Nano Today (2014) 9, 132—157

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/nanotoday

REVIEW

Metal nanoclusters: New fluorescent probes for sensors and bioimaging

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Received 14 December 2013; received in revised form 11 February 2014; accepted 12 February 2014
Available online 12 March 2014

KEYWORDS
Metal nanocluster;
Fluorescent probe;
Biolabels;
Sensor;
Imaging

Summary Fluorescent metal nanoclusters (NCs) as a new class of fluorophores have attracted more and more attention due to their unique electronic structures and the subsequent unusual physical and chemical properties. The size of metal NCs approaches the Fermi wavelength of electrons, between metal atoms and nanoparticles, resulting in molecule-like properties including discrete energy levels, size-dependent fluorescence, good photostability and biocompatibility. These excellent properties make them ideal fluorescent probes for biological application. Up to now, significant efforts have been devoted to the synthesis, property and application studies of gold and silver NCs. Recently, a growing number of studies on copper and other metal clusters have also been reported. In this review article, we focus on summarizing recent advances in controllable synthesis strategies, chemical and optical properties, and sensing and imaging applications of metal NCs (mainly including Au, Ag, Cu, etc.). Finally, we conclude with a look at the future challenges and prospects of the future development of metal NCs.

Introduction

Nanomaterials have been recognized as the most modish research topics in the past decades [1—3]. Nobel metal nanomaterials with interesting size-dependent electrical, optical, magnetic, and chemical properties have been intensively pursued, not only for their fundamental scientific interest, but also for their many technological applications [4—6]. Especially, metal nanoclusters (NCs) have attracted special attention due to their attractive features and molecule-like properties [7—16]. Metal NCs usually consist

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http://dx.doi.org/10.1016/j.nantod.2014.02.010
1748-0132/

of a few to a hundred atoms, and the sizes are comparable to the Ferimi wavelength of electrons [7], which endows them an important role-the missing link between single metal atoms and plasmonic metal nanoparticles. In this size regime, the continuous density of states breaks up into discrete energy levels [16,17]. Due to the electrons of metal atoms confined in molecular dimensions and the special discrete energy levels, metal NCs exhibit dramatically different optical, electronical and chemical properties, including strong photoluminescence, excellent photostability, good biocompatibility and sub-nanometer size. Such novel properties make metal NCs an ideal nanomaterial for promise applications in biological analysis and imaging, environmental monitoring, industrial catalysis and electronic devices.

Fluorescent metal NCs have been developed as a new class of fluorophores. Current fluorescence applications mostly involve organic fluorophores, semiconductor quantum dots (QDs) [18] or fluorescent proteins [19]. Organic fluorophores exist in a wide range of chemical structures and spectral properties; however, they are prone to photobleaching, which may limit their many applications. Semiconductor QDs are fluorescence-tunable and photostable; however, their large physical size may hinder their use as fluorescent reporters of binding events, which may compromise their use for in vivo applications. Fluorescent proteins are genetically encodable, which can be produced by the cells and organisms themselves. Consequently, there is no need for additional labeling and/or other chemical procedures in studies of live cells and organisms. Metal NCs show strong photoluminescence, combined with good photostability and high emission rates, and have a sub-nanometer size and size or scaffold-dependent tunable fluorescence. They have an appealing set of features that complements the conventional fluorophores. These properties establish them as a new class of ultra-small, biocompatible fluorophores for applications as biological labels or optoelectronics emitters.

It should be pointed out that several excellent review papers have been dedicated to the metal NCs [8—14]. However, these previous reviews focused on either one kind of metal or metal NCs with actually a wide size range and different focusing aspects. In this article, we will mainly summarize recent advances in the synthesis, special properties and the applications of metal NCs (Au, Ag, Cu, etc.) as new fluorescent probes for analytical sensing and biological imaging. In the final section, we will give a brief outlook on the challenges and opportunities for future metal NCs research.

Energy levels: from bulk metals to nanoclusters

The physical and chemical properties of metals depend greatly on their size. With the varying size, their behaviors go through several noticeable transitions (Fig. 1) [17]. Bulk metals are good optical reflectors and electrical conductors. The electronic situation in bulk metals is characterized by the existence of energy bands. They result from the combination of an infinite number of energetically very similar orbitals. The valence band contains the relevant valence electrons. The conduction band of metals overlaps to some extent with the valence band and so becomes partially occupied with electrons. These electrons are finally respon-

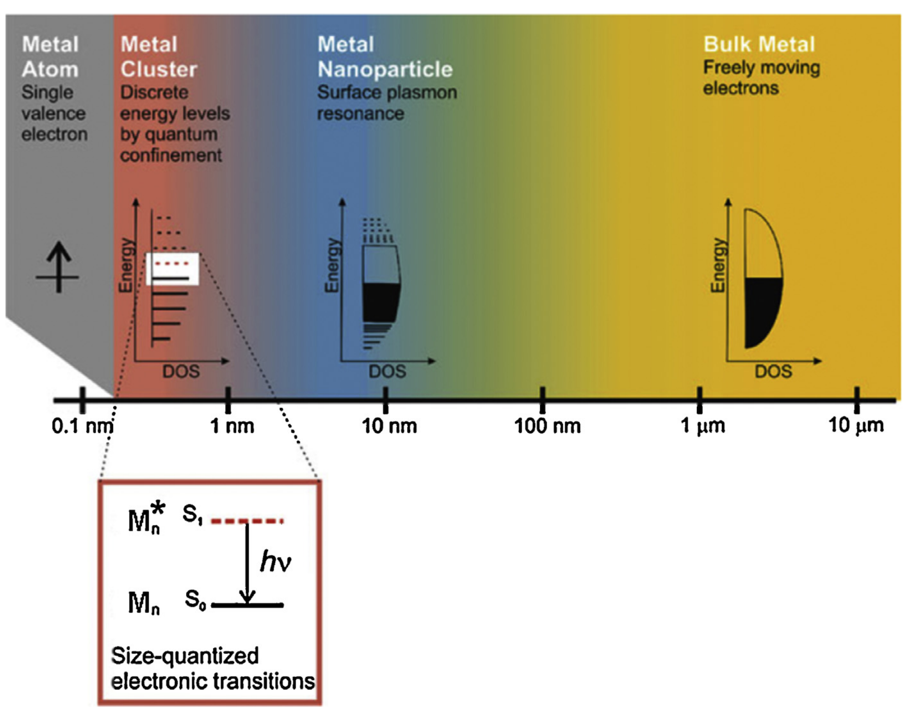

Figure 1 The effect of size on metals. Whereas bulk metal and metal nanoparticles have a continuous band of energy levels, the limited number of atoms in metal nanoclusters results in discrete energy levels, allowing interaction with light by electronic transitions between energy levels. Metal nanoclusters bridge the gap between single atoms and nanoparticles.
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