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# Recycling of non-product outputs containing rare elements originating in nanomaterial syntheses

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Recycling of non-product outputs containing substantial amounts of rare elements originating in nanomaterial syntheses is relatively attractive as rare elements tend to be more valuable than abundant elements. Compared with disposing these outputs, such recycling may reduce risks and modestly contribute to resource conservation. However, there are few scientific papers regarding this recycling. The published papers touch upon only 6 of the at least 51 rare elements that are present in commercially available nanomaterials. There appears to be a case for a substantially increased research effort aimed at a preferentially low-cost, recycling of non-product outputs with rare elements generated in nanomaterial syntheses, leading to the synthesis of nanomaterials of at least acceptable functionality. Such research may improve the economics of nanomaterial production.

### Environmental significance

The paper recycling of non-product outputs containing rare elements originating in nanomaterial syntheses deals with a topic that was found to be largely neglected in investigations dealing with nanomaterial synthesis and processing. The paper focuses on non-product outputs with rare elements, as they tend to be relatively valuable, and hence the recycling of these non-product outputs are likely to be financially interesting. In the case of chemical synthesis of gold nanoparticles and biosynthesis of nanomaterials containing rare elements, a few papers were found in the scientific literature that deal with the recycling of a non-product output originating in these syntheses giving only 0.01% of the number of papers dealing with the syntheses. The papers found in the scientific literature touch upon only 6 of the at least 51 rare elements that are present in commercially available nanomaterials. This is at variance with the admonition of Hansen *et al.* (*Nature Nanotechnology*, 2022, **17**, 682–685), namely that researchers of nanomaterials should consider key questions posed by the circular economy as early as possible in the commercialization process. A case is made for a substantially increased research effort aimed at a preferentially low-cost recycling of non-product outputs containing substantial amounts of rare elements originating in nanomaterial syntheses, leading to the synthesis of g recycled nanomaterials of at least acceptable functionality.

## 1. Introduction

Arvidsson *et al.*[1] have distinguished abundant and rare elements. Elements that can be characterized as abundant and used in commercially available nanomaterials include Al, C, Ca, Fe, Mg, Si, and Ti.[2,3] Commercially available nanomaterials include at least 51 rare elements: Ag, As, Au, B, Be, Bi, Cd, Ce, Co, Ce, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, Ir, La, Li, Lu, Nb, Nd, Ni, Os, Pb, Pd, Pt, Pr, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Tl, Tm, W, Y, Yb, Zn and Zr.[2,3] Rare elements are generally more valuable than abundant elements,[4] and several of them (Ag, Au and the Pt group elements) are often called precious. When substantial amounts of rare elements are present in non-product outputs of nanomaterial syntheses, functional recycling—in this case recycling non-product outputs to starting materials for the synthesis of functional nanomaterials—is relatively attractive (see also Wang *et al.*[5]). Functional recycling supports circular resource flows. In the case of nanomaterials, such recycling may contribute to resource conservation in a modest way.[2] Also, when compared with disposing these non-product outputs, recycling them may reduce risks linked to hazardous nanomaterials and elements.[2] The attractiveness of the recycling of non-product outputs containing rare elements may be increased when it can be combined with other relatively valuable substances that may be present in non-product outputs (*e.g.*, ionic liquids).[5] Non-product outputs that may contain substantial amounts of rare elements include, off-specification nanomaterials containing rare elements,[6] sacrificed nano-templates containing rare elements,[5] soot with rare elements originating in electric-arc-based synthesis,[7] and media remaining after synthesis and separation of nanomaterials containing rare elements[8]—as well as biological residues remaining after nanomaterial synthesis, in the view of adherence or binding of substances containing rare elements to biological materials.[9,10] Section 2

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deals with published scientific studies regarding the recycling of non-product outputs of chemical nanomaterial synthesis containing rare elements that originated in nanomaterial syntheses. A discussion thereof and a perspective on research needs is the subject of section 3.

## 2. Studies regarding the recycling of non-product outputs that contain rare elements originating in nanomaterial syntheses

Searching the databases of major publishers of scientific literature, such as ACS, Elsevier, Frontiers, IOP Publishing, MDPI, Sage, Springer-Nature, RSC, Taylor and Francis, Wiley, Web of Science core collection and Google Scholar generated several studies, as described below, dealing with the recycling of non-product outputs that contain, or may contain, rare elements originating in chemical and biological nanomaterial syntheses.

Stevenson *et al.*[7] and Wynne *et al.*[11] addressed the non-product output waste soot from electric-arc-based synthesis of the metallic nitride fullerene $Sc_2N@C_{80}$. The waste soot studied contained fullerenes, nanotubes and about 50% $Sc_2O_3$. Such waste soot was subjected to thermal oxidation, generating $Sc_2O_3$ feedstock for the synthesis of new metallic nitride fullerenes. In the synthesis of $Sc_2N@C_{80}$ the recycled feedstock gave, for at least three cycles, yields comparable to the original feedstock.

