Erratum

Erratum to "Synthesis, stabilization and applications of nanoscopic siloxane-metal particle conjugates" [J. Organomet. Chem. 686 (2003) 24–31]

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This has come to our attention that the introductory sections (1 and 2) of this account contain text, which was directly quoted without quotation marks and proper citations and attributions. A corrected version with quotation marks and proper citations is provided below. We sincerely regret these errors and tender our apologies. In addition to existing references, three new Refs. [a–c] should also be added. These corrections have no bearing on any data, results or conclusions presented in this account.

1. Introduction

As detailed by Carotenuto [a], "Interest in condensed matter at size scales larger than atoms but much smaller than bulk solids has grown rapidly over the last few years. Matter containing from tens to thousands of atoms can have structures and properties significantly different from those of conventional materials [1]; consequently, the current research on nanostructured materials is principally devoted to the synthesis, characterization and understanding of changes in the fundamental properties.

Particularly interesting is the study of metal properties behavior on a nanometric scale [2,3]. Size dependent changes in band-gap energy, excited-state electronic behavior, and optical spectra are generated that differ drastically from those known for the bulk limit. In addition, the new characteristics of this class of materials make them really attractive for a number of technological applications [4–6], including photonic devices, catalysis, corrosion protection, solar energy conversion, and chemical or biochemical sensors.

Preparation and characterization of nanocrystallites is a very critical area of research for fundamental understanding and tailoring of materials properties of practical use. Nanocomposite materials require nanometric particles with uniform size, controlled dimensions, and regular shape. Such particles can be obtained by solution chemistry (chemical precipitation and sol–gel technique) and by vapor deposition (gas evaporation, laser ablation, and sputtering) [7]. However, solution chemistry is the only technique that provides a cost-effective method for the production of large quantities of nanoparticles and allows one to manipulate matter at the molecular level. Solution chemistry is the most practical route for the synthesis of nanoscale particles, but the control of size distribution, particle morphology, and crystallinity still need further investigation."

Widegren and Finke [b] have elegantly summarized that "the synthesis of soluble transition-metal nanoclusters has been accomplished using five general methods [8,9]: (i) the chemical reduction of transition-metal salts; (ii) the electrochemical reduction of transition metal salts; (iii) thermal or photochemical decomposition of transition-metal precursors; (iv) ligand reduction and displacement from organometallic compounds; and (v) metal vapor synthesis. Some synthetic techniques use a combination of these five methods; e.g., sonochemical [10] preparations of nanoclusters involve either (i) or (iii) or a combination of (i) and (iii) [10–15]. Of the five methods, the chemical reduction of transition-metal salts is by far the most common.

Transition-metal nanoclusters are only kinetically stable because the formation of bulk metal is the thermodynamic minimum [16,17]. Therefore, nanoclusters that are freely

dissolved in solution must be stabilized in a way that prevents the nanoclusters from diffusing together and coalescing—any such agglomeration would eventually lead to the formation of the thermodynamically favored bulk metal [16]. Nanocluster stabilization is usually discussed in terms of two general categories of stabilization, electrostatic and steric [18,19]. Electrostatic stabilization is achieved by the coordination of anionic species, such as halides, carboxylates or polyoxoanions, to the coordinatively unsaturated surface metal atoms of the metal particles [18]. This results in the formation of an electrical double-layer (really a diffuse electrical multi-layer) [20], which causes coloumbic repulsion between the nanoclusters. Steric stabilization is achieved by the presence of bulky, typically organic materials that, due to their bulk, impede the nanoclusters from diffusing together [18]. Polymers, dendrimers and large alkylammonium cations are examples of organic steric stabilizers. The choice of stabilizer also allows one to tune the solubility of the nanoclusters [21,22].''

