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Review

Carbon nanomaterials as potential substitutes for scarce metals

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ABSTRACT

There is growing evidence of resource problems related to the use of scarce metals in society, including the long-term risk of world-wide depletion of high-grade ores, shorter-term supply deficits and mineral related conflicts. In this study, we explore the idea that scarce metals may be substituted by nanomaterials based on the abundant element carbon, primarily graphene, nanotubes and fullerenes. We depart from a list of 14 geochemically scarce metals: antimony, beryllium, chromium, cobalt, gallium, germanium, gold, indium, niobium, platinum, silver, tantalum, tin and tungsten. We then review scientific papers and patents for carbon nanomaterial technologies that, if successfully implemented, could reduce or eliminate the need for each metal in its main application. For all main applications except for gold in jewelry, such technologies were identified. Most of the identified technologies were described in more than 100 papers. This suggests that there is an ongoing promising development of carbon nanomaterial technologies for applications currently relying on scarce metals. However, we recommend further studies to scrutinize these technologies regarding their environmental performance to avoid problem shifting from metal scarcity to (eco)toxic effects of the carbon nanomaterials themselves or other impacts related to their production and use.

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1. Introduction

1.1. Metal scarcity and dematerialization

In a paper with the suggestive title *Dining at the Periodic Table*, Johnson et al. (2007) discussed the increased societal use of different elements in the periodic table. For example, while a circuit board in the 1980s typically used 11 elements, this increased to 15 in the 1990s and to 60 in the 2000s. They also report how the global mine production of ten metals have increased considerably between 1900 and 2000: aluminum, chromium, nickel, tungsten, copper, zinc, iron, gold, lead, silver and tin. Along the same lines, Ljunggren Söderman et al. (2014) report an increased use of scarce metals in vehicles. They also write that a transition to electric vehicles may further raise the use of scare metals, such as lithium, cobalt, nickel, manganese, silver and copper. This increased demand for a large variety of metals – together with the uneven distribution of metals in Earth's crust – has caused concerns over metal scarcity. The European Commission (2014) has developed a list of critical raw materials, of which most are scarce metals. Criticality is defined there as the combination of high supply risk and high economic importance. The purpose of this list is to ensure a continued supply of these raw materials to the European economy. Other ways to define and assess resource criticality have been developed, which take additional aspects, such as substitutability and environmental impact, into account (Erdmann and Graedel, 2011; Graedel et al., 2012; Nassar et al., 2015). The role of some scarce metals in conflicts has also been highlighted. Similar to drugs, oil and diamonds, profits from selling these minerals are used to fund ongoing conflicts. Important minerals in this context are those containing tin, tungsten, tantalum and gold (3TG) in the Democratic Republic of the Congo (Fitzpatrick et al., 2015).

Taking a longer time perspective, there is growing evidence of long-term depletion of high-grade ores of geochemically scarce metals. By comparing predicted future use to lithospheric stocks, Gordon et al. (2006) concluded that providing today's industrialized country level of services worldwide would require the depletion of all recoverable resources of copper, zinc and platinum as well as near-complete recycling of these metals from that point forward. Skinner (1976) suggested that the depletion of geochemically scarce metal ores would lead to an increased use of iron and other more common metals in different applications, which he termed “a new iron age”. Note that these sources do not speak of depletion in terms of ‘lack of metal atoms’, but the depletion of high-grade ores, which would leave only common rock as source of virgin metals. Although extraction of rare metals from common rock is technically possible, it is very expensive in terms of exergy and money.

There are thus both short- and long-term reasons for reducing the societal use of scarce metals. One strategy for that is to make the use more efficient by *dematerialization*. Dematerialization means a reduction in material and energy use per produced unit of service or utility (Cleveland and Ruth, 1998; Herman et al., 1990; Holmberg and Karlsson, 2000; Reijnders, 1998). A related concept is *dissipation*, which refers to the loss of concentrated material resources due to emissions to the environment, dilution in other materials or landfills (Ayres, 1998, 1999; Zimmermann and Gößling-Reisemann, 2013). According to an assessment by Zimmermann and Gößling-Reisemann (2013), all of the European Union's designated critical materials have dissipation rates higher than 30% and most have dissipation rates higher than 50%. Dematerialization is about reducing dissipation in absolute terms, for instance by reuse, recycling and decreased demand for material products (de Bruyn, 2002; van der Voet et al., 2008).

1.2. Transmaterialization and carbon nanomaterials

Another strategy for reducing the societal use of scarce metals is *transmaterialization*. It can refer to change of the materials used in society in general (Labys, 2002; Labys and Waddell, 1989), but is here used in the stricter meaning of substituting materials that are scarce and hazardous (Holmberg and Karlsson, 1995, 2000). A number of previous studies have discussed and investigated the potential for substituting scarce materials. Reijnders (2016) discussed the substitution of chromium, manganese, molybdenum, niobium, nickel, vanadium and tungsten in steel by more common materials, such as aluminum, magnesium, nitrogen and silicon. Graedel et al. (2015) investigated the substitution of approximately 60 different metals by substitutes available in the near term. Several studies have investigated the availability and potential substitution of scarce materials in solar cells, such as cadmium, telluride, selenium, gallium, indium and ruthenium (e.g. Andersson et al., 1998; Espinosa et al., 2012; Tao et al., 2011). Many experimental studies investigating the technical performance of potential substitutes to scarce materials also exist.

The present analysis is about the potential substitution of scarce metals by the abundant material carbon. It is the tenth most common element in Earth's crust (Wedepohl, 1995). The annual societal carbon turnover includes almost 10 000 million metric tonnes in the form of coal, petroleum and natural gas (U.S. Energy Information Administration, 2012) and about 2000 million metric tonnes of biogenic carbon harvested in forests and on agricultural land (Berndes, 2014). These numbers exceed the production volume of iron, the most common industrial metal (1200 million metric tonnes of pig iron were produced in 2015 (Fenton, 2016)), and are vastly greater than the turnover of any scarce metal (see e.g. Table 1).

Recent years' research and development have expanded the applications of carbon far beyond those of the traditional allotropes graphite and diamond, mainly by the discoveries of carbon nanomaterials (CNMs). The most commonly mentioned ones are fullerenes, carbon nanotubes and graphene, but there are also others that are being researched, such as graphyne, graphdiyne, graphone, graphane (Peng et al., 2014) and carbon quantum dots (Shen and Liu, 2016). Some CNMs have properties similar to those of metals, such as high strength, high electric and thermal conductivity, and high chemical and structural stability also at high temperatures (Geim and Novoselov, 2007). They can also be dispersed in other materials, such as polymers, whereby the polymer obtains some of the CNMs' properties (Kim et al., 2010).

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