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Straightforward Light-Driven Synthesis of Ultrasmall, Water-Soluble Monolayer-Protected Platinum Nanoparticles

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A facile synthetic methodology to obtain, in one-step, ultrasmall (ca. 1 nm) and water-soluble carboxylate-terminated platinum nanoparticles is reported. It involves visible light as a reaction trigger and platinum acetylacetonate and thioglycolic acid as the only chemical reactants. These nanoparticles are stable for weeks and can be easily transferred into organic solvents such as toluene, chloroform or dichloromethane by using the cationic surfactant tetraoctylammonium bromide as the phase-transfer agent. To the best of our knowledge, they are among *the smallest* water-soluble platinum nanoparticles prepared to date and represent the *first example* of preparation of thiol-protected platinum nanoparticles exclusively driven by light.

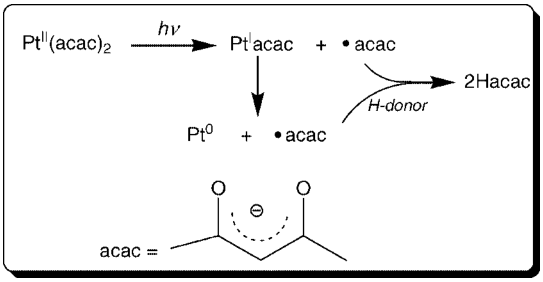
Introduction

Metal nanoparticles are continuing to draw a great deal of attention by interdisciplinary areas of the scientific community due to their exciting optical, electronic, magnetic and catalytic properties.[1] Potential applications of metal nanoparticles span indeed from molecular electronics and optoelectronics to medicine and biology.[2] The modification of metal nanoparticles with monolayers of thiol derivatives, has been proven to be an appropriate strategy to achieve monolayer-protected clusters which are air-stable, isolable and dispersible in organic solvents.[3] In contrast to the large number of reports focused on the preparation of thiol-capped gold nanoparticles, only limited examples have addressed the synthesis of thiol-protected platinum nanoparticles.[4–7] The interest on these hybrid nanostructures is strongly motivated not only by their well-established catalytic activity, but also by their biomedical relevance. Furthermore, as these nanoparticles are characterized by negligible plasmon absorption into the visible region,[8] they represent ideal platforms for the fabrication of hybrid optical nanodevices by self-assembling of functional chromogenic units.[9] Many practical applications necessitate platinum nanoparticles to be dispersible in water with preservation of their physicochemical properties over long time.[10] In this regard, Chen and Kimura have shown simple synthetic protocols to prepare water-soluble platinum nanoparticles, with diameters ranging from 2.5 to 4.7 nm, capped with mercaptosuccinic acid and involving the chemical reduction of water-soluble platinum salts.[7]

Herein we report a facile synthetic methodology to obtain ultrasmall (ca. 1 nm), water-soluble and stable platinum nanoparticles, implying visible light as a reaction trigger and platinum acetylacetonate, Pt(acac)$_2$, and thioglycolic acid (TA) as the only chemical reactants.

Results and Discussion

Differently to β-diketonate complexes with metals such as Cu, Ni, and Pd, Pt(acac)$_2$ undergoes photodecomposition with comparable efficiency upon irradiation with both UV and Vis light due to the absence of low-lying d,d states which deactivate the reactive π,π^* state.[11] In hydrogen-donating solvents Pt(acac)$_2$ undergoes efficient photodegradation to yield colloidal platinum and β-diketones.[11a] The main steps for this photoprocess are recalled in Scheme 1 for the sake of clarity. They involve the homolytic cleavage of the metal–ligand bond followed by hydrogen abstraction by the ligand-centered radical.



Scheme 1. General photodecomposition mechaism of Pt(acac)$_2$ in the presence of hydrogen donors.

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We have recently demonstrated that colloidal platinum can also be obtained in water medium by irradiation of Pt(acac)$_2$ caged in a β-cyclodextrin cavity acting as suitable host and excellent hydrogen donor.[12] Accordingly, when Pt(acac)$_2$ is irradiated in acetonitrile, which is not a hydrogen donor, the photodecomposition is negligible and does not lead to the formation of platinum colloids. On these grounds, we irradiated with visible light an acetonitrile solution of Pt(acac)$_2$ in the presence of TA. The role of TA is expected to be twofold. In fact, it is a good hydrogen donor (the hydrogen atom bound to the sulfur atom is highly reactive towards free radicals) and represents a suited capping agent to obtain platinum nanoparticles with negatively charged surface due to the presence of carboxylate groups. The almost colorless solution turned yellow upon irradiation. As shown in Figure 1, the disappearance of the Pt(acac)$_2$ absorption was accompanied by the appearance of the typical absorption band of Hacac (see dotted spectrum, for comparison) and a structureless absorption extending up to the visible region, attributed to colloidal platinum. The quantum yield for the photochemical reaction (see Experimental Section) was $\Phi = 0.02 \pm 0.005$.

