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Quantitative study on the interaction of Ag^+ and Pd^{2+} with CNT-*graft*-PCA (polycitric acid) in aqueous solution

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ABSTRACT

The reactions between multi walled carbon nanotube graft polycitric acid (MWCNT-*graft*-PCA) and Ag^+ and Pd^{2+} ions at 25 °C are investigated spectrophotometrically. Encapsulation of Ag (I) and Pd (II) on the surface of (MWCNT-*graft*-PCA) as a function of pH, sonication time and reaction time was studied. The results indicated that the absorbance increased until pH = 6 and pH = 8 for Ag and Pd respectively and then decreased. The effects of sonication time on the reactions were studied and 20 min was selected for both of reactions. Also the time of reaction between MWCNT-*graft*-PCA and (Ag, Pd) vs. absorbance was studied and the stirring time of 160 and 100 min was selected for these reactions respectively. Also knowing the number of light-absorbing species is a critical step for subsequent quantitative and qualitative solution equilibrium studies. Behind the number of various complexes formed the stability constants for the combination of MWCNT-*graft*-PCA (ligand L) with Ag^+ and Pd^{2+} ions at 25 °C and variant pH, and various mole ratios are estimated by the SQUAD program.

1. Introduction

Recently, nanotechnology has become an important field in science and technology, allowing one to manipulate matter at the nanometer scale and to incorporate nanostructures and nano-processes into working technological innovations [1–5]. Considerable interest has been focused on the possibility of the construction of new assemblies from nanoparticles (NPs) and other components to yield superstructure nanomaterials with unique and useful optical, electronic, and magnetic properties [1–4].

Carbon nanotubes (CNTs) are potentially excellent one-dimensional nanoscale materials because of their excellent physical properties [6] and morphology that can be carefully functionalize [7,8].

The chemical modification and the covalent functionalization of carbon nanotubes with organic species like long chain alcohols and amines, dendrimers and polymers have been reported recently [9–11]. Also there are few reports about the functionalization of carbon nanotubes that open the area of metallo-organic chemistry to nanotubes such as the synthesis of nanotubes covalently complexed to molecular coordination compounds [12], interconnecting carbon nanotubes with an inorganic metal complex [13], sidewall oxidation and complexation of carbon nanotubes by base-catalyzed cycloaddition of transition metal oxide [14]. Recently a method has been developed for the attaching of self-assembled gold nanoparticles (Au-NPs) onto the surface of sidewalls and ends of thiol-terminated multi-walled carbon nanotubes (MWNTs) functionalized with orthomercaptoaniline which acts as a bridging agent [15].

Among them, one of the most intriguing applications of CNTs is the polymer/CNT nanocomposites. In the past decade, there has been an increasing interest in the studies of polymer/CNT nanocomposites due to the unique combination of promising properties and construction of multifunctional structures of each component [16]. Lately biodegradable nanocomposites containing multi walled carbon nanotubes (MWCNT) and polycitric acid (PCA) were successfully synthesized which hereby metal nanoparticles could be trapped through the conjugating of polymers to CNTs [17].

CNT grafted polymer (CNT-g-polymers) hybrid materials are good candidates to support metal nanoparticles such as platinum group metals (silver, palladium and so on). The unique properties of palladium, silver and other platinum group metals account for their widespread use.

In this work, MWCNTs were opened and functionalized by acid (MWCNT-COOH) and citric acid was polymerized on their surface. Trapping of Ag^+ and Pd^{2+} ions by MWCNT-g-PCA hybrid materials was led to encapsulated silver and palladium nanoparticles onto the surface of MWCNTs via complexation reactions. The parameters for complexation reactions of (Ag^+, Pd^{2+}) ions with MWCNT-g-PCA were optimized using UV–Visible spectrophotometry and then the complex-forming equilibriums and the stability constants of MWCNT-g-PCA-Ag and MWCNT-g-PCA-Pd were calculated using SQUAD

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program. It is one of the most widespread programs and algorithms for determining the stability constant from absorbance data.

Conceptually, the novelty of this derivatization is that nanotube can be considered as a primary ligand with respect to the metal atom. To the best of our knowledge, this is the first report of optimizing the parameters of reaction between MWCNT-g-PCA and platinum group metals (Ag and Pd) and it is the first report of applying SQUAD program for studying MWCNT complexation reactions with metal ions.

2. Experimental

2.1. Chemicals and solutions

All the chemicals were of analytical reagent grade. Carbon nanotubes were prepared by Cheap Tubes Inc. The outer diameter of CNT was between 20 and 40 nm. Monohydrate citric acid, $AgNO_3$ and $PdCl_2$ were purchased from Merck. Two stock solutions of metal ions which were obtained from their various salts ($AgNO_3$ and $PdCl_2$) were prepared in 100 ml volumetric flasks and the solutions were used for the preparation of the various mole ratio mixtures of MWCNT-g-PCA. Buffer solutions were prepared using (Na_2HPO_4, NaH_2PO_4) 0.2 M and the concentrated (HNO_3, NH_3) solutions for adjusting pH of reaction solutions of hybrid materials with $PdCl_2$ and $AgNO_3$ respectively which were purchased from Merck. All experiments were carried out at 25 °C, and all titrations were repeated at least three times.

