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Autonomously propelled microscavengers for precious metal recovery

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We report biogenic micromotor design consisting of porous chalky elongated tubes (~60 µm length) coated with Fe-Pt for dual functionality i.e. metallic gold formation and rapid isolation. These autonomously propelled scavengers once introduced in the reaction environment, showed rapid bubble-propulsion followed by high-purity separation of the visually-distinguishable gold metal particles (yellow in colour) from the reaction mixture. The concept presented here has excellent potential towards environmentally sustainable metal recovery, micron-level metal/mineral particulate extraction, electronic waste treatment and similar redox product separation among others.

Since the onset of human civilization, gold has been greatly appreciated owing to its material properties and cultural/monetary significance. There are several key-challenges in the current mining scenario including the need to process low-grade ores due to rapid depletion of high grade ores in an environmentally sustainable manner.[12] Another major challenge faced by current mining and waste reclamation industry is effective capturing of micron/sub-micron range particle size for almost all types of precious metals and minerals.[3] For example, over 10% of gold tends to get lost in tailings owing to the absence of adequate re-capturing processes to extract smaller size particles[4]. Gold in particular has found tremendous usage as a precious metal in jewellery, standard for global currencies, electronics industry, biomedical applications thereby requiring long-term planning and management.[5] Therefore, judicious mining of gold with focus on sustainable environmental practices together with its prompt recovery and reuse is the need of the hour. Gold as a metal is generally recovered from dilute solution via a precipitation method with granulated zinc,[6] physical adsorption,[7] solvent exchange and ionic exchange resins.[8] However, most of these processes are limited in terms of low selectivity for Au, low efficiency under dilute reaction conditions, toxic reaction by-products and associated high costs including constant regeneration of the catalyst/adsorbent[9,10]. The most common method for gold processing involves the use of highly toxic inorganic cyanides to convert Au(0) into a water-soluble $Au(CN)_2^-$ coordination complex followed by the addition of H_2O_2 to precipitate gold from the reaction mixture. This process is known as leaching and subsequently involves further down-streaming processing steps to recover gold metal together with an ever persistent problem of cyanide containing toxic slurries disposal. In fact, efficient recovery of gold grains (<75 µm) requires specialized processing methods[11] (like cyanidation) that are prohibitively expensive to implement with a serious environmental threat. Utilization of cyanide for the recovery of gold has often resulted in severe environmental catastrophes due to accidental leakages and exposures.[12] In fact, many alluvial processing systems for gold mining immediately separate and discard all sub-75 µm sized material from the ore (in a process known as desliming) which a considerable financial loss for precious metals processing and re-use.[13]

Therefore, it is imperative that developing environmentally benign processes for gold recovery is the need of the hour as demonstrated by a recent trend in biogenic synthesis and recovery of metallic particles.[14, 15, 16, 17, 18] Torres et al. suggested the use of alginate based hydrogels for gold and silver nanoparticles uptake from the reaction solution.[19] Likewise, Tasdelen et al. reported DEAE-cellulose biopolymer composites for gold recovery under room temperature conditions.[20] Similarly, Ogata et al. reported tannin gel particles for the extraction of gold via simultaneous oxidation of –OH groups resulting in the reduction of trivalent gold ions into metallic gold over the gel-particle surface. [21] The state-of-the-art in gold recovery from spent sources has been investigated with pyrometallurgy,[22] hydrometallurgy[23] and bio-recovery[24] among others. [25] However, in most of the cases involving precious metal extraction/recovery, these metals are needed in their bulk state rather than in colloidal or nanoparticle state. In fact, adsorption based mechanisms for gold recovery has been extensively investigated but as is the case, it has its drawback in terms of mandatory downstream processing to recover gold in the bulk state (if any) and inability to mimic the actual gold ore extraction conditions involving hydrogen peroxide.[26] This can be understood

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by a recent study by Liu et al. reporting a novel host-guest chemistry from gold recovery (in $KAuBr_4$ solution) by utilizing corn starch (alpha-dextrin) as an inexpensive and eco-friendly process.[27] The idea utilized here is essentially based on the self-assembly mediated co-precipitation of α·Br in presence of the gold solution together with the cyclodextrins facilitating gold recovery from the reaction solution. All these interesting studies indicate the ongoing trend towards the extraction and recovery of precious metals based on the principles of green chemistry and sustainable environmental practices.

