XIV CONGRESSO INSTM
sulla Scienza e Tecnologia dei Materiali

CAGLIARI
9-12 giugno 2024

STRUCTURE AND MORPHOLOGY OF E-WASTE-DERIVED HIGH VALUE METAL NANOPARTICLES

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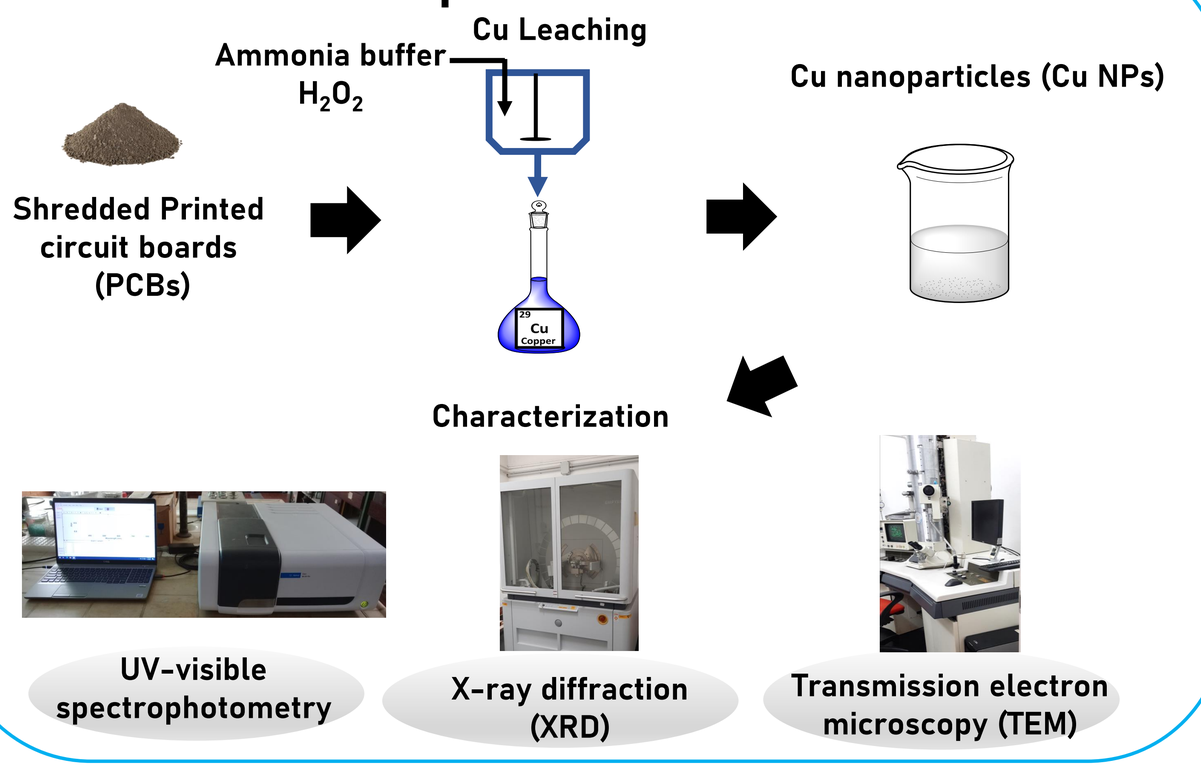
Graphical abstract



Introduction

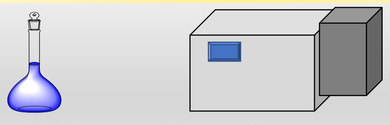
The rapid pace of technological advancement, the growing demand for electronic devices, and the short lifespans of appliances lead to a depletion of primary resources and a rising rate of electronic waste (e-waste). E-waste recycling helps to diversify the sources of raw materials market and alleviate their impact on the environment. E-waste such as TVs, DVD/CD players, computers, and mobile phones, contains a common valuable component: Printed Circuit Boards (PCBs). Spent PCBs can be considered urban mines as they typically contain valuable metals (12-16%) including precious metals such as Cu, Ag and Au.[1,2] The most dominant hydrometallurgy methods for recovery metals from PCBs involve inorganic acids such as HCl, HNO_3 or aqua regia, which may result in a reduced leaching selectivity, as well as potential environmental threat related to their use and by-products formation.[3] Therefore, the solution needs to be further processed, adding extra costs to the process.[4] Herein, a selectively leaching approach involving the use of ammonia buffer as a leaching solution in the presence of H_2O_2 at room temperature under vigorous stirring has been used to recover Cu as tetraamine copper (II).[1] The Cu-rich leach solution has been used as a precursor to synthesize copper nanoparticles (Cu NPs) at room temperature using trisodium citrate dihydrate ($C_6H_5Na_3{\cdot}2H_2O$) and potassium borohydride (KBH_4) as stabilizing and reducing agents, respectively. The characterization of the as-recovered Cu NPs and their stability were investigated by XRD, UV-vis and TEM techniques.

