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Nitrene-functionalized ruthenium nanoparticles: Selective manipulation of nanoparticle electronic conductivity by vinyl derivatives

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ABSTRACT

The electronic conductivity of solid films of nitrene-functionalized ruthenium nanoparticles was measured and compared in the presence of organic vapors of various relative polarity that included ethanol, acetone, *n*-hexane, 1-hexene, toluene, and styrene. The nanoparticle conductivity was found to decrease upon the exposure to the vapors tested, and the largest drop was observed with styrene and toluene. Interestingly, the diminishment of the nanoparticle conductivity was found to be 2.5 times more sensitive to styrene than to toluene, despite their similar relative polarity and nanoparticle solubility. This was accounted for by the combined contributions of (i) increased distance between nanoparticle metal cores as a result of film swelling from solvation as well as (ii) selective chemical reactivity of the Ru=N interfacial bonds to vinyl moieties that altered the tunneling pathway for interparticle charge transfer. These results suggest that functional nanoparticles may serve as a unique platform for chemical vapor detection with enhanced sensitivity and selectivity.

1. Introduction

In a series of recent studies [1–4], metal nanoparticles functionalized with conjugated metal–ligand interfacial linkages have been found to exhibit extensive intraparticle charge delocalization, which leads to the emergence of unprecedented optical and electronic properties of the nanoparticles. In addition, the strong metal–ligand interactions and hence the low interfacial contact resistance provide a means of facile charge transfer through the interface and between nanoparticles [5]. For example, ruthenium nanoparticles protected by carbene fragments have shown interesting nanoparticle-mediated intervalence charge transfer between ferrocene-terminated carbene ligands on the particle surface [1], where the electron delocalization through the metal cores renders the particle-bound functional moieties to behave analogously to dimeric species [6]. Similar behaviors have also been observed with nitrene-functionalized nanoparticles where the nitrene fragments are prepared by controlled thermolysis of azide derivatives [7]. Interestingly, the ruthenium-nitrene interfacial bonds are found to exhibit unique chemical reactivity towards vinyl derivatives through imido transfer (Scheme 1) [7]. Such a unique property may be exploited as a powerful variable in the further manipulation of interparticle charge transfer and hence nanoparticle film conductivity.

Films of organically capped metal nanoparticles have been widely used as vapor sensors due to a measureable change in electronic conductivity when exposed to vapors of low concentrations [8–10]. In essence, these films consist of metal centers embedded in an organic framework of the capping ligands, and the electrons travel through the films by tunneling between metal centers with the organic ligands as the energy barriers. The effect is similar to charge transfer through a mixed valence system. Following this electron tunneling model as well as the Marcus theory, the ensemble conductivity may be defined by Eq. (1) [5,11,12],

$$\sigma(\delta, T) = \sigma_0 \exp(-\beta\delta) \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where σ_0 is the intrinsic conductivity of the nanoparticle film based on the number and mobility of the charge carriers, β is the electronic coupling term, δ is the distance between particles, and E_a is the activation energy which is given by Eq. (2),

$$E_a = \frac{e^2}{8\pi\varepsilon\varepsilon_0}\left(\frac{1}{r} - \frac{1}{r+\delta}\right) \tag{2}$$

with r being the metal core radius. From these two equations it is apparent that there are multiple parameters that may be exploited to alter the conductivity of the nanoparticle films. For instance, by increasing the interparticle distance the first exponential term in

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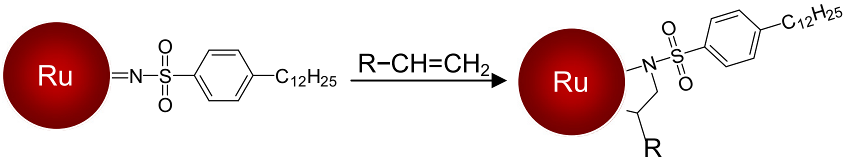

Scheme 1. Schematic of imido transfer reactions of nitrene-functionalized ruthenium nanoparticles with vinyl derivatives.

Eq. (1) will decrease and the activation energy (Eq. (2)) will increase resulting in a loss of conductivity. An increase of the interparticle distance can be readily accomplished through solvation of the particles comprising the film. As the particles are solvated, the film will swell leading to larger interparticle distances and thus a larger barrier for electron tunneling and a lower overall conductivity. Such behaviors have been observed in a number of prior studies with solid films of gold nanoparticles functionalized with mercapto derivatives [9,13]. However, in these studies, with nanoparticle solvation being the leading parameter in controlling the interparticle charge transfer, it is not surprising that the selectivity and sensitivity of the nanoparticle film conductivity towards organic vapors are rather limited.

