

Original Research

Recovery of gold from hydrometallurgical leaching solution of electronic waste *via* spontaneous reduction by polyanilineYuanzhao Wu^{a,b,c,1}, Qingming Fang^{a,b,c,1}, Xiaohui Yi^{a,b,c}, Gang Liu^{a,b,c,*}, Run-Wei Li^{a,b,c,*}^a CAS Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China^b Zhejiang Province Key Laboratory of Magnetic Materials and Applied Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China^c University of Chinese Academy of Sciences, 19 A Yuquan Rd, Shijingshan District, Beijing 100049, China

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ABSTRACT

The present study is primarily designed to develop an environmentally-benign approach for the recovery of precious metals, especially gold, from the ever increasingly-discarded electronic wastes (*e-waste*). By coupling the metal reduction process with an increase in the intrinsic oxidation state of the aniline polymers, and the subsequent re-protonation and reduction of the intrinsically oxidized polymer to the protonated emeraldine (EM) salt, polyaniline (PANi) films and polyaniline coated cotton fibers are able to recover metallic gold from acid/halide leaching solutions of electronic wastes spontaneously and sustainably. The current technique, which does not require the use of extensive extracting reagents or external energy input, can recover as much as 90% of gold from the leaching acidic solutions. The regeneration of polyaniline after gold recovery, as confirmed by the X-ray photoelectron spectroscopy measurements, promises the continuous operation using the current approach. The as-recovered elemental gold can be further concentrated and purified by incineration in air.

1. Introduction

As one of the most useful and precious metals mined from the earth, gold (Au) has been widely used in jewelries, financial field (as a medium of exchange), dentistry/medicine, aerospace equipment, industries, and *etc.* Among these, the manufacture of electronic devices has become the most important industrial consumption of gold today [1]. Due to its highly efficient electrical conductivity, which can be used to carry tiny current while resistant to interruption by corrosion or tarnish at the contact points, gold is usually the most preferred material choice for low-voltage, low-current and low-contact-force applications [2–4]. It is reported that a total amount of 311 t of gold has been consumed in electronic industries in 2007, more than that has been purchased in the form of jewelry in US in the same year [1]. In the meanwhile, around 20–50 million tons of electronic products, containing as high as 40% of metal contents by weight, are discarded annually across the globe [5]. The direct disposal of electronic waste (*e-waste*) has addressed a series of problems, including environmental pollution by hazardous materials and loss of secondary metal sources. Thus, recycling of *e-waste* has been taken into consideration by both the

government and the public, not only from the point of waste treatment, but also from the aspect of recovery of valuable metals [6–8].

Numerous state-of-the-art technologies for the recovery of gold from *e-waste* are available in forms of (1) pyrometallurgical, (2) hydrometallurgical, and (3) biometallurgical processing of the solid waste and subsequent recovery of various metals [2]. Comparing with the conventional pyrometallurgical processing which may emit hazardous material (*e.g.* dioxins) into the environment [9], or the newly-developed biometallurgical processing which exhibits limited bacterial leaching rate [10], hydrometallurgical method is more exact, more predictable, more easily controlled, and more economically viable for the recovery of metals from *e-waste* [11–13]. However, the subsequent treatment of the hydrometallurgical leaching solutions usually involves the extensive use of sacrificial metals (cementation), organic solvents and metal cyanide complexes (solvent extraction), the elaborate resin regeneration steps (ion-exchange), or the input of external/additional energy (electrochemical reduction) [14,15]. Thus, a more environmentally-benign process, utilizing less metal extracting reagents or energy input, appears to be necessary.

Because of their high intrinsic electrical conductivity, environmental stability, solution processability and interesting redox properties,

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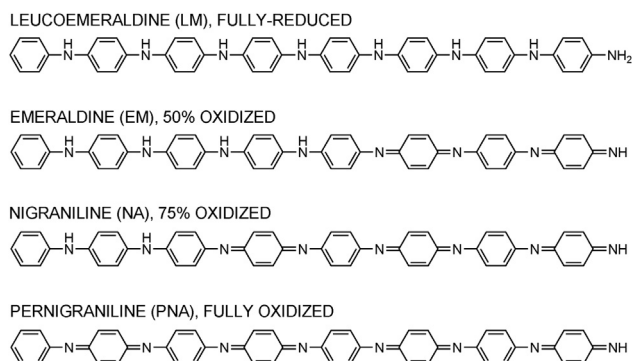


Fig. 1. Octameric structures of polyaniline in various intrinsic oxidation states.

the century-old aniline families of polymers (chemical structure shown in Fig. 1) are promising candidates for the spontaneous recovery of gold from acid leaching streams of e-waste [16–18]. Associated with the chain nitrogen, the interconversion between various intrinsic oxidative and protonated states of polyaniline (PANi) can be coupled with the metal reduction process in acid solutions, to recover gold to their elemental form spontaneously and sustainably. The aim of this work is to develop a novel and environmentally-friendly semi-pilot process for the spontaneous reduction of gold by electroactive aniline polymers during hydrometallurgical leaching of the e-waste.

