e., rods versus rounded particles) as compared with TiO₂ (Fig. 3b,d).

Load-displacement curves, as obtained by nanoindentation, are shown in Fig. 5. The loading portion of the load-displacement curves do not show any events that could be assigned to cracking or delamination of
As was the case in photocatalytic activity, WO₃ is superior to TiO₂ in terms of mechanical properties. Overall, both TiO₂ and WO₃ films are mechanically stiffer than pure brass at low loads, whereas only WO₃ films are better than brass at higher loads. It is particularly important to note that WO₃ films show significantly less plastic deformation and stronger elastic recovery, as evident from the unloading portion of the curve.

Values of Young’s modulus and hardness calculated for TiO₂ and WO₃ films on brass, as well as for the brass substrate, are shown in Table I. WO₃ films exhibit higher values of both parameters, 163.4 and 5.9 GPa, respectively, which exceed those for the brass substrate. Thus, it is possible to use WO₃ films for improving mechanical properties of brass, such as surface hardness and scratch resistance.

Table I. Young’s Modulus and Hardness of Brass and the Titanium Dioxide (TiO₂) and Tungsten Oxide (WO₃) Films on Brass

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>141.1 ± 8.1</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>TiO₂ on brass</td>
<td>120.9 ± 9.7</td>
<td>2.7 ± 0.6</td>
</tr>
<tr>
<td>WO₃ on brass</td>
<td>163.4 ± 9.2</td>
<td>5.9 ± 0.6</td>
</tr>
</tbody>
</table>

The authors are thankful to Boris Dyatkin for assistance with Raman spectroscopy analysis, Maria Lukatskaya for EDX analysis, and the Centralized Research Facility of Drexel University for use of SEM, XRD, and nanoindenter.

Conclusions

Tungsten oxide and TiO₂ films were deposited on brass substrates by a simple wet-chemical method and their structure, morphology, mechanical properties, and photocatalytic activities were evaluated. WO₃ films showed rod-like crystals whereas TiO₂ films contained rounded particles. Despite the fact that TiO₂ is known for its excellent photocatalytic activity, often surpassing other photocatalysts, WO₃ was found to be superior for photocatalytic films on brass substrates. Nanoindentation studies also showed that WO₃ films have better mechanical properties than TiO₂ films. Results of this study confirm that there is not a single one-size-fits-all solution to photocatalytic films and that it is important to select the photocatalytic films based on their compatibility with the substrate. While this study shows that photocatalytic coatings can be produced on brass, further optimization of coating structure and mechanical and optical properties should be conducted.

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References


