Research paper

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Jianqiang Ma, Sarthak Mandal, Corin Bronsther, Zhenghan Gao, Ken B. Eisenthal

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Second Harmonic Study of Acid-Base Equilibrium at Gold Nanoparticle/Aqueous Interface

Jianqiang Ma[1], Sarthak Mandal[2], Corin Bronsther[1], Zhenghan Gao[3] and Ken B. Eisenthal*[1]

1. Department of Chemistry, Columbia University, New York, NY 10027

2. Current affiliation: School of Molecular Sciences, Arizona State University

3. Department of Physics, Columbia University, New York, NY 10027

Abstract

Interfacial acid-base equilibrium of the capping molecules is a key factor to stabilize gold nanoparticles (AuNP) in solution. In this study we used Second Harmonic (SH) generation to measure interfacial potential and obtained a surface pKa value of 3.3±0.1 for the carboxyl group in mercaptoundecanoic acid (MUA) molecule at an AuNP/aqueous interface. This pKa value is smaller than its bulk counterpart and indicates that the charged carboxylate group is favored at the AuNP surface. The SH findings are consistent with the effects of the noble metal (gold) surface on a charge in solution, as predicted by the method of images.

Keywords

Surface pKa, noble metal/aqueous interface, method of images.

Introduction

An interface has unique properties that derive from their intrinsic asymmetry. The singular composition and structure of interfaces are manifested in both their equilibrium and dynamic processes. Although the special opto-electronic properties of noble metal plasmonic nanoparticles have been studied extensively, their effects on chemical phenomena at the interface of the nanoparticles with the aqueous solution in which they are suspended, has not been extensively studied[1]. The primary focus of the research presented in this paper is the application of the nonlinear second harmonic (SH) method to probe chemical processes at the AuNP/aqueous interface. SH is an excellent method to study interfacial phenomena because it enjoys the advantages of being interfacial selective for reasons of symmetry, non-invasive, label-free, being able to investigate colloidal interfaces ranging from nano to macro dimensions, and being able to measure time evolution of interfacial phenomena from slow to ultrafast[1,2]. We have selected to study a class of reactions that are of central importance in science and technology. They are proton transfer reactions engaged in acid-base equilibria at interfaces. In this study, the interface is that of a 50nm AuNP in contact with the aqueous bulk solution in which it is suspended.

In our experiment, we use mercaptoundecanoic acid (MUA) (**Figure 1(a)**) as the capping molecule attached to a gold nanoparticle by the formation of a covalent S-Au bond. The free suspension of AuNP in an aqueous solution is strongly dependent on the degree of ionization of the carboxyl group in the capping molecules. In other words, the acid-base equilibrium of the