2. Experimental

2.1. Acid/halide leaching of gold from electronic waste

Prior to chemical leaching of metals from electronic waste, the raw waste materials were subjected to mechanical crushing to reduce the particle size as well as enhance the access of leaching reagent to the internal layers. Then the crushed particulates were poured into robust reactors containing concentrated nitric acid and hydrochloric acid consequently, to dissolve most of the silver and base metals. After solid-liquid separation, aqua regia was used to dissolve gold from the solid residues. Special attention should be paid during the hydrometallurgical leaching of the solid e-waste materials, as both the concentrated nitric acid and aqua regia are dangerous corrosive and oxidizing reagents. The flow diagram for chemical leaching of various metals from e-waste materials is illustrated in Fig. S1.

2.2. Preparation of polyaniline powder, film, and PANi coated cotton fiber

Polyaniline was synthesized in its emeraldine (EM) salt form *via* oxidative polymerization of aniline and converted to EM base by deprotonation with sodium hydroxide. Dense and pinhole-free thin films of about 20–50 μm in thickness were cast from 1-Methyl-2-Pyrrolidone (NMP) solution of EM base on glass substrates (Fig. S3(a)). The field emission scanning electron microscopy (FE-SEM) image of the cross section of the EM base film is shown in Fig. S4. PANi coated cotton fibers were also prepared during the oxidative polymerization of EM salt (Fig. S3(b)). Leucoemeraldine (LM) powders and films were also prepared by treatment with hydrazine monohydrate. The as-prepared LM products were kept in vacuum and used soon after preparation.

2.3. Recovery of gold from acid gold leaching solution

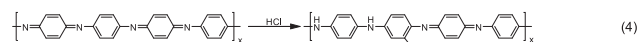
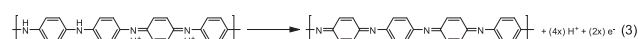
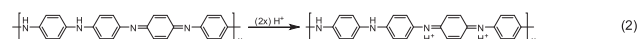
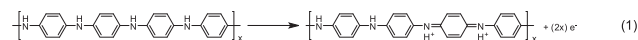
All gold recovery experiments were performed at room temperature. Standard chloroauric acid aqueous solutions were also used for comparison purpose. $2 \times 2 \text{ cm}^2$ polyaniline films, or PANi coated cotton fibers of comparable polymer weight ($\sim 10.0 \text{ mg}$), were soaked in the

Au-containing solutions to recover elemental gold. The rate of gold recovery and the concentration of gold ions remaining in each solution were determined from the UV-visible absorption peak at about 312 nm. The reduction of AuCl_4^- ion to elemental gold and its deposition on the surface of polyaniline films or PANi coated cotton fibers were readily confirmed by the XPS measurements. The recovered gold was further concentrated and purified by incineration in air at 600 $^\circ\text{C}$.

3. Results and discussion

3.1. Redox properties of polyanilines

In order to achieve spontaneous reduction of precious and heavy metals by electroactive polymers during hydrometallurgical leaching of the e-waste, the redox states or potentials of the polymers are desired to match the reduction potential of specific metal ions in specific media. The aniline polymers have the general formula of $[(-\text{B}-\text{NH}-\text{B}-\text{NH}-), (-\text{B}-\text{N}=\text{Q}=\text{N}-)]_{1-y}$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively (Fig. 1). The oxidation state of polyanilines can range from that of the fully reduced leucoemeraldine (LM, $y=1$), through that of the 50% oxidized emeraldine (EM, $y=0.5$), to that of the fully oxidized pernigraniline (PAN, $y=0$). In acidic solution with pH in the range of 1–4, reversible electrochemical oxidation of LM base occurs initially with no deprotonation to give EM salt; EM salt can also be obtained through the protonation of the imine nitrogen ($=\text{N}-$ structure) in its EM oxidation state; continued oxidation of EM salt occurs subsequently with spontaneous deprotonation to give PNA base:



Reaction (1) is pH independent and has an oxidation potential of about 0.1 V *vs* saturated calomel electrode (SCE) while the oxidation potential for reaction (3) is about 0.7 V *vs* SCE [19]. The reduction potential of gold ion in the form of chloroauric acid (AuCl_4^-) is about 1.0 V *vs* SCE [20], well matching the oxidation potentials of LM or EM form of polyaniline. Thus in acidic solutions containing chloroauric acid, the amine nitrogen of the LM and EM form of polyanilines can act as the reducing agent to reduce Au (III) ions to the metallic gold. Nevertheless, it is reported that the treatment of the fully oxidized polymer with hydrochloric acid involves reduction to regenerate protonated EM salt, with a portion of the benzenoid hydrogen atoms substituted by chloride species, probably attributed to the hydrolysis of some quinoid units in the aqueous medium [21,22]. Thus, by coupling the gold reduction process in hydrochloric acid aqueous solutions with an increase in the intrinsic oxidation state of polyaniline, the subsequent re-protonation and reduction of the intrinsically oxidized pernigraniline, the spontaneous and sustainable recovery of gold can be achieved.

The oxidative states of polyaniline powders, films as well as PANi coated cotton fibers were readily studied by X-ray photoelectron spectroscopic (XPS) measurements. The proportion of quinoid imine ($=\text{N}-$), benzenoid amine ($-\text{NH}-$) and positively charged nitrogen (N^+) atoms corresponding to a particular intrinsic oxidation state and protonation level of polyaniline can be quantitatively differentiated in the properly curve-fitted N 1s core-level spectrum. The N 1s core-level XPS spectrum of the EM base powder is shown

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