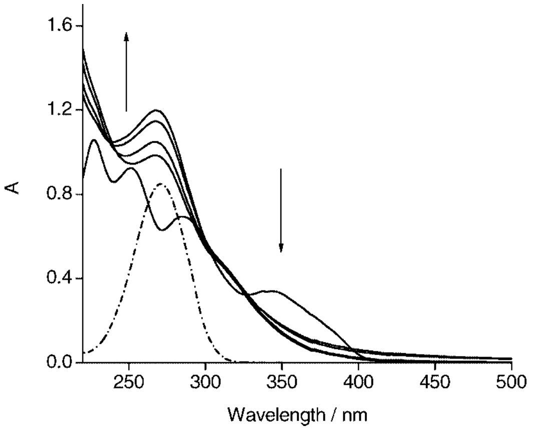


Figure 1. Absorption spectral changes observed upon 0, 8, 16, 40, 50 min of light irradiation of a 0.5 mM acetonitrile solution of Pt(acac)$_2$ in the presence of 1 mM TA. The dotted line shows the absorption spectrum of Hacac in acetonitrile. The arrows indicate the direction of the spectral evolution with time. Cell pathlength 1 mm.

A control experiment carried out with an acetonitrile solution of Hacac provided unambiguous evidence for the quantitative release of the ligand from Pt(acac)$_2$ upon irradiation. As Hacac does not absorb the exciting light, it is not photodecomposed during the course of the photoreaction and thus, can be easily removed from the reaction mixture by drying the irradiated solution under vacuum at 70 °C for 1 h. The dried sample was very soluble in water at pH = 8 but not at pH = 2, according to the presence of the ionizable carboxylic groups bound to the metal surface. This pH dependence allowed the removal of the unbound TA through few cycles of redispersion/centrifugation at pH = 2. The absence of free TA in the supernatant was verified by ESI-MS. At last, the precipitate was solubilized in water at pH = 8 and the absorption spectrum was recorded. As shown in Figure 2A, the spectrum obtained does not show any detectable absorption associated to Hacac but is exclusively characterized by a structureless absorption extending into the visible region which is in full agreement with the spectra reported in the literature for other platinum nanoparticles.[4a,7,8a,8b] High-resolution transmission electron microscopy (HRTEM) on this sample (Figure 2B) shows that the platinum nanoparticles are quite well dispersed and are characterized by an average diameter of (1.0 ± 0.3) nm. The FFT analysis (inset Figure 2B) reveals that the nanoparticles are single crystals with fcc structure.

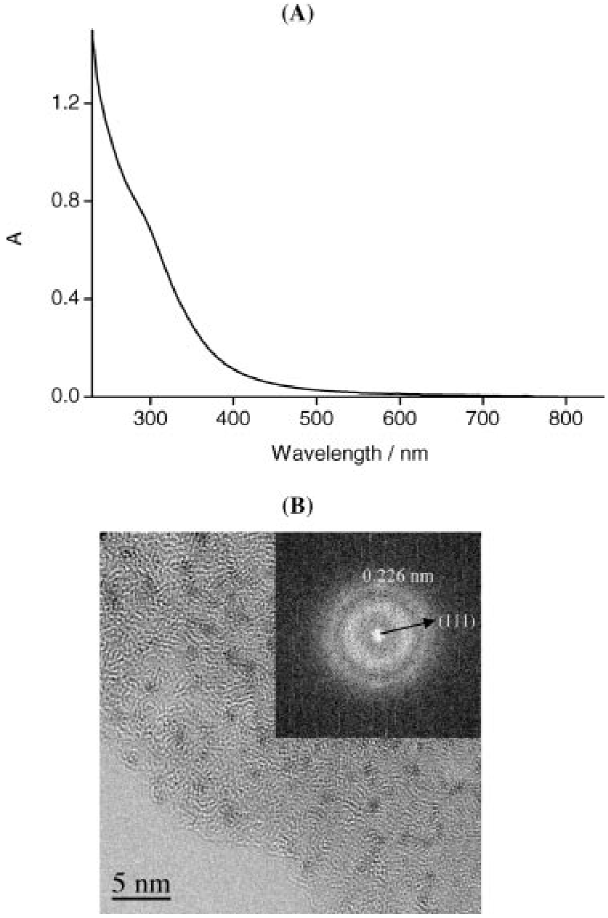


Figure 2. (A) Absorption spectrum in water solution at pH = 8, cell pathlength 1 mm and (B) HRTEM micrograph of the TA-modified platinum nanoparticles. The inset shows the FFT analysis showing an fcc packing arrangement.

