Electrochemical Cr(VI) Reduction over Terpyridine-Derivatized Ti Sheets

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ABSTRACT

Cr(VI) reduction has been used to diminish the high toxicity of the Cr(VI) ion in the environment. Herein, electrochemical (EC) reduction was demonstrated using Au NP-loaded Ti electrodes functionalized with 2,2':6',2''-terpyridine-4'-thiol (STpy). Cyclic voltammetry tests were performed and these revealed Cr(VI) reduction potentials around -0.55, -0.35, and -0.55 V (vs Ag/AgCl) for bare Ti, Au NP-loaded Ti, and STpy-functionalized Au NP-loaded Ti (Ti-AuNP-STpy) electrodes, respectively. The reduction potential and Cr(VI) reduction performance varied with Ti oxidation state as well as surface functionalization. The EC Cr(VI) reduction using the Ti-AuNP-STpy electrode was found to have the best reduction performance. In addition, for future potential applications, the surface plasmon resonance response was also demonstrated for Cr(III) and Cr(VI) sensing over the Au-STpy surface. Thus, these novel electrode systems provide very useful information for developing improved detoxification methodologies.

Keywords: Cr(VI) reduction, Electrochemical reduction, Terpyridine-derivatized Au NPs, Cyclic voltammetry, Surface plasmon resonance

1. Introduction

Decontamination of hexavalent chromium Cr(VI) is a major environmental challenge [1-3]. Low limit-of-detection Cr(VI) ion sensing and safer treatments methods are actively being researched both in industry and academia [4-7]. Various safer Cr(VI) treatment methods have thus far been developed, including adsorption removal, photocatalytic reduction, and electrochemical reduction methods [8-23]. As an example of adsorption-reduction removal of Cr(VI), mesoporous polydopamine/TiO₂ composite nanospheres have been prepared for the adsorption of Cr(VI) ions via electrostatic interactions followed by reduction to Cr(III) [9]. The design of a material with suitable surface charge and electron-transfer properties is important for adsorption-reduction treatments [10-12]. Photocatalytic reduction of Cr(VI) to the less toxic Cr(III) ions using existing catalysts has been extensively been studied. The photocatalysts used include TiO₂-impregnated ceramic hollow fibers [13], TiO₂/g-C₃N₄ microspheres/reduced graphene oxide, AgI/TiO₂ [14], Zn-Al-layered double hydroxide and TiO₂ composites [15], TiO₂-coated cellulose acetate monolithic structures [16], hollow TiO₂ from polystyrene@TiO₂ [17], and CoO_x NP-loaded TiO₂ nano-sheets [18]. A key factor in this method is to design a material with a good UV-visible absorption cross section and efficient charge separation for Cr(VI) reduction [19]. Electrochemical (EC) reduction has also been an effective approach for the detoxification of Cr(VI) ions present in an acidic electrolyte. The design of a stable and efficient electrode is a major challenge. Furthermore, electrochemical behaviors (e.g., reduction-oxidation potentials) on the electrode surface are a crucial factor [1,2]. The redox potential is known to be highly dependent on

the electrode surface. Various electrodes have been developed, these include PANI/graphene QDs on screen-printed carbon electrodes (SPCEs) [20], α -Fe₂O₃/TiO₂ [21], Au-TiO₂ (rutile)/FTO [22], and BiVO₄ NP-modified SPCEs [23].

Motivated by the abundant literature, to further develop the EC method and obtain new information, we demonstrated the EC reduction of Cr(VI) ions using a newly developed EC electrode consisting of terpyridine-derivatized AuNPs on Ti. It was found that the terpyridine-derivatized surface played a positive role in the electrochemistry. This new methodology could be employed for improving EC reduction methods as well as other related applications.

