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Thermostable gold nanoparticle-doped silicone elastomer for optical materials

Lei Yan[a], Jihong Li[a], Na Liu[a], Xiongwen Hao[a], Chunfang Li[a], Wanguo Hou[b], D.X. Li[a,*]

[a] *State Key Laboratory Base of Eco-chemical Engineering, Lab of Colloids and Functional Nanostructures, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*

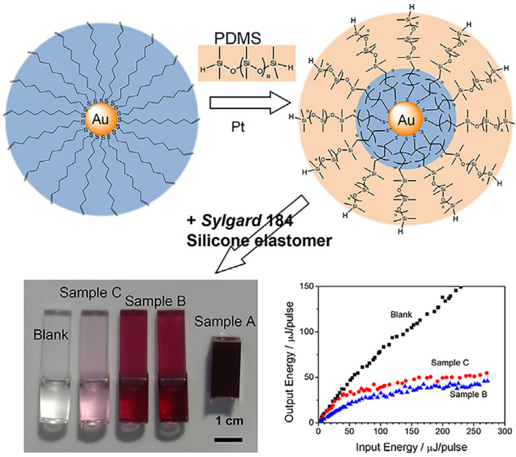
[b] *Key Laboratory of Colloid and Interface Chemistry, Ministry of Education (Shandong University), Jinan 250100, China*

HIGHLIGHTS

- Poly(dimethyl siloxane) (PDMS)-capped gold nanoparticles were synthesized via hydrosilylation.
- AuNP@PDMS nanocomposite were well dispersed in *Sylgard* 184 silicone elastomer base prepolymer.
- Uniform AuNP-doped silicone elastomer showed red color with lowered molar absorption coefficient.
- AuNP-doped elastomer material showed good thermostability and optical limiting performance.

GRAPHICAL ABSTRACT

Poly(dimethyl siloxane)-capped gold nanoparticles were synthesized via hydrosilylation and were demonstrated to have a well dispersed state after blending with polysiloxane elastomer prepolymer. The subsequently obtained uniform gold nanoparticle-doped silicone elastomer material showed high thermostability and obvious optical limiting performance.



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ABSTRACT

When gold nanoparticles (AuNPs) are blended with matrix polymers for material engineering of a nanoparticle doped polymer matrix, one frequently observes nanoparticles' aggregation due to their large interface energy. In this work, poly(dimethyl siloxane)-capped AuNPs (AuNP@PDMS) were successfully synthesized via hydrosilylation from alkenyl-terminated AuNPs and hydride-terminated PDMS polymer. The AuNP@PDMS particles have a well dispersed state after blending with polysiloxane elastomer prepolymer because the same component of the shell polymer to matrix polymer should decrease maximumly the interface influence between the nanoparticles and the polymer matrix. Therefore, uniform AuNP-doped silicone elastomer material with brilliant red color was obtained after vulcanization. The average molar absorption coefficient of doped AuNPs in silicone elastomer was deduced to be $3.06 \times 10^{7}\ \mathrm{cm^{-1}\ mol^{-1}}$. Such AuNP-doped silicone elastomer showed good thermostability and

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* Corresponding author at: College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Zhengzhou Road No. 53, Qingdao 266042, China.
E-mail address: lidx@iccas.ac.cn (D.X. Li).

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obvious optical limiting performance. The intrinsic homogeneity of shell polymer on nanoparticles and matrix polymer is a remarkable advantage to diminish the interface influence in blending of nanoparticles with polymer matrix, thus could provide uniform nanoparticle-doped polymeric materials.

1. Introduction

Recently, the nanocomposites consisting of AuNPs and polymers have attracted much attention because of their fascinating potential applications in stabilized nanoassembly [1], smart nanodevices [2], and biological nanomaterials [3]. This topic involves two branches concerning the discriminating role of the polymer components. The first branch mainly focuses on polymer-stabilized AuNPs with well-defined core-shell structures [4–6], in which the surface-initiated polymerzation methods are usually empolyed as a construction strategy [7,8]. The anchored polymer layer intensively enhances the nanoparticle stability due to the steric hindrance and simultaneously render the core various functional properties [9–11]. In the second case, AuNPs are incorporated into the polymer matrix to produce nanoparticle-doped polymer matrix for material engineering. The obtained AuNP-doped monoliths or films showed great potential for optical [12] and biosensing materials [13]. For example, natural rubber latex-supported AuNPs were in-situ synthesized for flexible surface enhanced Raman scattering (SERS) substrates for sensitive Raman-scattering detection [14,15]. The nanogold hybrided polysiloxane films had an ability to switch colors in the swelling process [16], and similar flexible films showed dichroism [17] and unusual optical properties [18]. The AuNP-doped polysiloxane films or microfluidic chips were used to construct biosensors [19,20].

