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# Soft-nanocoupling between silica and gold nanoparticles based on block copolymer

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ABSTRACT

A novel triblock copolymer of ABC type was synthesized by RAFT polymerization with good control and successfully acts as a specific "adhesive" to "glue" the $SiO_2$ nanoparticles (NPs) and Au NPs together to make a hybrid. This method, with the coined name, soft-nanocoupling, is based on specific anchoring of organic groups onto the surface of inorganic nanoparticles with all-covalent interactions. $SiO_2$ and Au NPs were used as a proof of concept in this contribution. For the triblock copolymer, namely POE-PGMA-PMPS {poly[oligo(ethylene oxide) methyl ether metharylate]-b-polyglycidyl methacrylate-b-poly[3-(methacryloxypropyl) trimethoxysilane]}, the POE block with oligo-PEG side chains was used to improve the dispersability in solvent media; the PGMA block that was further reacted with lipoic acid was used to anchor onto the Au NPs; and the silane-containing PMPS block can "grab" the $SiO_2$ NPs. It was found that the resulting $SiO_2$-Au hybrid has a corona shell of $SiO_2$ NPs with Au NPs tightly embedded inside, and can even tolerate a harsh sonication process of 1 h. Since the soft triblock copolymer functions as a bridge to couple Au and $SiO_2$ NPs together, the process is called soft-nanocoupling. Compared to the conventional hard-coupling process, which requires specific case by case procedures, soft-nanocoupling is more straightforward, and especially can be designed in a modular way depending on the specific NPs used. With the well-established synthetic methodologies of NPs of single components to date, such as $SiO_2$, Au, $Fe_xO_y$ etc., all that is needed to make hybrid NPs is the proper design of a specific "glue" with anchoring moieties targeting the selected NPs. Thus, the soft-nanocoupling methodology affords a new platform for fabricating hybrid nano-objects from NPs using block copolymers.

## 1. Introduction

One of the most pursued techniques in nanotechnology nowadays is to synthesize a large variety of nanometer sized objects, including metals [1–2], rare earth compounds [3], semiconductors [4], elementary oxides [5–7] and so on. They can be magnetic, fluorescent, or plasmonic, or function as inert fillers, etc. in versatile applications. A more challenging topic is to fabricate hybrid nano-objects composed of more than one component to gain combined functions [8–9] or functions of the same type but from different components [10], which greatly stimulated the interests of synthetic chemists recently. Various approaches were applied, such as deposition-precipitation, galvanic replacement, coprecipitation and templated growth [10–11]. Seed-mediated growth [12] is a typical example for preparing multi-component nanoparticles, such as for applications regarding magnetism [13]. Since the methods for obtaining these hybrid nanoparticles usually require harsh conditions such as refluxing at high temperatures [13–15], or onerous and delicate procedures such as sequential nucleation on preformed nanoparticles [16–18] or through coating of encapsulations [19–21], even followed by partial etching [11], the synthetic method may be called hard-nanocoupling, where the word "coupling", invented by Plato, means that different elements coexist in a whole [22], and "hard" implies harsh conditions or complex procedures and the hard nature of inorganic particles.

From the beginning of the synthetic study of the inorganic NPs, organic molecules have played a very important role. For example, oleic acid and oleylamine help to stabilize magnetic NPs and their precursors during syntheses involving temperatures up to 300 °C [14]. Similarly, trioctylphosphine and its oxide (TOP and TOPO) have been widely used in the synthesis of quantum dots (QDs) [23]. Water-soluble thiol ligands were later developed to make the synthesis possible in water, and thus much greener [24]. Besides, polymers with suitable pendant groups were used as very powerful multidentate ligands to stabilize NPs in ligand exchange process [25]. This further facilitated the tuning of energy transfer in organic-inorganic semiconductor hybrid NPs when π-conjugated ligands were used [26]. More complicated and

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very interesting asymmetric particles can be synthesized by taking advantage of the phase separation of organic molecules binding to the surface of NPs [27]. The fundamentals behind these examples are the anchoring of organic molecules onto the surface of NPs through physical or chemical interactions, such as by electrostatic, dipole interactions, van der Waals force or covalent bonding [27–28].

In this contribution, and inspired by the efforts just reviewed, we developed a novel way to make hybrid inorganic NPs with two components, that is, to make a polymeric “adhesive” to “glue” two different NPs together, using $SiO_2$ and Au NPs as a proof of concept. As a demanding requirement, the resulting hybrid must tolerate robust sonication to confirm the strong adhesion of the synthetic glue. The idea is illustrated in Scheme 1. Since the adhesive is made from polymer, which is “soft”, the method is herein called “soft” nanocoupling. Compared to “hard” nanocoupling processes, “soft” nanocoupling is applied in mild conditions, and, most important, the design of hybrid nano-objects is simplified using polymeric “glue”, since selective anchoring of organic groups onto the NP surfaces is almost the only thing that needs to be considered to make the “glue” effective (Scheme 1A).

It should be noted that this approach is different from the “decoration” method, which involves a much bigger central object that is “decorated” by much smaller ones around it, such as shown in Scheme 1B. The decoration can be via in-situ formation of much smaller NPs on the surface of the bigger ones of different type, such as the syntheses of Ag or Au NPs in the hydrophilic corona of Janus NPs by Kirillova et al. [29], or can be via a bottom-up method of grafting polymers from the surface of the central NPs followed by binding a much smaller second type of NPs by Yuan et al. [30]. In the current contribution, a special decoration strategy using a single synthetic polymer to “glue” the previously prepared silica (big) and Au (small) NPs is reported; the selection of different sizes of NPs of different types was to facilitate the identification of specific species of NPs and does not take away from the explicit elaboration of the idea of “soft” nanocoupling.

