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The effect of protonation and oxidation state of polyaniline on the stability of gold nanoparticles

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ABSTRACT

It has been shown that Au NPs are stabilized by PANI through (1) a charge transfer from the imine nitrogens on PANI to the AuNPs and (2) by H-bonding between PANI and unreduced AuCl_4^- ions adsorbed on Au NPs. The addition of electrolytes such as NaCl or NaOH which do not cause structural changes to PANI that could affect either the charge transfer or the H-bonding did not cause any particle aggregation. Aggregation of Au NPs stabilized by PANI was only observed when solutions of NaBH_4 , HCl, and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were added to dispersions of AuPANI. Sodium borohydride reduces PANI by transforming the imine groups on PANI to amine groups. In addition, NaBH_4 reduces further the “unreduced” AuCl_4^- ions that are adsorbed on AuNPs. This results in a reduction in the attractive forces between Au NPs and PANI. The addition of a solution of HCl to a suspension of PANI causes the formation of polysemiquinone cation radicals through the protonation of PANI. This leads to the reduction in the ability of PANI to form H-bonds. Similarly, the addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to the AuPANI suspension oxidizes PANI by transforming amine groups to imine groups. However the polymer degrades through the hydrolysis of the imine group under high electrochemical potentials ($E > 0.7$ V). All these conditions lead to the aggregation of Au NPs. Chain-like aggregates (nanowires) form when agglomeration is induced by the reduction of PANI while close-packed aggregates form when PANI is oxidized or protonated.

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1. Introduction

Among the conjugated polymers, polyaniline (PANI) has been extensively studied because of its tunable electrical properties (the polymer can be easily converted to different oxidation states) [1], and its ability to stabilize dispersed metal nanoparticles [2]. A very useful method for the synthesis of gold-polyaniline (AuPANI) systems involves the use of a redox coupling [3] as applied to the formation of nanoparticles of gold, silver, palladium or copper in PANI or the related complexation approaches [4]. The size of the Au nanoparticles can be controlled very finely in the 2–10 nm range by adjusting the synthesis conditions [4] and the resulting preparations have been shown to exhibit useful catalytic properties [5]. However, the nanometal-polymer composites synthesized by the redox or complexation methods are necessarily heavily loaded with metal (at least in the initial as-prepared state) and consequently the question of metal particle stability arises. The present paper emphasizes the physical chemistry of the system and discusses factors affecting the stability of the Au nanoparticles, a theme not well studied to date.

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The interaction of PANI (emeraldine base) with metal ions is well documented. These interactions fall into two categories; *pseudo-protonation* and oxidative doping. The former, similar to protonation of PANI by acids such as hydrochloric acid, involves the interaction of a metal cation with imine nitrogens of PANI without a change in the number of electrons associated with PANI [6,7]. The latter is believed to occur in a twostep redox process in which the amine nitrogen is first oxidized to imine by a metal cation with subsequent coordination of the reduced metal cation to an imine nitrogen. The final step of this process is a reversal of the first [8]. While there seems to be a consensus on the interaction of PANI with metal cations, the literature is scant of reports on the interaction of PANI and metal nanoparticles. Although Pillalamarri and coworkers [9] reported that metal nanoparticles were fairly strongly attached to polymer fibers in their PANI-silver (and gold) nanocomposites, they were however unable to probe the polymer-metal interaction in depth as the polyaniline signal dominated both the uv-vis and FT-IR spectra. A recent report by Tseng and co-workers also suggested a strong bond between gold nanoparticles and PANI with charge transfer between PANI and the metal [10]. A shift in the binding energy of Au_{4f} from 87.7 eV to 87.5 eV for Au-PANI compared with pure Au film, as well as a shift in the Raman bands of C=N and C=N₊ to high wavenumbers in Au-PANI was said to suggest charge transfer from the positively charged nitrogen on PANI to the slightly negatively charged Au nanoparticles [11].

