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## Direct cyanidation of silver sulfide by heterolytic C-CN bond cleavage of acetonitrile†

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\*\*a\*\* Table 1. \*\*A\*\* Table 1. \*\*A\*\* Table 2. \*\*A\*\* Table 2.

Extraction of silver as silver cyanide from silver sulfide was made possible using acetonitrile as the source of cyanide. The process of cyanidation took place through the oxidation of sulfide to sulfur oxides and cleavage of the C–CN bond of acetonitrile. The reaction was found to be catalyzed by vanadium pentoxide and hydrogen peroxide. The different species involved in the cyanidation process were duly characterized using FTIR, ESI-MS, HRMS, XPS and UV-vis spectroscopic analysis. The mechanism of the cyanidation process was confirmed through *in situ* FTIR analysis.

Silver (Ag) is a precious noble metal that has found applications in photography, nanocatalysis, antibacterial agents and jewelry. <sup>1-3</sup> Most importantly, it contributes to the economic growth of numerous countries. Silver metal extracted from its main ores contributes to a high percentage (~30%) of the total world production of Ag. Silver sulfide (Ag<sub>2</sub>S) is the most common ore from which it is extracted. <sup>4-5</sup> However, the traditional way of extracting Ag from Ag<sub>2</sub>S ore has many disadvantages, as it involves the use of poisonous sodium cyanide (NaCN) or potassium cyanide (KCN), which are also used in gold (Au) extraction. <sup>4-5</sup> The use of cyanide to achieve Ag leaching has led to great public concern, due to the damage it can cause to

most commonly ammonium acetate buffer at pH = 4, has drawn great attention, and has been found to be a potential candidate for Ag extraction from its ores. Although the method is cheaper, it consumes a high concentration of the reagent and also depends on different conditions such as pH and the kinetics of oxygen reduction. The reaction of silver ions (Ag\*) with thiosulfate solution in the presence of a base (NH $_3$ ) is thermodynamically favorable, but the slow oxygen reduction process leads to deliberate leaching of Ag as silver thiosulfate complex, Ag(S $_2$ O $_3$ ) $_3$ <sup>5</sup>-. Hence, the search for an alternative method is still an ongoing research process.

Apart from alkali cyanides, alkyl nitriles such as acetonitrile