2. Experimental details

The following chemicals were used as received: 2,2':6',2''-terpyridine-4'-thiol (STpy, 95%, Shanghai iChemical), potassium chromate (K₂CrO₄, 99.0%, Ducksan Pure Chem.), sulfuric acid (H₂SO₄, 95-97%, Emsure), and dimethyl sulfoxide (DMSO, GR 99%, Kanto Chem.). As-received Ti sheets (MSL Tools Store, China) were cleaned repeatedly by ultrasonication in acetone, isopropyl alcohol, and water and then dried under an IR lamp. The cleaned Ti sheets (0.5 cm × 2.0 cm) then underwent thermal treatment at 400 °C for 2 h to obtain oxidized Ti (TiO_x) surfaces. For the preparation of AuNP-loaded Ti (Ti-AuNP) electrodes, Au (~10 nm) was sputter-coated on bare (or oxidized) Ti sheets using an SPT-20 ion sputter coater (COXEM Company, Korea). For the preparation of terpyridine-functionalized AuNP-loaded Ti (Ti-AuNP-STpy) electrodes, a Ti-AuNP electrode was dipped in 1 mM STpy DMSO solution for 4 h, carefully rinsed with DMSO and

Figure 1. Terpyridine functionalization of bare or oxidized Ti sheets.

ethanol, repeatedly, and finally dried in a stream of N_2 gas.

The morphologies of the electrodes were examined using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The concentration of Cr(VI) ions was examined using UV-visible absorption spectrometry (SCINCO NeoSys-2000 UV-Vis spectrophotometer) before and after electrochemical testing. Top monitor changes in the chemical states of the electrodes before and after the EC experiments, X-ray photoelectron spectroscopy was carried out (Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer, equipped with a monochromated Al K α X-ray source and hemispherical energy analyzer). Cyclic voltammetry and EC amperometry testing was conducted using a typical three-electrode system with a counter Pt wire, a Ag/AgCl reference, and a WPG100 Potentiostat/Galvanostat (WonATech Co., Ltd.). The electrolytes used were 1.0 M H_2SO_4 (aq.), 1 (and 10) mM Cr(VI)/1.0 M H_2SO_4 (aq.), and 1 (and 10) mM Cr(VI)/1.0 M H_2SO_4 (aq.) solutions. The working electrodes tested were bare Ti, Ti-AuNP, Ti-AuNP-STpy, bare TiO_x , TiO_x -AuNP, and TiO_x -AuNP-STpy electrodes.

3. Results and discussion

A key aspect of this study was the preparation of the Ti-AuNP-STpy electrode, which is depicted in Fig. 1, and described in the Experimental details above. In our method for the preparation of the Ti-AuNP-STpy electrode, Au NP-loaded Ti sheets are immersed in a 1 mM STpy DMSO solution for 6 h and then carefully rinsed. During the immersion, Au-S covalent bond formation occurs between the Au NPs and STpy ligands [24]. This newly developed electrode system is expected to function via strong interactions between three N atoms in the STpy ligands and guest Cr(VI) ions.

Figure 2 shows the morphologies of bare Ti, Ti-AuNP-STpy, Ti-AuNP after Cr(VI) reduction, and Ti-AuNP-STpy after Cr(VI) reduction, all obtained via SEM. The image of the AuNP-loaded Ti sheet displays a uniform distribution of Au NPs before and after STpy functionalization. The surface morphology is clearly different before and after Au sputter deposition. For the Ti-AuNP and Ti-AuNP-STpy electrodes after EC Cr(VI) reduction, the morphology is markedly changed compared to that of the intact Ti-AuNP-STpy sample. The Au NP aggregate, forming a large Au island. Electric-field-assisted Au NP aggregation has been reported in the literature [25]. When Au aggregates, it is plausible that the EC efficiency may be reduced.

Figure 3 shows cyclic voltammetry (CV) curves for bare Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes acquired between -0.8 and $+0.2$ V (vs. Ag/AgCl) at a scan rate of 100 mV/s in blank 1.0 M H_2SO_4 , 1 mM Cr(III)/1.0 M H_2SO_4 , and 1 mM Cr(VI)/1.0 M H_2SO_4 electrolyte solutions. In blank 1.0 M H_2SO_4 , no redox peaks are observed. Instead, a current density (CD) increase is seen at negative potentials. For the Ti-AuNP and Ti-AuNP-STpy electrodes, the CD increases more sharply above -0.3 V. The sharp CD increase is attributed to the hydrogen evolution reaction (HER) [26,27]. For the 10 mM Cr(III)/1.0 M H_2SO_4 electrolyte, no reduction peak occurs in the negative potential region

Figure 2. SEM images of (a) bare Ti and (b) Ti-AuNP-STpy electrodes before electrochemical testing, and of (c) Ti-AuNP and (d) Ti-AuNP-STpy electrodes after electrochemical testing.

