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Selective recovery of pure copper nanopowder from indium-tin-oxide etching wastewater by various wet chemical reduction process: Understanding their chemistry and comparisons of sustainable valorization processes

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ABSTRACT

Sustainable valorization processes for selective recovery of pure copper nanopowder from Indium-Tin-Oxide (ITO) etching wastewater by various wet chemical reduction processes, their chemistry has been investigated and compared. After the indium recovery by solvent extraction from ITO etching wastewater, the same is also an environmental challenge, needs to be treated before disposal. After the indium recovery, ITO etching wastewater contains 6.11 kg/m^3 of copper and 1.35 kg/m^3 of aluminum, pH of the solution is very low converging to 0 and contain a significant amount of chlorine in the media. In this study, pure copper nanopowder was recovered using various reducing reagents by wet chemical reduction and characterized. Different reducing agents like a metallic, an inorganic acid and an organic acid were used to understand reduction behavior of copper in the presence of aluminum in a strong chloride medium of the ITO etching wastewater. The effect of a polymer surfactant Polyvinylpyrrolidone (PVP), which was included to prevent aggregation, to provide dispersion stability and control the size of copper nanopowder was investigated and compared. The developed copper nanopowder recovery techniques are techno-economical feasible processes for commercial production of copper nanopowder in the range of 100–500 nm size from the reported facilities through a one-pot synthesis. By all the process reported pure copper nanopowder can be recovered with > 99% efficiency. After the copper recovery, copper concentration in the wastewater reduced to acceptable limit recommended by WHO for wastewater disposal. The process is not only beneficial for recycling of copper, but also helps to address environment challenged posed by ITO etching wastewater. From a complex wastewater, synthesis of pure copper nanopowder using various wet chemical reduction route and their comparison is the novelty of this recovery process.

1. Introduction

In the industry, the ITO wastewater gets generated basically from two different resources; i.e., (i) from the ITO deposition process, and (ii) from the ITO patterning process. During the ITO deposition process, on the evaporation chamber wall, the ITO gets deposited, which subsequently cleaned through the etching process. During ITO patterning, through a wet chemical etching process, deposited undesired ITO are etched out using HCl, is the source of the etching wastewater. During the deposition process various kinds of substrates are used and during patterning various kinds of deposited coatings are used, which are associated with undesired metallic impurities. In the industry, these impurities are a cause of concern for the production process and the reason for the ITO etching wastewater generation leads to an environmental challenge. In the ITO etching wastewater, along with indium and tin, significant amount copper also wasted out into the wastewater stream. The ITO etching wastewater can be treated as reported process elsewhere (Swain et al., 2015a; Swain et al., 2015b). Exploration companies estimated the average grade of copper ores in the 21st century is below 0.6 percent copper, with a proportion of ore minerals being less than 2 percent of the total volume of the ore rock (The Investing News Network (INN), World-class Copper Deposits, 2015). Copper development association inc. has reported that for commercial exploitation, copper deposits generally need

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to be in excess of 0.5% copper, and preferably over 2% (Calcutt, 2001). The ITO etching wastewater contains 6.11 kg/m^3 of copper, which no need of beneficiation processing unlikely from primary resources, can be profitable urban mining resources.

Because of its unique properties, i.e., the combination of high electrical and thermal conductivity, and functional application in various fields such as optical, catalytic, electrical equipment, and electronic, copper nanopowder occupies a significantly prime position in powder metallurgy (Agrawal et al., 2006; Cheng et al., 2011). The copper nanopowder being used in chemical, pharmaceutical, welding and alloying industry for decades. Conductive pastes made from copper nanopowder have been used for the formation of thick film conductors such as electrodes or conductive patterns in multilayered electronic parts and printed circuit boards (Hai et al., 2007; Tang et al., 2010; Xue et al., 2006). The replacement of precious metal powders like; gold, silver or palladium by copper nanopowder for the production of conductive paste for hybrid integrated circuit and for the metallization of multilayer ceramic capacitor (MLCC) is a current trend in the electronic industry (Hai et al., 2007; Zhang et al., 2010). Metal powder, in particular, copper nanopowder is a potential raw material for the future additive manufacturing industry.