As summed up by Crooks and co-workers [c] the ''Monolithic ceramic and polymeric templates have also been used for preparing nanomaterials. For example, the well-defined pores in alumina or polymeric filtration membranes can be used to define the geometrical and chemical properties of metal, semiconductor, and polymeric nanomaterials [23]. In many cases the template can be removed chemically or thermally, leaving behind the naked nanomaterial. The obvious advantage of this technique is that highly monodisperse particles with a variety of shapes, sizes, and chemical compositions can be prepared [24]. The polymer template usually serves to both control particle size and passivate the surface of the nanoparticles against agglomeration.''

As detailed by Carotenuto [a], ''A number of polymers can be used as protective agents (e.g., poly(vinylalcohol), poly(methylvinylether), sodium polyacrylate, poly(N-vinyl-pyrrolidone) (PVP)) [25]; such a component allows one to recover the fine particles as a polymer-based composite. Moreover, diblock copolymers with metal-ion affinities can be used to sequester metal ions into localized domains that can subsequently be converted into metal nanostructures. A wide range of metal particles have been formed within such polymer templates including Cu, Ag, Au, Pt, Pd, and Rh.''

While our group is involved in devising versatile and practical routes to semiconductor and metallic nanocrystals and their property profiling, due to space limitations, we will limit our discussion to novel metals. In this account, we will summarize, the synthesis and characterization of polysiloxane-encapsulated metal nanoparticles their thermal, catalytic, optical and photothermal properties.

2. Motivations and rationale for approach

Siloxane polymers are a very versatile class of polymers, which have been used as additives to produce or enhance a number of physical properties ranging from water repellency to thermal stability. Monomeric hydrosilanes are known reducing agents and have been successfully used for the generation of Pt, Pd, and Rh nano-sized particles in the context of metal catalyzed hydrosilylation of alkenes [26]. On the other hand, investigations of polyhydrosilanes as reducing agents for the generation of nano-sized silver particles have not been explored. Though, their property profile may provide the means of directing metallic particles into specific physicochemical environments in addition to their utility as reducing agents. In our approach, well-defined silicon polymers (polysiloxanes) are envisioned to act as reducing agents, as well as templates to control the size, stability, and solubility of nanoparticles ranging in diameter from less than 1 nm up to 10 nm.

As in the case of dendrimeric systems described by Crooks and co-workers [c] same arguments can also be borrowed and adopted for polysiloxanes. Thus, ''the polysiloxanes are particularly well-suited for hosting metal nanoparticles for the following reasons'': (1) the selected polysiloxane templates themselves are of fairly uniform composition and structure, and therefore they may yield well-defined nanoparticle replicas; (2) unusual freedom of rotation around the Si–O bond allows these polymers a high degree of flexibility while maintaining their integrity; (3) polysiloxanes with Si-H functionalities can act as reducing agents thus can eliminate the need for extra reducing agents; (4) the encapsulated nanoparticles are confined primarily by steric effects, and therefore a substantial fraction of their surface is unpassivated and available to participate in surfactant exchange and catalytic reactions; (5) the substituent branches can be used as selective gates to control access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles; and (6) the terminal groups can be tailored to control solubility of the hybrid nanocomposite and used as handles for facilitating linking to surfaces and other polymers. As will be discussed later, these attributes take full advantage of the unique structural and chemical properties of polysiloxanes. Indeed, ''polysiloxanes/nanoparticle composites can represent an unusual case of the template and replica working in concert to exhibit functions that exceed those of the individual components. That is, in the studies reported here the polysiloxane templates play a role well beyond that of a simple casting mold.''

Following changes should also be incorporated on page 27 (paragraph 2, lines 16–27).

As described for other systems [b] in our strategy also ''presence of... particles can grow to definite size.''

Additional references

[a] G. Caotenuto, Appl. Organomet. Chem. 15 (2001) 344–351.
[b] J.A. Widegren, R.G. Finke, J. Mol. Catal. A 191 (2003) 187–207.
[c] R.M. Crooks, M. Zhao, L. Sun, V. Chechik, L.K. Yeung, Acc. Chem. Res. 34 (2001) 181–190.