Figure 3. Cyclic voltammetry curves at 100 mV/s for bare Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes obtained in (a) blank 1.0 M H_2SO_4 , (b) 10 mM Cr(III)/1.0 M H_2SO_4 , and (c) 10 mM Cr(VI)/1.0 M H_2SO_4 . CV curves measured at various scan rates for (d) bare Ti, (e) Ti-AuNP, and (f) Ti-AuNP-STpy electrodes in 10 mM Cr(VI)/0.1 M H_2SO_4 . The insets of (c1), (c2), and (c3) are plots of CD (and potential) vs square root of scan rate ($v^{1/2}$) for the Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes.

as expected, and HER CD is also observed. In the 10 mM Cr(VI)/0.1 M H_2SO_4 electrolyte, peaks are generated in the CV curves of all three electrodes, and this is attributed to the reduction of Cr(VI) to Cr(III). The Cr(VI) reduction potentials are observed at approximately -0.55 , -0.35 , and -0.55 V (vs Ag/AgCl) for the bare Ti, Au NP-loaded Ti, and STpy functionalized Au NP-loaded Ti electrodes, respectively. A lower negative potential is demonstrated for the Ti-AuNP electrode compared to those for the other two electrodes, although the CD is relatively lower. The less negative (or more positive) potential for Ti-

Figure 4. Cyclic voltammetry curves at 100 mV/s for bare TiO_x , $\text{TiO}_x\text{-AuNP}$, and $\text{TiO}_x\text{-AuNP-STpy}$ electrodes obtained in (a) blank 1.0 M H_2SO_4 , (b) 10 mM $\text{Cr(III)}/1.0$ M H_2SO_4 , and (c) 10 mM $\text{Cr(VI)}/1.0$ M H_2SO_4 . CV curves measured at various scan rates for (c1) bare TiO_x , (c2) $\text{TiO}_x\text{-AuNP}$, and (c3) $\text{TiO}_x\text{-AuNP-STpy}$ electrodes in 10 mM $\text{Cr(VI)}/1.0$ M H_2SO_4 . The insets of (c1), (c2), and (c3) are plots of CD (and potential) vs square root of scan rate ($v^{1/2}$) for the TiO_x , $\text{TiO}_x\text{-AuNP}$, and $\text{TiO}_x\text{-AuNP-STpy}$ electrodes.

AuNP could be due to the activity of the Au NPs. Similar observations have been reported in the literature [28]. In the CV curves acquired at various scan rates—100, 200, 300, 400, and 500 mV/s—the reduction potential does not significantly shift toward more negative potentials as the scan rate increases. However, the corresponding CD levels increase with scan rate. The CD intensities of the electrodes at a given scan rate increase in the order $\text{Ti-AuNP} < \text{Ti-AuNP-STpy} < \text{bare Ti}$. The bare Ti electrode generates the highest CD, but the signal is much broader than those found in the other two electrodes. The CD increase is observed to be linear with the square root of the scan rate, which is typical of a diffusion-controlled reaction process [7,16].