In the past decade, there has been increasing interest on synthesis of copper nanoparticles due to their various applications involving their physical and chemical properties (Agrawal et al., 2006; Cheng et al., 2011; Hai et al., 2007; Xue et al., 2006; Zhang et al., 2010). Various methods like, chemical reduction (Agrawal et al., 2006; Dhas et al., 1998; Hai et al., 2007), thermal reduction (Ma et al., 2014; Mohammad Hossein et al., 2010), microemulsion techniques (Ohde et al., 2001; Solanki et al., 2010; Wu and Chen, 2004), laser ablation (Muniz-Miranda et al., 2013; Sadrolhosseini et al., 2013), polyol method (Park et al., 2007), and the DC arc discharge method (Wei et al., 2006; Wei et al., 2007) has been reported in literature for the preparation of copper nanoparticles. However, most of these methods required either larger volume of organic solvents/reagent, which are either highly reactive under atmospheric conditions or required higher energy consumption, very expensive instrumental setup and expertise, if scaled up to industrial scale. When such particles are produced in the higher volumes required by the industry, there is a greater risk against the environment and occupational safety. Among these methods, wet chemical reduction exhibits the greatest feasibility for further applications because of simplicity, cost effectiveness and environmental friendliness (Nicola Cioffi et al., 2009). Toxicity of nanoparticles is now a very important issue thus, wet chemical closed method system can be an advantageous process for nanoparticles synthesis from the environment and occupational safety perspective.

In our current study, on the course of total recycling of Indium-Tin-Oxide (ITO) etching wastewater process development along with the indium recovery process, for selective recovery of copper nanopowder from ITO etching wastewater by wet chemical reduction has been investigated. A state of the art hydrometallurgical indium recovery process to deal with 1 t/day of ITO etching wastewater has been developed (Swain et al., 2015a; Swain et al., 2015b), where only recovery of indium and the process development aspect has been discussed. In continuation to the reported work, in the current research selective recovery of pure copper nanopowder from the ITO etching waste by various wet chemical reduction process and their aqueous chemistry has been addressed. Finally, the sustainable valorization processes have been compared. After indium recovery by a solvent extraction process, the ITO etching wastewater contains 6.11 kg/m^3 of copper and 1.35 kg/m^3 aluminum, pH of the wastewater is very low converging to 0 and contain a significant amount of chlorine in the media. After the indium recovery, the wastewater stream contains such amount of heavy metals is an environmental challenge, needs pretreatment before disposal has been addressed by this process. In this study, pure copper micro and nano sized powder were recovered by wet chemical reduction using three different categories of reagents like; metal (iron powder), inorganic acid (hypo-phosphorous acid), and organic acid (ascorbic acid). Different reducing agents like metallic, inorganic acid and organic acids were used to understand reduction behavior of copper in the presence of aluminum in a strong chloride medium, i.e. indium free ITO etching wastewater and compared. The polymer surfactant Polyvinylpyrrolidone (PVP) was used to control the size of reduced copper powder in all three processes. In the presence of the PVP, which was included to prevent aggregation and give dispersion stability to the resulting colloidal nanoparticles, their behavior was investigated and compared. Our literature investigation and a review of Cooffi et al. suggest that such a value added micro and nanosized copper powder recovery process is scarce in the literature (Nicola Cioffi et al., 2009). The importance and novelty of the reported process explained below.

(i) Most of the copper nanopowder preparation reported literature are from the pure chemical precursor, whereas in our current method Indium-Tin-Oxide (ITO) etching wastewater has been used as the precursor.
(ii) Most of the copper nanopowder syntheses reported in the open literature are about a gram to sub-gram material synthesis process, but our process offers a versatile and flexible approach for mass production capability up to kilogram scale.
(iii) The developed copper nanopowder recovery techniques are techno-economical feasible processes for commercial production of copper nanopowder in the range of 100–500 nm size from the reported facilities through a one-pot synthesis.
(iv) More importantly, the aqueous chemistry of wet chemical reduction and ITO etching wastewater has been discussed thoroughly is an important exploration worth to be reported, presented in Section 3.
(v) As reported process is a simple process, through which semiconductor manufacturing industry can address various issues like; (i) waste disposal as well as value added copper recovery, (ii) brings back the material to production stream and address the circular economy, and (iii) can be part of cradle to cradle technology management and lower the futuristic carbon economy, simultaneously.

2. Experimental

2.1. Materials

Indium rich Indium-Tin-Oxide (ITO) etching wastewater was supplied by TSM Co. Ltd, Republic of Korea. All chemicals like Ascorbic acid, Hypophosphorous acid, Polyvinylpyrrolidone (PVP), and NH_4OH were of analytical grade, supplied by Daejung chemical and metal Co, Ltd, Republic of Korea. All chemicals of reagent grade quality were used without further purification.

2.2. Methods

ITO etching wastewater which was supplied by TSM was processed as explained in our earlier publication (Swain et al., 2015a; Swain et al., 2015b). After quantitative recovery of indium by solvent extraction, copper present in the waste raffinate stream (indium free ITO etching wastewater), was reduced using various reducing agents through wet chemical reduction route. From onward unless otherwise mentioned, the indium, tin, and molybdenum free