An interesting concept of micromotor technology involving autonomously-propelled microswimmers has been emerged as a means to provide motility-based process improvements along with several novel applications akin to small-scale robotics. These micromotors can be regarded as assemblies of MEMS/NEMS fabricated materials,[28] (in some cases, bottom-up or hybrids)[29] showing stimuli responsive behaviour under specific reaction conditions thereby contributing to mechanical motion or work. The motion of individual micromotors can be induced by different energy sources including light, [30 31] magnetic fields,[32 33] electric fields,[34] ultrasound waves,[35] and/or chemical fuels.[36] Several studies have been reported for various micromotor applications like effective recovery/isolation of value-added products,[37] destruction of environmental pollutants,[38] microsurgery coupled drug delivery for cancer treatment (medibots),[39] assisted-fertilization[40] and motile microsensors.[41]

Chemically powered micromotors accelerated by the bubble-recoil mechanism[42] have been well studied, both for their motion mechanisms[43 44] and associated inter-mixing effects.[45] These bubble-propelled micromotors can be understood as generally confined and/or asymmetric geometries of heterogeneous catalysts/active materials exhibiting a gas evolution reaction (like H_2 or O_2) coupled with a high-turnover number which is sufficient to "push" the microbot under the aqueous reaction environment. However, to date there is no technological report where a miniature nano/microbot can effectively catalyse and collect precious metals from its reaction mixture (akin to ore solution) via autonomous propulsion resulting in facile separation of the desired metal via a physical process like magnetic separation. The potential benefits are huge in terms of recovery of precious metals among others where the metal particles can easily be scavenged by the microbot and can be easily recovered by simply swirling a magnet in the reaction volume. This complex design parameter can be well-understood by a recent review by Li et al. where they went on to suggest that "Extending these microrockets to more challenging environments and operations introduces new limitations and challenges that have not have been faced before in any other field".[46]

In this study, we are reporting the first-ever micromotor based study for rapid extraction of precious metals like gold via 'biogenic microminers'. This was achieved by extracting chalky biotubes (length 60 µm) from the *D.Marginata* plant in significantly high yield (see Supplementary Information Figure S1). These biotubes were purified of remaining cellular debris which was confirmed by XPS analysis (see Supplementary Information Figure S2) and were subsequently coated with a Pt-Fe layer for imparting chemical functionality. In the presence of ionic gold solution, these micromotors exhibit bubble propelled motion by the virtue of catalytic decomposition of hydrogen peroxide in the reaction solution. The reduction of gold ions was catalysed by hydrogen peroxide in presence of the Pt-incorporated catalyst (microbot). It is interesting to note that while hydrogen peroxide can reduce the gold stock solution into nanoparticle/colloidal solution, the presence of the calcified ferromagnetic micromotor assembly (acting as both stabilizing agent and adsorbent)[47] facilitate 'relaxation sites' to form a bulk metal state. This was clearly evident as the resulting gold nuggets were visually distinguishable in the reaction mixture and were easily recovered manually by a magnet. Figure 1A shows the schematic representation of biogenic gold scavenging microbots for gold recovery (in bulk state). We extracted calcified porous tubes (40-60 µm long) from the Dracaena sp. plant that are largely composed of calcium carbonate and calcium oxalate (known as 'raphides').[48, 49] The extracted chalky biotubes were then purified and coated with Fe-Pt to allow dual-functionality for motion (Pt catalysed H_2O_2 decomposition reaction) and magnetic control (Fe-ferromagnetic layer). Finally, these Fe-Pt coated microbots were analysed by SEM showing characteristic metal coating over the biotube surface. The detailed fabrication process can be looked up in the supplementary information. The application of biogenic materials like raphides plays a crucial role because similar structures with comparable properties have never been produced *in vitro* regardless of the synthesis conditions.[50] Another major advantage of using biogenic materials is the fact that contrary to elaborate clean-room fabrication techniques (like photolithography, 3D-printing, electroplating etc.), a large amount of material can be obtained in relatively short time with minimal process control. Further, the calcified matrix facilitates facile product separation by dissolving the substrate under acidic conditions.