For comparison with the Ti surface, the oxidized Ti surface was also tested. Figure 4 shows CV curves for bare the TiO_x , $\text{TiO}_x\text{-AuNP}$, and $\text{TiO}_x\text{-AuNP-STpy}$ electrodes acquired in the range of -0.7 to $+0.2$ V (vs Ag/AgCl) at a scan rate of 100 mV/s in blank 0.1 M H_2SO_4 , 10 mM $\text{Cr(III)}/1.0$ M H_2SO_4 , and 10 mM $\text{Cr(VI)}/1.0$ M H_2SO_4 electrolytes. In blank 1.0 M H_2SO_4 and 10 mM $\text{Cr(III)}/1.0$ M H_2SO_4 , no redox peaks are observed, as for the Ti electrodes shown in Fig. 3. Instead, CD increases are observed at negative potentials. The CD levels of the Au NP-loaded electrodes are seen to sharply increase above -0.3 V. In 10 mM $\text{Cr(III)}/1.0$ M H_2SO_4 , the CD increases for the electrodes occur, starting at the lowest potential, in the order $\text{TiO}_x\text{-AuNP} < \text{TiO}_x < \text{TiO}_x\text{-AuNP-STpy}$. The CD increase for the $\text{TiO}_x\text{-AuNP-STpy}$ electrode occurs at a much lower negative potential. In the 10 mM $\text{Cr(VI)}/1.0$ M H_2SO_4 electrolyte, Cr(VI) reduction potentials are observed around -0.55 , -0.35 , and -0.55 V (vs Ag/AgCl) for the bare TiO_x , Au NP-loaded TiO_x , and STpy functionalized Au NP-loaded TiO_x electrodes, respectively. The reduction potentials are shifted negatively, compared

Figure 5. UV-visible absorption spectra for $\text{Cr(VI)}/0.1$ M H_2SO_4 after amperometry reduction testing for 2 h at -0.6 V of (a) bare Ti, Ti-AuNP, and Ti-AuNP-STpy, (b) bare TiO_x , $\text{TiO}_x\text{-AuNP}$, and $\text{TiO}_x\text{-AuNP-STpy}$ electrodes. The UV-visible absorption spectra of 1 mM $\text{Cr(III)}/0.1$ M H_2SO_4 and 1 mM $\text{Cr(VI)}/0.1$ M H_2SO_4 are shown for reference. Insets show the decrease in peak (350 nm) intensity for the corresponding absorption spectra.

with -0.55 , -0.35 , and -0.55 V for the bare Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes, respectively. The reduction peaks are also broader than those of the bare Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes. This indicates that the support plays a significant role in the electrochemistry. The CV curves acquired at 100, 200, 300, 400, and 500 mV/s indicate that there is no significant change with scan rate for the reduction potential. However, the corresponding CD levels are seen to increase with scan rate. At a each scan rate, the CD intensities of the electrodes increase in the order $\text{TiO}_x\text{-AuNP} < \text{TiO}_x\text{-AuNP-STpy} < \text{bare TiO}_x$. The TiO_x electrode produces the highest CD and sharpest CD increase with scan rate. As for the Ti-supported electrodes, behavior typical of a diffusion-controlled reaction process is seen, that is, CD increases linearly with the square root of the scan rate ($v^{1/2}$) [7,16].

The Cr(VI) reduction performances of the bare Ti, Ti-AuNP, Ti-AuNP-STpy, bare TiO_x , $\text{TiO}_x\text{-AuNP}$, and $\text{TiO}_x\text{-AuNP-STpy}$ electrodes were further examined by amperometry at a potential of -0.6 V in a test solution of 1 mM $\text{Cr(VI)}/0.1$ M H_2SO_4 . The corresponding UV-visible absorption spectra are shown in Fig. 5. The UV-visible absorption spectrum of yellow 1 mM $\text{Cr(VI)}/0.1$ M H_2SO_4 solution includes a broad absorption peak at 350 nm. The UV-visible absorption spectrum of 1 mM $\text{Cr(III)}/0.1$ M H_2SO_4 solution does not include the same absorption peak. Therefore, the absorption intensity at 350 nm was used for monitoring Cr(VI) reduction [19]. In the amperometry tests carried out at -0.6 V for 2 h over the bare Ti, Ti-AuNP, and Ti-AuNP-

Figure 6. (a) Survey, (b) Ti 2p, (c) Au 4f, (d) O 1s, (e) Cr 2p, and (f) S 2p XPS spectra for as-prepared Ti-AuNP-STpy electrode, Ti-AuNP-STpy electrode immersed in the 1 mM Cr(VI) solution, and Ti-AuNP-STpy electrode after EC testing in the Cr(VI) solution.