2.2. Apparatus and software

The pH values were measured by a model Jenway 3015 pH meter using a Metrohm combined glass electrode. A Pharmacia model LKB UV–visible Ultraspect (III) single beam spectrophotometer that connected to a Pentium II computer with 1-cm quartz cells was used for recording the absorbance measurements. An ultrasonic bath (30 kHz, manufactured in United Kingdom) was used to well disperse metal ions in the polymeric shell of hybrid material. The calculations were made with a Pentium 4 computer and the SQUAD Program for determination of stability constants was used. Also third dimension diagrams were drawn with MATLAB R2007b software.

2.3. Procedure

2.3.1. Preparation of MWCNT-g-PCA hybrid materials

MWCNTs were opened according to reported procedures in the literatures [18]. MWCNT-g-PCA hybrid materials were prepared according to the following procedure [17]. Functionalized MWCNT-COOH (0.05 g) was added to a polymerization ampoule equipped with magnetic stirrer and vacuum inlet then monohydrate citric acid (2.5 g) added to ampoule and it was sealed under vacuum. The mixture was heated up to 120 °C and stirred in this temperature for 30 min. After removing the water by vacuum inlet, reaction temperature was raised to 140 °C and stirred at this temperature for 1 h. Water as a byproduct of reaction was removed by vacuum inlet and reaction temperature was raised to 160 °C. Polymerization continued in this temperature under dynamic vacuum for 1.5 h. The mixture was cooled and dissolved in THF and product was precipitated in cyclohexane. Purified product was obtained as a viscous coffee-brown compound in %85 yields.

2.3.2. Preparation of MWCNT-g-PCA nanocomposites containing silver nanoparticles

Preparation of MWCNT-g-PCA containing Ag nanoparticles was reported recently [17], but we prepared this nanocomposite in optimum reaction conditions such as pH, sonication time and the stirring time of reaction between hybrid materials and Ag^+ ions. Dilute solution of MWCNT-g-PCA was mixed with aqueous solution of silver nitrate containing 1 M ($AgNO_3$) at pH 6. After 20 min dispersing in an ultrasonic bath (22 kHz) the solution was stirred at room temperature for 160 min. Water was evaporated by vacuum and residue was dissolved in THF and precipitated in cyclohexane. With optimization reaction conditions, the time needed for maximum loading of Ag nanoparticles in polymeric shell decreased from 8 h [17] to 160 min.

2.3.3. Preparation of MWCNT-g-PCA nanocomposites containing palladium nanoparticles

MWCNT-g-PCA-Pd nanocomposite was prepared recently [19] but we prepared it in optimum reaction conditions (pH, sonication time, stirring time). Water solutions of $PdCl_2$ (0.26 g in 3 ml) and MWCNT-g-PCA (0.2 g in 10 ml) were mixed at pH 8 and placed in an ultrasonic bath (22 kHz) for 20 min to well disperse metal ions in the polymeric shell of hybrid material. Then it was stirred at room temperature for 100 min. Water was evaporated by vacuum oven and residue was dissolved in THF and precipitated in cyclohexane. Product was dried by vacuum oven at 60 °C for 2 h. With optimization reaction conditions, the time needed for maximum loading of Pd nanoparticles in polymeric shell decreased from 8 h [19] to 100 min.

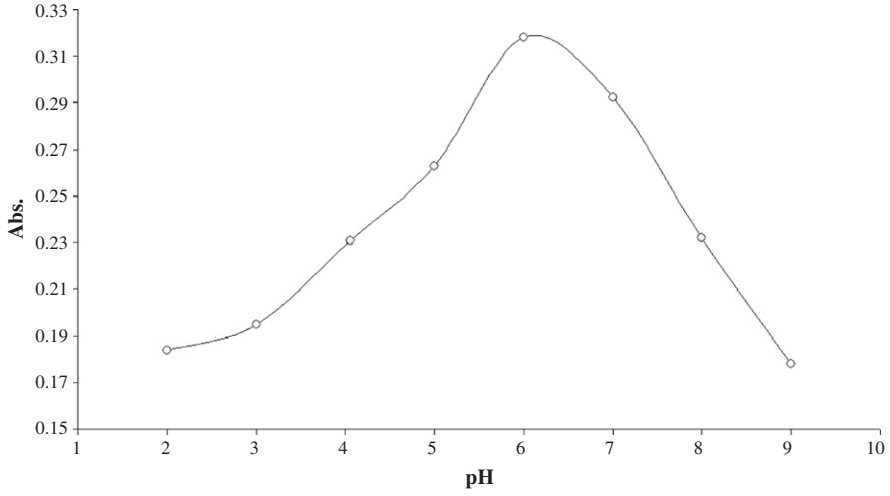

Fig. 1. Effect of pH on the interaction of MWCNT-g-PCA with Ag^+ at $\lambda = 350$ nm in $C^+_{Ag} = 1.2\times10^{-3}$ M, $C_L = 4.1\times10^{-4}$ M.