



## Layer-by-layer modification of high surface curvature nanoparticles with weak polyelectrolytes using a multiphase solvent precipitation process



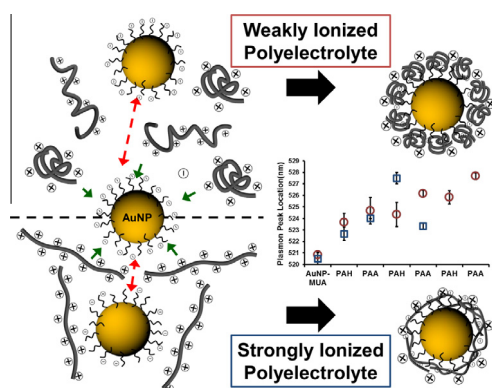
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### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 12 November 2015

Revised 19 December 2015

Available online 22 December 2015

#### Keywords:

Layer-by-layer

Gold nanoparticle

Solvent precipitation

Quantum dot

Poly(4-styrenesulfonic acid-co-maleic acid)

### ABSTRACT

The layer-by-layer modification of  $\approx 5$  nm mercaptocarboxylic acid stabilized gold nanoparticles was studied in an effort to illustrate effective means to overcome practical issues in handling and performing surface modification of such extremely small materials. To accomplish this, each layer deposition cycle was separated into a multi-step process wherein solution pH was controlled in two distinct phases of polyelectrolyte adsorption and centrifugation. Additionally, a solvent precipitation step was introduced to make processing more amenable by concentrating the sample and exchanging solution pH before ultracentrifugation. The pH-dependent assembly on gold nanoparticles was assessed after each layer deposition cycle by monitoring the plasmon peak absorbance location, surface charge, and the percentage of nanoparticles recovered. The selection of solution pH during the adsorption phase was found to be a critical parameter to enhance particle recovery and maximize surface charge when coating with weak

**Abbreviations:** PAH, poly(allylamine hydrochloride); PDADMAC, poly(diallyldimethylammonium chloride); PSS, poly(sodium-4-styrenesulfonate); PAA, poly(acrylic acid); QD, quantum dot; LbL, layer-by-layer; MPA, mercaptopropionic acid; MUA, 11-mercaptoundecanoic acid; AuNP, gold nanoparticle; PSS-co-MA, poly(4-styrenesulfonic acid-co-maleic acid); SS, styrene sulfonate; MA, maleic acid; DI, deionized; NP, nanoparticle.

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<http://dx.doi.org/10.1016/j.jcis.2015.12.040>

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Electrosteric stabilization  
Poly(allylamine hydrochloride)  
Poly(acrylic acid)

polyelectrolytes. One bilayer was deposited with a high yield and the modified particles exhibited enhanced colloidal stability across a broad pH range and increased ionic strength. These findings support the adoption of this multi-step processing approach as an effective and generalizable approach to improve stability of high surface curvature particles.

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## 1. Introduction

Nanomaterials exhibit unique size, shape, and surface dependent properties that can be tailored for the development of nanotherapeutic and diagnostic devices [1–5]. A subset of such nanomaterials are inorganic in nature; these nanoparticle (NP) colloids are typically synthesized in organic solvents as a variety of core and core/shell nanomaterials that require further surface modification for stabilization, functionalization, and transfer to aqueous conditions [6]. Facilitating nanomaterial interaction with biological media requires passivation of the inorganic core with an organic shell to prevent degradation and aggregation that would otherwise compromise the nanomaterial physiochemical properties, leading to undesirable nanotoxicological effects [7]. Numerous surface modification techniques currently exist with varying tradeoffs between method complexity, resulting colloidal stability, chemical reactivity, and coating thickness [8]. Modification with charged polymers is of particular interest due to the combination of a steric barrier and electrostatic repulsion that provides a superior electrosteric stabilization [9]. Layer-by-layer (LbL) is recognized as a low-cost and versatile nanofabrication technique to modify a broad range of templates with a diverse array of materials to produce tunable, responsive, and multifunctional devices [10–13].