STpy electrodes, 60, 90, and 100 % reduction efficiencies are indicated, respectively, for the UV-visible absorption intensities. The Ti-AuNP-STpy electrode shows the best rection performance. For this electrode, the yellow color of the solution is completely lost during the test, an indication of complete Cr(VI) reduction. For the oxidized Ti supports, the Cr(VI) reduction performance is poorer. However, the unmodified oxidized electrode performs better than the bare Ti electrode. In amperometry tests at -0.6 V for 2 h over bare TiO_x , TiO_x -AuNP, and TiO_x -AuNP-STpy electrodes, 80, 62, and 72% reduction efficiencies, respectively, are indicated by the UV-visible absorption intensities. The modified TiO_x electrodes have lower efficiencies than the corresponding Ti electrodes. It is well-known that Cr(VI) ions in acidic conditions are mainly present in the form of $\text{Cr}_2\text{O}_7^{2-}$ via $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ [29]. The electrochemical reduction mechanism has been proposed to be $\text{HCrO}_4^- (\text{VI}) + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}(\text{III}) + 4\text{H}_2\text{O}$ [28,30].

X-ray photoelectron spectroscopy (XPS) was carried out on the Ti-AuNP-STpy, Ti-AuNP-STpy (immersed in the Cr^{6+} solution), and Ti-AuNP-STpy (after the EC tests in the Cr^{6+} solution) electrodes and the results are displayed in Fig. 6. The survey XP spectra include peaks that are assigned to Ti (Ti Support), Au (overlayer), C (functionalized STpy), and S (S of STpy or sulfate ions) species, as expected. Peaks assigned to Cr species were detected in the spectra for the Ti-AuNP-STpy electrodes measured whilst immersed in the Cr^{6+} solution and after EC testing. In the Ti 2p spectrum of the as-prepared Ti-AuNP-STpy electrode, the Ti 2p signal is weak, due to thick overlayer of Au and terpyridine. For the Ti-AuNP-STpy electrode in the Cr^{6+} solution, two strong peaks in the Ti 2p spectrum are observed, at 464.7 and

Figure 7. SPR responses of 1 mM Cr(III) and Cr(VI) solutions measured over Au-STpy film surface.

458.9 eV, suggesting a spin-orbit splitting of 5.8 eV and an assignment to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ levels, respectively, of Ti(IV) species [31]. A smaller signal is observed at a binding energy (BE) of 454.0 eV, assigned to the Ti $2p_{3/2}$ peak of metallic Ti(0) [32]. The increase in the Ti 2p XPS signal upon immersion of the electrode into the Cr(VI) solution is due to the fact that some Au NP aggregation occurs during the interaction between Cr(VI) and the terpyridine ligand. Three Lewis basic N groups of STpy are expected to strongly interact with the Lewis acidic Cr(VI) ions [7]. Therefore, the Ti support surface is exposed outwards because of Au NP aggregation. After EC testing, the Ti 2p signal assigned to metallic Ti(0) showed no critical change, remaining at a BE of 454.0 eV, while the Ti 2p signals of the Ti(IV) species shifted to a 0.5-eV higher BE. This indicates that surface Ti species may interact with Cr species during the EC. In the Au 4f spectrum of the as-prepared Ti-AuNP-STpy electrode, the BEs of the Au $4f_{7/2}$ and $4f_{5/2}$ electrons are observed at 84.2 and 87.8 eV, respectively, with a spin-orbit splitting of 3.6 eV. This BE position is attributed to the attraction between the metallic Au and thiol. Upon immersing the electrode in the Cr^{6+} solution, the Au 4f signal is diminished as a result of the aggregation of Au NPs during the interaction between Cr(VI) and the terpyridine ligand, as mentioned above in discussing the Ti 2p XPS. After the EC test, the Au 4f signal is markedly diminished, which is attributed to the removal from the surface of the Au NPs during the 2 h reduction test. The O 1s spectrum of the as-prepared Ti-AuNP-STpy electrode features the O 1s BE at 531.7 eV, a peak that is attributed to surface-adsorbed oxygen [31]. Upon immersing the electrode in the Cr^{6+} solution, the O 1s BE appears at 530.6 eV, and this signal is attributed to lattice oxygen of Ti(IV) oxide species. The appearance of lattice oxygen is a result of aggregation of overlayer Au NPs, as mentioned above. After the EC testing, the O 1s peak at 530.6 eV remained unchanged but the peak at 532.3 eV was significantly enhanced, due to an increase in surface OH species such as Ti-OH. As a consequence, the Ti 2p BE was shifted to a higher BE position after the EC tests, as mentioned above. In the Cr 2p XP spectrum of the Ti-AuNP-STpy electrode dipped in the Cr^{6+} solution, two peaks are clearly observed at BEs of 578 and 587.5 eV, attributed to Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks, respectively, of Cr(III) [33]. These Cr 2p peaks of Cr(III) reflect the fact that the terpyridine ligand plays a significant role in the reduction of Cr(VI) to Cr(III). After the EC testing, the Cr