One can envision that if the electron tunneling pathways and hence the electronic coupling can be selectively manipulated, the detection sensitivity and/or selectivity may be further enhanced with an apparent change of the ensemble intrinsic conductivity. This is rendered possible with the emergence of metal nanoparticles functionalized with conjugated metal–ligand interfacial bonds [1–4]. In principle, if exposure to an organic vapor leads to the conversion of the conjugated metal–ligand bonds to saturated ones, the ensemble conductivity will be altered significantly as a consequence of the change of the electron tunneling pathway. This will provide sensing based on the exact chemical makeup of the vapor rather than a general feature such as solvation properties, a major limitation of most prior research. Such selectivity is essential for proper sensing technology and is the primary motivation of this study, which is exemplified by the selective reactivity of nitrene-functionalized ruthenium nanoparticles towards vinyl derivatives, as a result of imido transfer reactions of the ruthenium-nitrene bonds with vinyl moieties (Scheme 1).

2. Experimental

2.1. Chemicals

Ruthenium chloride ($RuCl_3$, 99+%, ACROS), 1,2-propanediol (ARCOS), sodium acetate trihydrate ($NaOAc \cdot 3H_2O$, MC&B), vinylferrocene (97%, Sigma-Aldrich), tetra-*n*-butylammonium nitrate ($TBANO_3$, ≥99%, Sigma-Aldrich), and 4-dodecylbenzenesulfonyl azide (Aldrich) were used as received. All solvents were obtained from typical commercial sources and used without further treatment. Water was supplied by a Barnstead Nanopure water system (18.3 MΩ cm).

2.2. Ruthenium nanoparticles

The synthesis of the nitrene-functionalized ruthenium (Ru=N) nanoparticles has been detailed previously [7]. In brief, ruthenium chloride (0.14 mmol) and sodium acetate (80 mg) were dissolved in 100 mL of 1,2-propanediol. The mixture was then refluxed at 165 °C under magnetic stirring for 1 h to allow for the reduction of the ruthenium salt into acetate-protected ruthenium colloids. The solution was then cooled down to 60 °C, and 0.52 mmol of dodecylbenzenesulfonyl azide and 20 mL of *sec*-butylbenzene were added to the solution which was then stirred for 1 h with the temperature maintained at 60 °C. Adsorption of the azide ligands onto the ruthenium colloids resulted in a phase transfer from 1,2-propanediol to *sec*-butylbenzene. The *sec*-butylbenzene phase was then collected and refluxed at 165 °C for 24 h where nitrene radicals were generated and attached onto the ruthenium colloid surface forming Ru=N bonds. The solution was then cooled down to room temperature and solvents were removed by a rotary evaporator. The particles were then rinsed extensively with acetonitrile to remove excessive ligands and the resulting particles remained stable and soluble in apolar solvents such as toluene, THF, chloroform, and dichloromethane, but insoluble in alkanes, ethanol or acetone.

2.3. Characterizations

Transmission electron microscopy (TEM) studies were carried out with a JOEP JEM-2010 TEM microscope operated at 200 kV. The samples were prepared by dropcasting a particle solution in toluene onto a Cu grid. ^1H and ^{13}C NMR spectroscopic measurements were carried out by using concentrated solutions of the nanoparticles in $CDCl_3$ or CD_2Cl_2 with a Varian Unity 500 MHz NMR spectrometer. The absence of any sharp features signified that the nanoparticles were free of excessive ligands. UV–vis spectroscopic studies were performed with an ATI Unicam UV4 spectrometer using a 1 cm quartz cuvette at a resolution of 2 nm. Photoluminescence characteristics were examined with a PTI fluorospectrometer.

2.4. Electronic conductivity

For electronic conductivity measurements, a particle film was formed by dropcasting 1 μL of a concentrated particle solution in toluene (ca. 60 mg/mL) onto an interdigitated array (IDA) electrode (25 pairs of gold fingers of 3 mm × 5 μm × 5 μm, from ABTECH). At least 30 min was allowed for solvent evaporation, and the film thickness was found to be greater than the height of the IDA fingers. Conductivity measurements were then carried out with the nanoparticle film sealed in a 20 mL vial where varied organic vapors were injected with a Hamilton microliter syringe at ambient temperature. In between each injection, the cell was purged with ultrahigh-purity nitrogen gas until a steady state was attained. The ensemble conductivity (σ) was evaluated by Eq. (3),

$$\sigma = \frac{1}{49R}\frac{L}{A} \tag{3}$$

where R is the ensemble resistance calculated from the slope of the I–V curves, L is the IDA electrode interfinger gap (5 μm), and A is the film cross-section area approximated by (finger height, 5 μm) × (finger length, 3 mm). The constant (49) reflects that there are totally 49 junctions which are in parallel within the IDA chip.

Prior to exposure to any organic vapors, the electronic conductivity of the nanoparticle films was measured and denoted as σ_i. Exposure to organic vapors changed the conductivity to σ. The variation of the normalized conductivity, which is defined as the ratio of σ/σ_i, with vapor concentration was then used to compare the sensitivity (S) of the nanoparticle ensembles to different organic vapors, where S is the tangent of σ/σ_i vs. vapor concentration.