The interaction of metal particles with polymer is proposed to affect the activity of the metal particle. For instance, Ishida and co-workers showed that even though Au particles on poly(melamine formaldehyde) (MF) were smaller to those on poly(methylmethacrylate), the later catalyst exhibited a higher catalytic activity in the decomposition of hydrogen peroxide [12]. This was said to be caused by the stronger interactions between Au particles and MF. In this article we probe the interactions between Au particles and PANI. In particular, we examine how the various oxidation states of PANI would affect the stability of the Au particles. We show that the Au nanoparticles are stable in emeraldine polyaniline. Addition of a reducing agent to a suspension of the Au-PANI, which reduces polyaniline, also induces the formation of irregular chainlike Au aggregates. When the polymer is oxidized using ammonium peroxydisulfate the size of gold nanoparticles increased. We also studied the effect protonation of PANI on the stability of Au particles. Regular close-packed Au aggregates formed when polyaniline was protonated by addition of hydrochloric acid at pH values lower than 2. PANI can easily interconvert between its various oxidation states but there are no reports in the literature on how the various oxidation states affect metal particles dispersed on PANI.

2. Experimental

All chemicals, except H₂AuCl₄·3H₂O, were obtained from Sigma-Aldrich. H₂AuCl₄·3H₂O was sourced from SA Precious Metals (Pty) Ltd. The gold-polyaniline (AuPANI) nanocomposites were prepared as detailed elsewhere [3,4]. A typical protocol for the synthesis of AuPANI is as follows. PANI was first deprotonated by mixing 1 g of PANI (emeraldine form) with 50 mL of 0.1 M NaOH solution. This mixture was stirred for 30 min and washed with distilled water until the pH of the filtrate dropped to 7. The moist cake was then suspended in 100 mL of distilled water to which 25 mL of 10⁻² M H₂AuCl₄ solution was rapidly added while stirring. After 2 h the mixture was filtered, washed with distilled water, and divided in two equal parts. One part was labelled AuPANI Complex (AuPANI-C) and dried while the other was suspended in 50 mL of water to which 15 mg of NaBH₄ in 10 mL of distilled water was rapidly added. After stirring for 1 h the final product was filtered, washed with distilled water, and dried. This product was labelled Au-PANI Reduced (AuPANI-R).

The stability of AuPANI-R nanocomposite was tested by soaking the nanocomposite in aqueous solutions to vary the oxidation state of PANI and its “degree” of protonation. For example, 500 mg of AuPANI-R powder was soaked in 25 mL aqueous solution of hydrochloric acid (concentrations ranging from 10⁻⁴ to 1 M) and then adjusted to a particular pH for 24 h. The solid was then collected by centrifugation, washed with water and dried. The dried samples were labelled AuPANI-R-pH_x where x (0–6) indicates the pH of the solution. To vary the oxidation state of PANI, NaBH₄ and (NH₄)₂S₂O₈ were used to reduce and oxidize PANI to leucoemeraldine and pernigraniline, respectively. In a typical experiment 50 mL 0.1 M aqueous solution of reducing/oxidizing agent was added to 500 mg AuPANI-R in a volumetric flask with constant stirring for 30 min. The solid was then collected by centrifugation, washed with distilled water and dried.

3. Results and discussion

3.1. Effect of NaBH₄ on the size and the stability of gold nanoparticles

The size of the gold nanoparticles is affected by the amount of reducing agent used in the synthesis [3]. When the molar ratio of NaBH₄ to gold (NaBH₄:H₂AuCl₄) was increased beyond 10 a number of networked Au structures were observed. Similar structures were also observed when AuPANI-R with Au particle diameters of 2.6 nm (NaBH₄:H₂AuCl₄ = 3.2:1) was treated with excess NaBH₄ (500 mg AuPANI-R in 50 mL 0.1 M NaBH₄), Fig 1. We suspect that in this case the reduction in the degree of oxidation of PANI at a high concentration of NaBH₄ (which converts imine N to amine N) weakens the attractive interactions between gold nanoparticles (Au NPs) and PANI. One or more Au nanoparticles then fuse and form networked structures. Indeed theoretical studies of the interactions between PANI and Pd atom have shown that PANI interacts strongly with Pd at the quinoid moiety by bonding with the imine N and the nearest C on the quinoid ring [13]. Pd was found to interact very weakly with the benzenoid moiety through weak bonds with C atoms of the benzenoid ring. Amine nitrogens were found not to donate their free electrons to bond with Pd unlike the imine nitrogens. A simple and commonly used technique

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