The application of LbL has been thoroughly investigated on planar substrates for the hierarchical assembly of multifunctional films for an assortment of applications [14–16] and was easily adapted for microparticle templates by exchanging the rinsing steps with multiple centrifugation/dispersion cycles [17]. However, translating this process to NP templates is significantly more challenging due to the added restrictions to prevent aggregation and becomes especially difficult for NPs smaller than 30 nm [18–30]. For very small NPs, the high surface curvature resists wrapping by rigid polyelectrolytes (PEs), with both theoretical and empirical work demonstrating that polyelectrolyte chain length should be approximately equal to NP circumference to promote stable wrapping [18,19,31,32]. Schneider and Decher contributed significantly to this area by finding the optimal conditions to prevent flocculation by mainly controlling stoichiometry between a dilute gold NP (AuNP) concentration and a large polyelectrolyte excess; demonstrating a correlation between the aggregation state of AuNPs viewed by TEM and the plasmon peak location of the UV–Vis absorbance [20,21]. We adapted this technique for coating dihydroliipoic acid modified quantum dots, but found that controlling stoichiometry alone was not sufficient to prevent aggregation and successful coating required careful control of solution pH throughout the process [33]. Solution pH is recognized as a critical parameter for controlling deposition thickness and morphology of the weak PEs poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) on planar [34–40], microparticle [41–45], and NP [46–48] templates. However, there has been no systematic investigation of the effect of solution pH on the interaction of weak PEs and high surface curvature NPs less than 10 nm [30].

Mayya and coworkers studied the coating of 7 nm AuNPs with strong PEs, poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium-4-styrenesulfonate) (PSS), maintaining solution

at pH 9 throughout the LbL process to ensure that the initial AuNP surface ligand remained fully ionized [23]. The effect of solution pH was not investigated and only strong PEs were used. Dorris and coworkers studied how pH affected the interaction of 5 nm cationic AuNPs with PDADMAC or PAH and PSS in terms of retention of the initial stabilizing ligand, but the study was limited to a single bilayer due to limited NP recovery [19]. Both of these publications considered the importance of choosing the correct solution pH in relation to the NP charge density, but the influence of polyelectrolyte charge density was not investigated. Furthermore, they did not address the resulting colloidal stability of the modified NPs.

Strong PEs maintain a high charge density over a broad pH range that enhances electrostatic stability and limits film reorganization. However, coating of high surface curvature NPs with strong PEs requires an increase in ionic strength to reduce chain rigidity [31,32], which simultaneously reduces NP surface potential, leading to flocculation if the concentration is not kept fairly low. In contrast, the advantage of PEs containing weak acid/base moieties arises from the ability to manipulate their linear charge density and conformation through solution pH. NPs coated with weak PEs exhibit pH dependent properties that can be exploited as stimuli responsive triggers but this also renders them susceptible to aggregation under pH extremes. Poly(4-styrenesulfonic acid-co-maleic acid) (PSS-co-MA) is an inexpensive, low molecular weight, commercially available, and high charge density weak-strong random copolymer of styrene sulfonate (SS) and maleic acid (MA). The deposition of this weak-strong copolymer can be tuned by controlling the MA ionization but shows more resistance to post exposure film reorganization because of the highly charged SS groups [49–53]. Using this copolymer for NP templates is expected to impart better colloidal stability for these same reasons, but to our knowledge this has not been reported on high surface curvature NPs. In this work, we explore the process for coating high surface curvature AuNPs with weak and weak-strong PEs with an emphasis on the effect of solution pH; assessing the polyelectrolyte modified AuNPs for aggregation, surface charge and colloidal stability.

## 2. Materials and methods

Poly(allylamine hydrochloride) (PAH) ( $M_w = 15,000 \text{ g mol}^{-1}$ ), poly(acrylic acid) (PAA) ( $M_w = 15,000 \text{ g mol}^{-1}$ ), poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSS-co-MA) ( $M_w = 20,000 \text{ g mol}^{-1}$ ), 11-mercaptoundecanoic acid (MUA) (98% or 95%), 3-mercaptopropionic acid (MPA) (99%), gold (III) chloride trihydrate (99.9%), tetraoctylammonium bromide (98%) and sodium borohydride (99%) were all obtained from Sigma Aldrich.

### 2.1. AuNP synthesis

The Brust–Schiffrin method was utilized to synthesize monodisperse gold nanoparticles (AuNPs) [23,54–55]. 3 mL of aqueous gold (III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 25.4 mM) was transferred into 8 mL of toluene by adding 25 mM of tetraoctylammonium bromide followed by cleaning three times of deionized (DI)  $\text{H}_2\text{O}$ . The cleaned gold salt in toluene phase was

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