Up to now, the developed approaches to achieve nanoparticle-polymer matrix materials can be sorted into two different strategies. The first one consists of an *in-situ* reduction of gold precursors dissolved in the polymer matrix into metal nanoparticles [21,22]. The gold precursor was usually reduced by the matrix polymers [20,23] or was converted under UV irradiation [24,25]. Such simple and fast method provides well-dispersed AuNPs in the matrix, but the nanoparticles always exhibited a broad size distribution as a disadvantage. The second strategy describes a post combination of pre-made AuNPs with pre-synthesized polymers [13,18,26]. This strategy provides full synthesis control over both nanoparticles and matrix polymers, thus could generate a wide variety of hybrid materials. Indeed, it is a critical difficulty to directly disperse metal nanoparticles into polymer matrix due to the nanoparticles' thermodynamic aggregation dominated by interface influence, even organic alkanethiol-monolayer coated AuNPs have been found to form aggregates of hundreds nanometers in the polymer matrix [13]. Therefore, it is necessary to modify AuNPs with proper mediators before mixing with polymers to diminish the interface effect. There are three mainly employed approaches for this purpose: (a) Organic alkylthiol and alkylamine can be used to decorate a stabilizing monolayer on AuNPs before blending with the polymer matrix [16,17,27,28]. (b) Utilization of silica shells around AuNPs could enhance the particle stability and provide compatibility to the polymer matrix [18,29–31]. (c) Particularly, polymer modified AuNPs can endow nanoparticles with more compatibility to polymer matrix [32]. These approaches for modifying AuNPs by mediators before blending with the matrix polymer could decrease partially the interface effect only in a limited degree.

If the polymer ligands capped on metal nanoparticles are chemically the same as the matrix polymer, it would be thermodynamically favorable to overcome the interfacial effect in a maximum limit [13]. To our knowledge, organosilicone elastomer mainly consisting of poly(dimethyl siloxane) (PDMS) was often employed in biological systems and abundantly used as sealing materials. However, we could find few color organosilicone rubber products because common organic dyes always could not fit the long-life organosilicone matrix. Thus, it is interesting that the AuNPs can be considered as a stable red dye to match the long-life of organosilicone materials. For polysiloxane polymer matrix, PDMS-capped AuNPs should be the best candidate for AuNP-doped polysiloxane elastomers, and how to chemically link PDMS molecules onto the surface of AuNPs is an important problem. In this work, hydrosilylation was successfully performed to covalently bind PDMS molecules onto the surface of AuNPs to overcome this problem, as schematically illustrated in Scheme 1. Undecenethiol was first grafted onto the gold surface to provide alkenyl-terminated AuNPs, subsequently a hydrosilylation reaction was used to link hydride-terminated PDMS and alkenyl bond in presence of a platinum catalyst. When these nanocomposites were doped into polysiloxane elastomer, the same polymer component should decrease maximally the interface influence between the nanoparticles and the polymer matrix. Additionally, the PDMS shell with reactive Si-H periphery could crosslink with the polymer matrix in the curing stage. The obtained flexible AuNP doped polysiloxane elastomer was characterized and further investigated with respect to thermostability and optical properties.

2. Materials and methods

2.1. Materials

Hydride-terminated PDMS (Mn 17500), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex (denoted as Pt(dvs)), potassium thioacetate and bromoundecene were purchased from Sigma-Aldrich, Shanghai, China. Undecenethiol was synthesized from bromoundecene and potassium thioacetate according to a thiourea procedure [33]. Sylgard 184 bi-component silicone elastomer, including base prepolymer and curing agent, was purchased from Dow Corning Inc., USA. All other chemicals were obtained commercially and used without purification.

2.2. Preparation of alkene-functionalized AuNPs

AuNPs were synthesized by reducing chloroauric acid with sodium citrate [34]. The alkene-modified gold nanoparticles were then obtained via a ligand exchange route by Au-S bond interaction. 300 mL freshly prepared colloidal gold was carefully added into 300 mL THF solution of 0.150 mL undecenethiol. The mixture changed into blue-purple after 12 h stirring and was rotary-evaporated to remove THF and water. The residue was dispersed with THF and washed by THF in centrifugation to discard free thiol. Then, 13.1 mg alkenyl-capped AuNPs were finally obtained.

2.3. Preparation of core-shell AuNP@PDMS nanocomposite

Hydrosilylation was used to covalently link the terminal Si-H bonds of PDMS molecules with the alkenyl groups anchored on