Finally, such interesting designs in nature extend our understanding towards bio-mimetic architectures which draws its inspiration from the nature and provide new avenues to utilize similar materials with enhanced properties in future.

Figure 1. Schematic representing metal-scavenging micromotor (A) fabrication and (B) gold recovery

Figure 1B shows the reaction scheme for gold scavenging microbots in action. Introduction of the gold ionic precursor solution under aq. reaction conditions consisting of H_2O_2 causes synthesis of colloidal gold particles as: $2AuCl_3 + 3H_2O_2 \rightarrow 2Au + 3O_2 + 6HCl$ However, the presence of calcified micromotors in the reaction mixture acts as the preliminary point of contact facilitating nucleation and subsequent deposition of Au particles over its surface. As the reaction proceeds, this microbot assembly owing to its autonomous motion, acts as the template for an ordered manner growth (similar to epitaxial growth) by moving around the

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reaction mixture and 'collecting' all the Au-particles resulting in a fairly large growth of pure gold cluster around its surface. These micromotors can then be easily collected by a magnet to recover pure gold cluster. In a similar study, Tasdelen et. al utilized DEAE-cellulose composites to recover metallic gold from gold chlorate solution where a key-finding was to increase the shaking rate and contact time leading to an increase in the gold recovery efficiency.[20] This motility-mediated enhancement is a key-feature of micromotor technology and the same was observed in our study. As expected, no aggregated metallic gold cluster formation was observed in the presence of biotubes alone (i.e. no Pt layer). Also, another control was carried out in the presence of Pt alone (no biotubes) where we noted formation of metallic Au particles in the reaction mixture which did not tend to cluster together as a nugget. This may be attributed due to the absence of any effective collection/adsorption site and stabilizing agents. (see SI Figure S4) The motion pattern of the biogenic microbots was also studied both in presence and absence of ionic gold solution. Figure 2 (a) shows microbot motion in absence of the gold stock solution so as to observe the effect of reaction parameters over the breaking of time-reversal invariance for effective micromotor motion.[51]

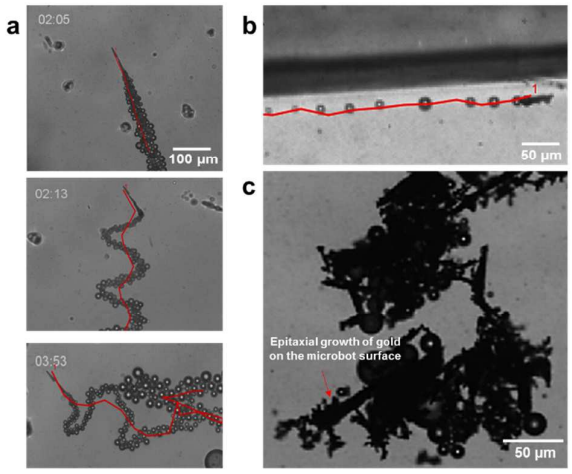

Figure 2. Analysis of micromotor motion patterns under (H_2O_2/SDS = 2.5% / 1%) : (a) linear motion, cork-screw motion and magnetically-guided motion; (b) an individual micromotor with Au-deposited on top in presence of Au reaction mixture (100 mM); (c) A cluster of Au-deposited micromotors.