Two other studies were about the chemical synthesis of Au nanoparticles. Pati *et al.*[12] used alpha-cyclodextrin to recover Au (as $AuBr_4$) from (simulated) citrate-capped waste Au nanoparticles. After $AuBr_4$ was subjected to oxidation in an aqueous medium in the presence of HBr, captured Au was reduced, precipitated and subsequently oxidized to generate an Au solution in *aqua regia*. This Au solution was used to synthesize Au nanoparticles. These nanoparticles were unstable, according to the authors[12] presumably due to unidentified impurities in the recovered Au. Oestreicher *et al.*[13] converted salted-out waste Au nanomaterial, originating in Au nanoparticle synthesis, into an aqueous $HAuCl_4$ solution, using HCl, NaCl and $H_2O_2$, with a claimed efficiency of 99.5%. The $HAuCl_4$ was then converted, using a seed-mediated growth approach, into stable Au nanospheres with acceptable functionality.

Another two studies were about chemical syntheses involving Ag nanomaterials. It was shown that templates of Ag nanomaterials with specifically defined shapes can be used to synthesize Au and Pt nanomaterials.[14] In this synthesis, the silver nanomaterials were sacrificed. AgCl can be recovered from sacrificed Ag nanomaterial to be used as feedstock for the production of Ag nanowires of good functionality, with reported efficiency levels of 69.8 to 84.6%.[14] Huang *et al.*[15] studied the synthesis of Ag nanowires using ethylene glycol as a solvent and reductant. Large nanowires were retrieved by subjecting to centrifugation. What remained (solvent with small Ag nanomaterials, surfactant and $Ag^+$) was recycled five times, after the adjustment of silver ion concentration, for the generation of Ag nanowires to be used as flexible transparent heaters.

Te nanowires can be used as templates for the synthesis of 1D nanomaterials (*e.g.*, those composed of metal tellurides or noble metals[16]). In this synthesis, Te nanowires are generally sacrificed to generate tellurite. Tellurite can in turn be used for the generation of new Te nanowires serving as templates, with reported efficiency levels of 65 to 81% and good nanowire functionality.[16]

There has also been a set of studies on the chemical synthesis of zeolite-imidazolate framework (ZIF) crystals with dimensions $<100$ nm or somewhat larger than 100 nm, containing relatively low contents of Co or Zn and produced from recycled mother liquors with replenished reagents (including Zn- or Co-salts) and compensation for lost solvent.[8,17–21] The crystals synthesized from recycled mother liquors appeared to be of good quality. Use of recycled mother liquors allowed substantial increases in product yield and reductions of non-product outputs.

Regarding the biological synthesis of nanomaterials containing rare elements, no study was found that demonstrated the recycling of rare elements present in non-product outputs; however, only one paper describing the recycling of a non-product output of nanomaterial synthesis was found. This paper[22] was about the reuse of residual organisms after the synthesis of Au nanoparticles by the microalga, *Klebsormidium flaccidum*, using $HAuCl_4$, with these nanoparticles subsequently released from the cells and able to be recovered from the culture medium. The authors did not address the eventual presence of Au in residual organisms and the fate of the Au, but it would seem likely that the residual organisms contained Au.[9,10] The residual organisms were recovered by subjecting to centrifugation. A sample of these recovered organism was incubated for growth and subsequently used for a new round of Au nanoparticle synthesis from $HAuCl_4$ without a negative impact on nanomaterial functionality. Testing for the presence of Au in residual organisms, and, if the result is positive, following the fate of this Au during further processing is a matter of additional research.

## 3. Discussion

The recycling processes regarding the non-product outputs of chemical synthesis of nanomaterials as discussed in section 2 led to the synthesis of nanomaterials displaying at least acceptable functionality, except for the case described by Pati *et al.*[12] However, these recycling studies touched upon only 6 of the at least 51 rare elements that are present in commercially available nanomaterials.[2,3] Regarding gold nanoparticles, a comparison may be made between the number of papers dealing with syntheses and the number of papers about the recycling of non-product outputs of syntheses. Until 2019, about 25 000 papers were published about the synthesis of gold nanoparticles, most of them were about chemical syntheses.[23] As noted in the previous section, two papers about the recycling of non-product outputs of chemical Au nanoparticle syntheses were found,[12,13] that is, only about 0.01% of the number of papers dealing with chemical Au nanoparticle syntheses.

All in all, publications about the recycling of non-product outputs of nanomaterial syntheses containing rare elements appear to be few and far between. This is at variance with the admonition of Hansen *et al.*,[24] specifically that researchers of nanomaterials should consider key questions posed by the circular economy as early as possible in the commercialization process. There is thus a need to change the emphasis in research regarding nanomaterial syntheses. There appears to be a case for a substantially increased research effort aimed at a preferentially low-cost recycling of non-product outputs, originating in nanomaterial syntheses, containing substantial amounts of rare elements, leading to the synthesis of nanomaterials of at least acceptable functionality (see also Wang *et al.*[5]). Such functional recycling of non-product outputs of nanomaterial synthesis may improve the economics of nanomaterial production.[7,12,25] Syntheses of nanomaterials containing rare elements used by industrial producers of nanomaterials that currently dispose off non-product outputs containing substantial amounts of rare elements and syntheses with relatively low yields of nanomaterials containing rare elements that are considered for near-term industrial applications may be prioritized in this context. This recycling may be conducive to substantial near-term improvements in the handling of non-product outputs containing rare elements.

## Conflicts of interest

There are no conflicts of interest to declare.

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