Elemental analysis conducted on the sample gave the following results: C 4.65, H 0.42, Na 4.48, O 6.40, Pt 74.49, S 6.33. The atomic ratio of C/H/O/S/Na is 1.94:2.15:2.05:1.01:1. This result provides evidence for the chemisorption of TA through the mercapto termination as well as for the existence of the carboxylate form ($C_2H_2O_2SNa$).

These colloidal nanoparticles exhibited good air stability. Indeed, they remained dispersed in water for several weeks with no relevant aggregation, as evidenced by the negligible variation of the absorption spectrum and the particle size noted after this period of aging.

Interestingly, the monolayer-protected nanoparticles can be easily transferred into organic solvents such as toluene, chloroform or dichloromethane by using the cationic surfactant tetraoctylammonium bromide (TOAB) as the phase-transfer agent. Figure 3A shows representative images of the aqueous solution of the TA-modified platinum nanoparticles before (left) and after (right) shaking with dichloromethane containing 0.1 м TOAB. The color change between the aqueous and organic phase clearly indicates that a complete phase transfer is achieved. It is also noteworthy that the phase transfer occurs without any aggregation as suggested by the negligible variation of the surface plasmon absorption after the nanoparticles transfer into the organic phase (Figure 3B).[13] In fact, particle aggregation would have led to significant broadening of the plasmon absorption.[15] These transference experiments provide a further confirmation that the platinum nanoparticles are negatively charged due to the presence of the carboxylate moieties. Pure electrostatic interaction between these functional groups and the positively charged TOAB has indeed pointed out by Chen and Kimura in the case of modified platinum and gold nanoparticles.[7,16]

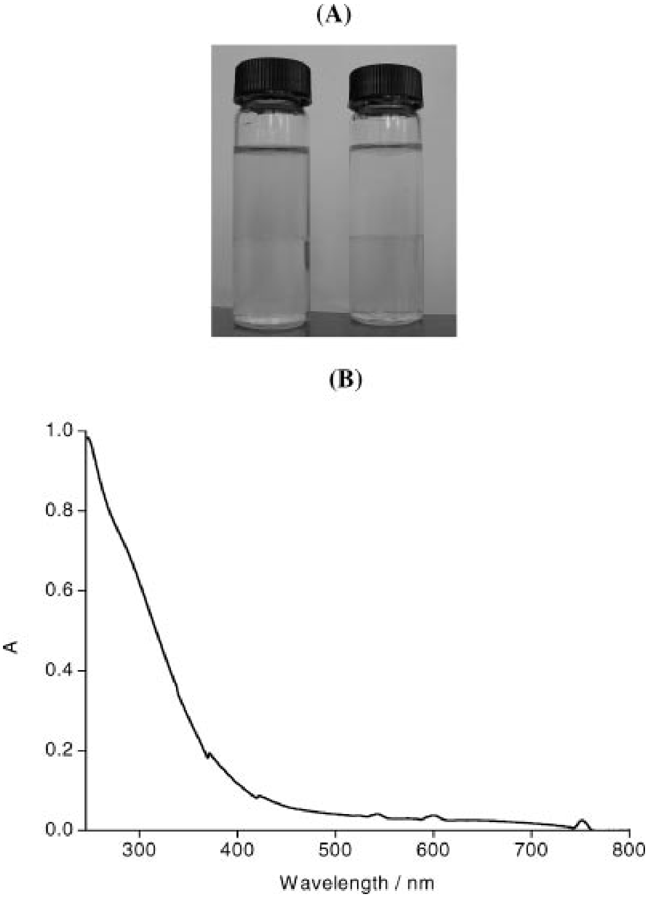
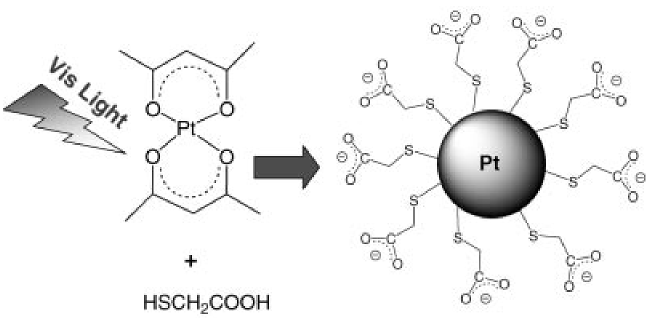