Figure 2(a) shows micromotor motion in a straight line resembling much a streamlined micro-rocket where a thrust of gases coming out from one end (O_2 evolution) causes the structure to jet forward. The observed speed was about 120 µm/sec (see Supplementary Information Video S1). The speed observed in case of screw-cork motion[43] and magnetically-guided zig-zag motion as shown in was found to be ~150 µm/sec. (see Supplementary Information Video S2, S3). The observed speed for the microbot during LbL-like gold formation (which is evident over the microbot surface in figure 2b) was found to be ~110 µm/sec (see Supplementary Information Video S4). Several of these microbots in the reaction medium acted as multiple templates for the accumulation of colloidal gold particles and tend to cluster together as highlighted in figure 2c. Please note that the clusters accumulated around the biotube is metallic gold.

Gold scavenging and associated characteristics of autonomously propelled biogenic microbots are presented in figure 3. Figure 3a shows microbot surface before the initiation of the reaction (smooth) as compared to micromotor surface after completion of the reaction (rough with clear signs of crystal growth). It should be noted that the above two images represent two different micromotors as upon completion of the reaction (owing to their motion and accumulation), it is fairly difficult to find the exact individual micromotors during the course of reaction.

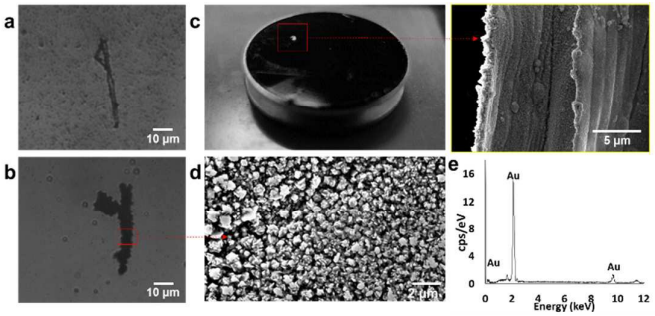

Figure 3. Micromotor mediated gold scavenging at the (a) initiation of the reaction and (b) upon completion of the reaction. Growth of Au particles over the micromotor surface is clearly visible. (c) Macroscopic gold particle obtained after the completion of reaction (inset highlightening uniform Au growth on the surface and associated (d) SEM image of Au microparticles; e) EDX spectra of the pure Au obtained after the completion of the reaction.

These biogenic micromotors then acted as a template over which reduction of gold into bulk metal took place until a visibly distinguishable metal cluster of pure gold (yellow in colour) was formed (size in mm) as shown in figure 3c. Subsequently, the macroscopic gold particle surface was analysed by SEM (figure 3d) showing multiple microscopic gold particles of size 0.5 – 1.5µm clustered together over the microbot assembly. Another interesting aspect of the study was purification of these gold nuggets by dissolving the supporting calcified biotube matrix in a mildly acidic solution of HCl (pH 2; time < 1 min) resulting in pure Au metal for further analysis. The same can be clearly observed in figure S5 and Video S5 (Supplementary Information).Finally, the resulting gold particle was washed with DI water analysed by EDX as shown in figure 3e. The absence of any other interfering peak suggests relatively pure 'gold nuggets' formed via the biogenic micromotors (see Supplementary Information figure S3 and figure S5).

In conclusion, we presented a novel proof of concept for a micromotor application in precious metal recovery. Salient features of this microbot assisted isolation technique includes an eco-friendly plant derived template with reaction parameters similar to that employed in gold mining industries. Further, this opens a new research focus in the area of mining and recycling of valuable metals and minerals (size < 100 µm) where a 'micro-scale carrier' can effectively target/adhere/attract metal particle and help in easy extraction. The same may be conceptualized by a host of active microparticle assembly comprising of proteins, peptides, chemical modifications or polymeric interfaces with an inherent mechanism to 'fish out' specific metallic particle of interest (size < 100 µm). The concept presented here can be extrapolated for chemical sensing, pollutant adsorption and other value-added product recovery reactions.

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