2p BE shifted to a higher BE position, possibly due to some interaction with sulfate residues. The corresponding S 2p signals appear at approximately 169.3 eV. The S 2p peak at 168.5 eV for the other two samples is assigned to thiol in the STpy-functionalized electrodes [7].

We demonstrated surface plasmon resonance (SPR) sensing performance to briefly show that the newly developed system can be applied to sensing using SPR [6]. Figure 7 shows the SPR signal response over a STpy-functionalized Au film chip upon introducing Cr(VI) and Cr(III) ions. Interestingly, a strong SPR response was observed for both Cr(VI) and Cr(III). However, the SPR signal did not change significantly when Cr(VI) was converted to Cr(III) and vice versa. This indicates that once the Cr ion has strongly interacted with the terpyridine ligand, no substitutional change occurs. When water is introduced, however, the signal quickly returns to its original levels. This indicates that an adsorption-desorption equilibrium may occur when changing between Cr ion solutions and deionized water. This preliminary result indicates that the STpy-functionalized Au chip can be used for Cr ion sensing based on SPR. Further investigations should be carried out, however.

4. Conclusions

Toward the safer electrochemical treatment of toxic Cr(VI) in solution, bare Ti, Ti-AuNP, Ti-AuNP-STpy, bare TiO₂, TiO₂-AuNP, and TiO₂-AuNP-STpy electrodes were newly developed and tested, by CV and amperometry, for the electrocatalytic reduction of Cr(VI) to Cr(III) under an acidic conditions. The Cr(VI) reduction efficiency was observed to be enhanced for the STpy functionalized Au NP-loaded Ti surfaces, compared with the those of the bare Ti and Au NP-loaded Ti. Cr(VI) reduction potentials were observed at approximately -0.55, -0.35, and -0.55 V (vs Ag/AgCl) for the bare Ti, Ti-AuNP, and Ti-AuNP-STpy electrodes, respectively. The reduction potentials were negatively shifted when oxidized Ti supports were used. The CD increased linearly with the square root of the scan rate ($v^{1/2}$), an indication of a diffusion-controlled reaction process. The Cr(VI) reduction performances of the electrodes, measured by amperometry at -0.6 V, were found to increase in the order bare Ti < Ti-AuNP < Ti-AuNP-STpy. The Ti-AuNP-STpy electrode showed 100% reduction efficiency. The electrodes based on the oxidized Ti support were demonstrated to possess poorer efficiencies, compared to the corresponding Ti supports. XPS data confirmed that the Ti electrode consisted of Ti(0) covered by Ti(IV) oxide states. Functionalized Au NPs were found to be partially removed from the surface. In addition, the SPR demonstration tests for Cr(VI) and Cr(III) highlighted the potential applicability of the Au-STpy electrode system in Cr sensing. Thus, we can conclude that these test results for the newly developed electrode systems demonstrate a new methodology for the development of electrochemical Cr(VI) treatment.

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