Advantages
+ No commercial Cu precursor
+ No dangerous surfactant
+ Low temperature

Disavantages
– The leaching solution may contain limited fraction of other metals

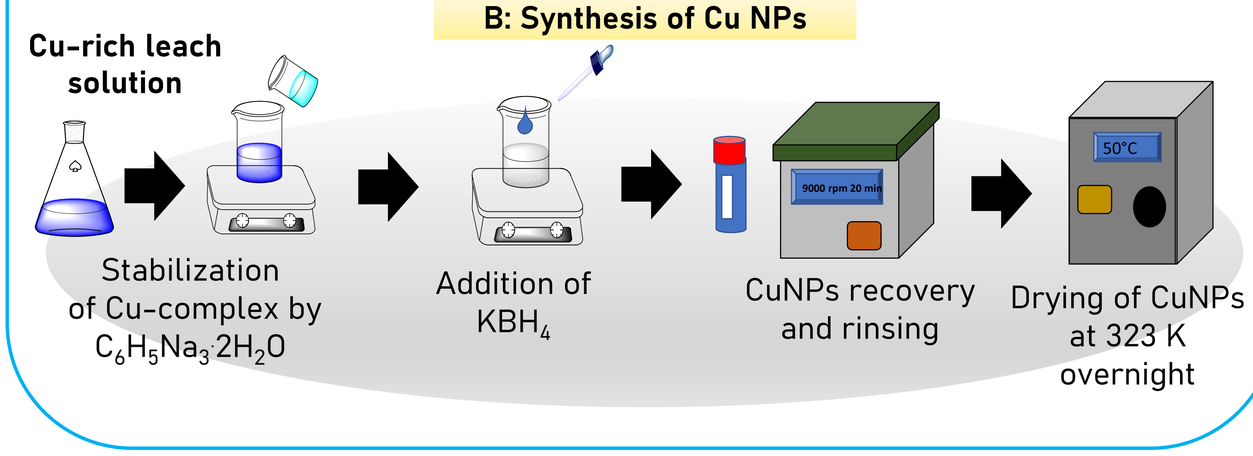
Method and materials

A: Determination of Cu concentration in solution



Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

B: Synthesis of Cu NPs



Results

- ICP-OES analysis showed the occurrence of Cu^{2+}, Ni^{2+} and Ag^{+}, where the most concentrated species is Cu^{2+} (4890 ppm), and both Ag^{+} and Ni^{2+} displayed significantly lower values (around 10 ppm).
- UV-vis spectrum confirmed the formation of the Cu NPs. Four broad plasmon absorptions at different wavelengths due to the formation of single NPs and aggregates are observed (**Figure 1a**). XRD pattern showed three dominant peaks at 2Θ ≈ 43°, 50° and 74° indexed as (111), (200) and (220) planes, respectively (**Figure 1b**). These are characteristic peaks for the cubic system of copper with an average particle size of 17±6 nm. Moreover, the Bragg reflection at 37° characterizes the crystallographic plane (111) of the cubic stucture of cuprous oxide (Cu_2O). TEM images revealed the occurrence of aggregates of nearly spherical nanoparticles (**Figure 1c**) with individual size in the order of tens of nanometers.