It is noteworthy that electrostatic interaction has been developed to date to absorb negatively charged Au NPs onto the positively charged surface of ammonium-functionalized $Fe_xO_y$ [31], such as by using polyaniline [32], aminosilane [33], poly(allylamine hydrochloride) [34], and lysine [35–36], either by post-attachment or in-situ synthesis. In a different strategy, covalent interaction through the thiol-Au bond was used recently by Zhao and coll. to make a corona of Au NPs on $Fe_3O_4$ NPs via surface-grating RAFT polymerization followed by cleavage of RAFT moieties to afford thiol groups [37]. In another example, electrostatic interactions were used to connect CdSe quantum dots (QDs) and $Fe_3O_4$ NPs to form magnetic luminescent hybrid particles through thioglycolic acid on CdSe and amine groups on an extra modified layer of $SiO_2$ on $Fe_3O_4$ NPs [38]. With the ideas described so far, three important aspects may be highlighted: firstly, the covalent bond is known to be more stable, and has no ion-exchange concerns such as when used in vivo with many electrolytes; secondly, grafting-from the surface is a “bottom-up” strategy, so NPs have to be handled during the polymerization process with great care; and thirdly, electrostatic interaction has no selectivity toward NPs, and any charged species will attract their counter-charged species. This contribution aims at covalently “gluing” two NPs ($SiO_2$ and Au) together. $SiO_2$ and Au NPs are chosen because firstly, their syntheses have been very well documented; and secondly, the surface chemistry of silane-$SiO_2$ and thiol-Au is well known and conveniently applied [39–42]. Very recently, Liu and coll. found a robust way to obtain stably anchored ultra-small Au NPs with single triblock copolymer chains [43], lending support to the “glue” idea in the present contribution.

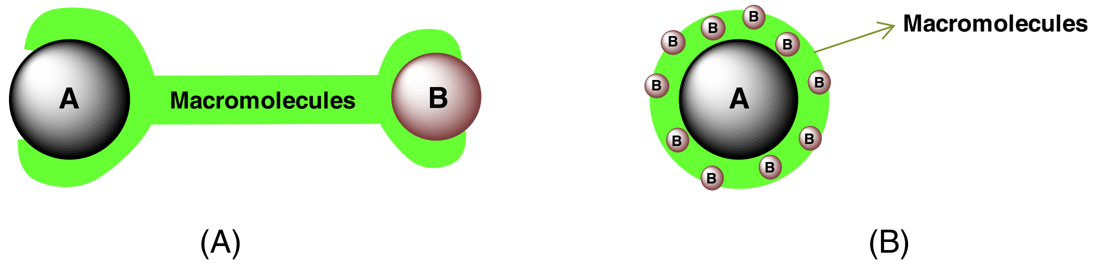
The synthetic route of the novel triblock copolymer is shown in Scheme 2. The triblock copolymer, POE-b-PGMA-b-PMPS, containing oligo(ethylene oxide) methyl ether metharylate (OE), glycidyl metharylate (GM) and 3-(methacryloxypropyl) trimethoxysilane (MPS) was synthesized by sequential RAFT polymerization. The POE block was used to improve dispersability in the solvent media. Silane groups were used for anchoring onto $SiO_2$ NPs. Similar silane containing monomers have been polymerized successfully through ATRP [44–45], and so is referred to in the synthetic route of this contribution by RAFT polymerization. The glycidyl groups on the GM moieties were further reacted with lipoic acid to afford anchoring onto Au NPs, proven to be very effective in reference 43. The advantages of the design of the triblock copolymer in this contribution are, firstly, that robust covalent connections between the NPs are used; secondly, that the building blocks in the triblock copolymer function separately to achieve both anchoring on NPs and dispersing in media, and thus is a modular design methodology; thirdly, that the anchoring strength on NPs can be conveniently tuned by the degree of polymerization (DP) during RAFT polymerizations.

## 2. Experimental section

### 2.1. Materials and characterization

Oligo(ethylene oxide) methyl ether methacrylate (OE, average $M_n = 300$) was purchased from Aldrich and glycidyl methacrylate (GMA, 96%) was purchased from J & K Technology. α-Lipoic acid (LA, 99%), sodium borohydride ($NaBH_4$), ammonia solution ($NH_3 \cdot H_2O$), tetrabutylammonium bromide (TBAB), hydrogen tetrachloroaurate(III) hydrate($HAuCl_4 \cdot 4H_2O$), aluminium oxide ($Al_2O_3$ basic, 200 mesh) and azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent. Tetraethyl orthosilicate (TEOS), sodium citrate dihydrate, and anisole were purchased from Aladdin Reagent. 3-(Methacryloxypropyl) trimethoxysilane (MPS, 98%) was purchased from Beijing HWRK Chemical. 4-Cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to a literature procedure [46]. All monomers were passed through a basic alumina column before polymerization to remove inhibitor. AIBN was recrystallized from methanol and stored in a refrigerator before use, petroleum ether and tetrahydrofuran (THF) were distilled from sodium under a nitrogen atmosphere. Unless otherwise specified, materials were obtained from commercial sources as the best grade and used without further purification.

$^1H$ NMR spectra were obtained using a 400 MHz Bruker Advance III spectrometer. The $CHCl_3$ singlet at 7.27 ppm was selected as the reference standard. Spectral features were tabulated in the following order: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet,



**Scheme 1.** Illustration of the general idea of “soft” nanocoupling (A), and the example of decoration of small NPs onto the surface of bigger ones through “soft” nanocoupling process (B).