Scientific Report: Functionalized nanoparticles capable of binding PGM ions from aqueous solutions

Platinum group metals (PGMs) which are widely used in car catalytic converters have been in high demand, in spite of a low natural abundance in the earth crust. Due to scarcity and high value of these metals, there is an increased interest towards their recovery from wastes such as spent catalyst.

Palladium together with platinum is the more used metal for catalyst devices. Platinum, palladium and rhodium are generally fixed in the washcoat surface of the catalytic converter and allow the oxidation of carbon monoxide (CO) and hydrocarbons \( (\text{H}_x\text{C}_y) \) and the reduction of nitrogen oxides \( (\text{NO}_x) \) in order to decrease the contamination caused by car exhaust fumes [1].

Several works have been dedicated to the recovery of these metals by different methods, including solvent extraction, ion exchange, membrane separation and so on. However, most of these methods suffer from some drawbacks such as high capital and operational costs.

In this context, some new materials for precious metals recovery have been developed, mostly utilizing ion-exchange technology. Furthermore, besides the conventional ion-exchangers, chelating resins have been also developed to take advantage of the intrinsic selectivity provided by functional groups. In conformity with the hard and soft acids and bases theory (HSAB), functional groups containing S and N donor atoms interact strongly with the soft acids like the precious metals. This fact leads to the development of chelators which contain chelating groups with S or N atoms for the selective extraction and separation of the PGMs.

Nowadays, efforts are made to develop low-cost materials for the recovery of metals [2-3] and the use of colloidal nanoparticles is a promising approach for this purpose. Nanomaterials have shown to possess distinctive mechanical, magnetic, optical, electronic, catalytic and chemical properties that contribute to promising applications in electronics, energy, biomedicine, environmental remediation and recently recovery of metals [4-5]. Their small size gives them a high surface area-to-volume ratio and facilitates the interaction with several kinds of chemical species.

In order to achieve this objective of iron oxide nanoparticles were synthesized. \( \gamma \)-Fe2O3 nanocrystals were prepared according to the method described by Hyeon and coworkers [6]. Briefly, 10 ml of octyl ether and 1.28 g of oleic acid where degassed in a 50 ml flask at 60 °C for 20 minutes. 0.29 ml of Fe(CO)\(_5\) were then added at 100°C and the solution was heated up to refluxing temperature (~295-300 oC) for 1 hour. The flask was then cooled down to room temperature, 0.34 g of \( \text{CH}_3\text{NO} \) were added and the mixture was heated at 130 °C for two hours, during which time it turned to dark brown. The flask was heated again to refluxing temperature for 1 hour, after which the solution was cooled to room temperature. Methanol was added to precipitate the nanocrystals, which were recovered upon centrifugation and redissolution in chloroform.

As colloidal stability is a key requirement to keep the maximal binding capacity. The use of amphiphilic polymers to disperse originally hydrophobic nanoparticles in aqueous solution is a suitable approach in
this direction [7]. The particles were characterized by transmission electron microscopy (TEM) and the average diameter of the inorganic nanocrystal cores was determined. The overall surface area of each nanocrystal was calculated by considering the effective nanocrystal diameter (deff (nm) = d + 2) as the sum of the diameter of its inorganic core plus the surfactant shell, which was assumed to be 1 nm in thickness. The concentration of the starting nanocrystal solution was determined by absorption measurements.

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The amphiphilic polymers that have been used so far for coating hydrophobic inorganic nanoparticles consist of hydrophobic side chains for the linkage to the nanoparticle surface and a hydrophilic backbone that provides water solubility through charged groups (in general –COO’) and also acts as an anchor for the attachment of selective chelators. Specifically the polymer is based on a poly(maleic anhydride) backbone. Reaction of a fraction of the anhydride rings with alkylamines leads to the formation of the hydrophobic side chains that are needed for intercalation with the hydrophobic surfactant layer on the nanoparticle surface.

As it is known, a fraction of the anhydride rings could be used to link functional organic molecules to the backbone. Organic molecules bearing amino-groups can be directly linked to the anhydride rings by reaction of the anhydride with the amino group In this way alkylamines and organic molecules with amino terminations can be linked to the polymer backbone in a one-pot reaction[8] (see figure 2).

In order to recover precious metals, we decide to integrate in the polymer ligands such as, Ethylenediamine, Ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate (EAC), PEG (known to chelate cations), γ-aminobutyric acid, 11-mercaptoundecanoic acid (MUA), L-Cysteine and Gd-chelator (DOTA) (as a control because it is used in previous work [9]).

<table>
<thead>
<tr>
<th>EAC</th>
<th>Ethylenediamine</th>
<th>PEG</th>
<th>DOTA</th>
<th>γ-aminobutyric acid</th>
<th>MUA</th>
<th>L-Cysteine</th>
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Figure 3. The different ligands used to recover precious metals
In order to improve magnetic separation the use of polyelectrolyte capsules as matrix to link several small particles together is considered. By linking several magnetic particles to one matrix particle the effective magnetic moment is increased, which facilitates magnetic separation. Multilayer-layer capsules contain magnetic NPs in the wall have already been synthesized [10]. By applying an external magnetic field their separation from the aqueous phase is fast and easy and has also already been demonstrated [11]. In parallel, the capsules could also be use as matrix for the selective chelators, by putting them into the capsules walls or cavities. Such enhanced chelator density would increase the capacity to recover ions from wastes.

Therefore, the synthesis of different capsules have been done.

![Synthesized capsules](image)

**Figure 4.** Synthesized capsules

The fast magnetic separation of the capsules with iron oxide nanoparticles embedded in the wall has been also probed.

![Image](image)

**Figure 5** (a) Polyelectrolyte capsule (b) magnetic NPs in the wall of the capsule. Picture reprinted from reference [10]. (c) magnetic separation

The same ligands that have been integrated in the polymer have been conjugated to dextrane in order to introduce the ligands in the cavities of the capsules.

Furthermore, first test of ion-binding to functionalized colloidal nanoparticles and ion-binding to ligand-modified dextrane have been developed. The results show that only few ions bind and not in a selective way.
Therefore, after doing a selection of specific chelators, thanks to some collaborations (Dr. Markus Klapper, Max Planck Institut für Polymerchemie, Mainz and Prof. Dr. Eric Meggers, Philipps Universität Marburg) new ligands have been prepared. These ligands are specific for precious metals and have a thiacycrown ether carboxylic acids structure.

Further work would probe the selectivity of these ligands and the capacity of them to catch precious metals from water solutions.