Figure 3. (A) Photograph of the TA-modified platinum nanoparticles in water at pH = 8 before (left) and after (right) shaking with a dichloromethane solution containing 0.1 м TOAB. (B) Absorption spectrum of the TA-modified platinum nanoparticles after transferring in dichloromethane. Cell pathlength 1 mm.

As shown in Scheme 1, the release of the free ligand involves hydrogen abstraction reaction by the ligand-centered radical. Since the occurrence of such a process from acetonitrile is, of course, out of question because thermodynamically not favored, it is reasonable to conceive that the acac$^{\cdot}$ radical leads to the formation of Hacac by abstraction of the –SH hydrogen atom, according to the high reactivity of thiols towards free radicals.[17]

Conclusions

The photochemical methodology pictorially sketched in Scheme 2 is very simple, and effective to produce ultrasmall, water-soluble and stable platinum nanoparticles in a single step. To the best of our knowledge, they are among *the smallest* water-soluble platinum nanoparticles prepared to date and represent the *first example* of preparation of thiol-protected platinum nanoparticles exclusively driven by light. The advantage offered by the light radiation as a reaction trigger is twofold. Firstly, the use of visible excitation produced by conventional lamps with moderate light intensity is environmentally friendly and cheap in contrast to the use of toxic chemicals and sophisticated laser sources. Secondly, the light radiation allows to produce a large number of atoms homogeneously and instantaneously, exerting a key function in the nucleation, growth and dispersion of the nanoparticles. In view of their small sizes and the well-known role of the carboxylic moiety in the formation of self-assembled supramolecular architectures,[18] these carboxylate-terminated platinum nanoparticles might be intriguing candidates for potential biological applications and building-up of two- and three-dimensional self-assembled nanocomposite devices.



Scheme 2. Pictorial view illustrating the single-step formation of the monolayer-protected platinum nanoparticles.

Experimental Section

All reagents were obtained from Sigma–Aldrich and used as received. The solvents used were of analytical and spectrophotometric grade. All glassware used was immersed in piraña solution (70:30 H_2SO_4/H_2O_2) at 70 °C for 1 h. ***Warning:** piraña solution should be handled with caution!* Next, the glassware was rinsed with large amounts of high-purity water and dried. Water was purified through a Millipore Milli-Q system. Irradiation was carried out under a continuous argon flux in a 10 mm quartz cuvette with

3 mL capacity using a Rayonet photochemical reactor equipped with 16 RPR lamps with an emission in the 380–480 nm range with a maximum at 420 nm. The incident photon flux on the sample was ca. 10^{16} quanta s^{-1}. The total irradiation time was 50 min, the concentrations of $Pt(acac)_2$ and TA were 0.5 mM and 1 mM, respectively. The photodecomposition quantum yield for the $Pt(acac)_2$ complex was determined spectrophotometrically by using the following equation: $\Phi = \Delta[C]V/\Delta t I_0 F$, where $\Delta[C]/\Delta t$ is the rate of disappearance of the platinum complex, V is the volume of the irradiated solution, I_0 is the intensity of the incident photons and F is the fraction of the photons absorbed by the platinum complex. Absorption spectra were recorded with a Jasco V-560 spectrophotometer. ESI mass spectra were recorded with an Agilent 1100 series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 kV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N_2 (10 L/min); carrier solvent, methanol (0.4 mL/min). HRTEM images were obtained by means of an FEG JEM 2010F instrument with a field emission gun operating at 200 kV. The electro-optical configuration guarantees ultrahigh spatial resolution (0.19 nm). This microscope is equipped with the GIF (Gatan Image Filter) apparatus which allows to realize images filtered to narrow windows of the electron energy loss spectrum. Elemental analyses were conducted by means of standard techniques.

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[17] At this point it is unclear if the sulfur-centered radicals generated upon hydrogen abstraction (i) directly bind to the naked platinum surface, (ii) dimerize to disulfides which at last chemisorb to the metal serface, or (iii) both.

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