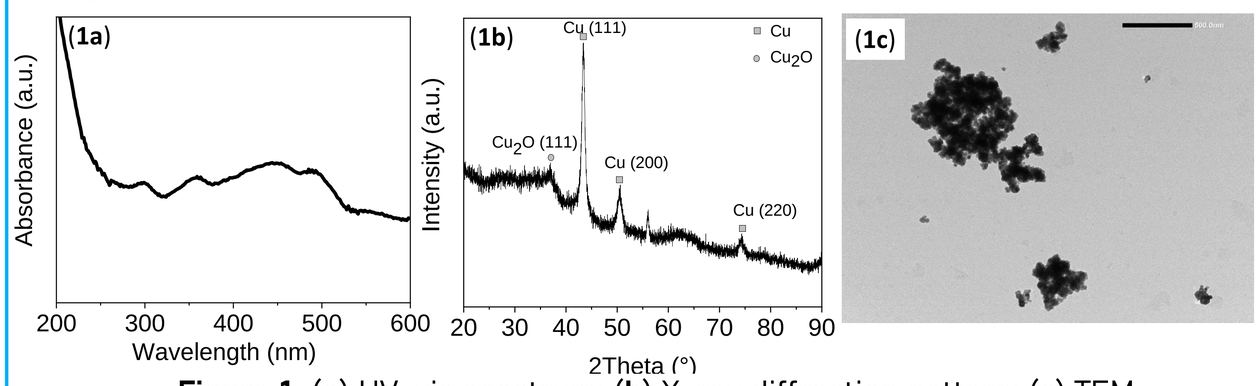


Figure 1. (**a**) UV-vis spectrum; (**b**) X-ray diffraction pattern; (**c**) TEM image magnification of as-synthesized Cu NPs.

- The stability of Cu NPs was conducted by measuring the XRD pattern and the UV-vis spectrum of the Cu NPs after six months of storage in static air at 323 K (**Figure 2 (a-b)**). XRD pattern confirmed the oxidation of Cu into Cu_2O and CuO while UV-vis spectrum showed a further narrow plasmon adsorption at 226 nm.

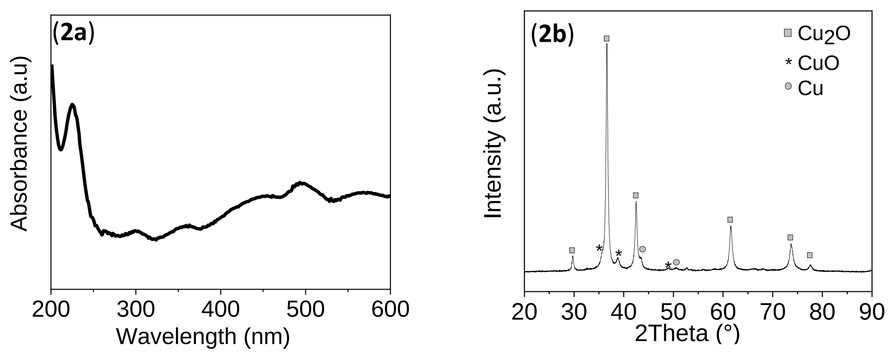


Figure 2. (**a**) UV-vis spectrum; (**b**) X-ray diffraction pattern of as-synthesized Cu NPs after six months of storage at 323 K.

Conclusion

- The ammonia leaching process under oxidizing environment was selective for the Cu recovery with an insignificant amount of Ag^{+} and Ni^{2+}.
- The Cu NPs were synthesized through an easy route at room temperature by the reduction of the Cu-complex by potassium borohydrate to form Cu NPs.
- XRD and UV-vis proved the formation of Cu NPs while TEM confirmed that the synthesized nanoparticles are nearly-round spheres.
- The as synthesized Cu NPs showed limited stability and phase changes after six months of storange at 323 K.

[1] Rigoldi, A., Trogu, E. F., Marcheselli, G. C., Artizzu, F., Picone, N., Colledani, M., Deplano, P. and Serpe, A., *ACS Sustainable Chemistry & Engineering*, **2018**, 7(1), 1308-1317.
[2] I. Birloaga, F.Vegliò, *Journal of Environmental Chemical Engineering* **2016**,4, 20-29
[3] El-Nasr, R. S., Abdelbasir, S. M., Kamel, A. H., & Hassan, S. S., *Separation and Purification Technology* **2020**, *230*, 115860.
[4] Gautam, P., De, A. K., Sinha, I., Behera, C. K., & Singh, K. K., *Environmental Research*, **2023**, *229*, 115951.

This work was carried out in the framework of the SMART PCBs project (MASE, bando RAEE 2021).
We thank the CeSAR (Centro Servizi Ricerca d'Ateneo) core facility of the University of Cagliari and Dr. A. Ardu for assistance with the generation of TEM images.

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