Nano-electronics and spintronics with nanoparticles

S Karmakar¹, S Kumar¹, R Rinaldi¹,² and G Maruccio¹,³
¹NNL Istituto Nanoscienze-CNR, Lecce, Italy
²Department of Innovation Engineering, University of Salento, Via Arnesano, 73100, Lecce, Italy
³Physics Department, University of Salento, Via Arnesano, 73100, Lecce, Italy

Email: shilpi.karmakar@unisalento.it, giuseppe.maruccio@unisalento.it

Abstract. We review the current research on nanodevices with nanoparticles which present unique challenges in both the realization of well-controlled interfaces at the nanoscale and the ability to adequately characterize their electrical properties. In particular, we discuss the fabrication and electrical characterization of such nanodevices with special attention to devices based on metal and magnetic nanoparticles.

1. Introduction

Over the past decades, progress in miniaturization of electronic devices has played a powerful role in the continuous technological development, increasing the performance and speed of the information exchange. Advances in nanolithographic fabrication techniques and chemical methods like self-assembly made possible to scale down the devices to few tens of nanometers or less [1-3]. This has already made a great impact on the performance of traditional semiconductor circuits and opened up new possibilities based upon quantum effects. The same has led to the birth of a new field called single electronics where the exploitation of charging effects in tunnel junctions with nanoscale islands allows transport/control of individual charge carriers [4]. In metals these carriers are electrons while in the case of superconducting materials at low temperature, they can be Cooper pairs.

In this review, we summarize recent studies of nanoelectronics with metallic and magnetic nanoparticles (NPs) with a view towards future applications and spintronics. Vertical electron transport has been studied extensively to elucidate functionalities like non-linear I–V characteristics and nanoscale ohmic contacts. The most prominent amount of the published work relies heavily on scanning probe microscopy [5-16]. However for practical applications, the deposition of clusters/single nanoparticles within nanojunctions fabricated on insulating surfaces is required. Patterning or positioning can be accomplished through self-assembly of the nanocrystals or could either be achieved via electrostatic interactions at the cluster-substrate interface [17, 18]. The ability to functionalize a nanoparticle network with linking molecules provides appealing low cost design flexibility.
2. Single Electron Transistors

One of the most promising nanoelectronic devices is the single-electron transistor (SET) [4], where single-electron charging effects are used to precisely control the charging of a conducting island by individual electrons. Electrons are transferred to the island from source and drain terminals by tunnelling across potential barriers and the charging process can be controlled by a gate terminal (Fig. 1). The SET has the advantages of very low power consumption and better immunity from statistical charge fluctuation, compared to conventional devices. In the past two decades SETs made from metallic nanoparticles have attracted extensive research interest for their potential applications in future nanoelectronics viz. integrated circuits and supersensitive electrometers [19-23].

The practical application of SET requires room temperature operation and silicon process compatibility. For room temperature operation, the single-electron charging energy of the island, \( E_C = \frac{e^2}{2C_{TOT}} \) (\( C_{TOT} \) is the total island capacitance and \( e \) is the elementary electronic charge) must be large compared to the thermal energy \( \sim k_B T \approx 26 \text{ meV} \) (\( k_B \) is Boltzmann's constant and temperature \( T = 300 \text{ K} \)). Therefore, the value of the \( C_{TOT} \) must be \( \sim 1 \text{ aF} \) or less and in practice this implies that the charging island must be \(<10 \text{ nm}\) in size. In addition, electrons must be localized on the island, which requires a large tunnel barrier resistance as compared to the quantum resistance \( R_Q \approx 26 \text{ kΩ} \) at the operating temperature. The use of very small metallic islands also improves the charge sensitivity of the electrometers beyond the operational temperature range.

For SET fabrication usually chemically synthesized colloidal nanocrystals are preferred since they have smaller and more uniform sizes, while another advantage is their potential for controlled assembly. However, integrating individual nanoparticles into devices and gating them effectively is extremely challenging. This is due to the challenges in (i) fabricating nanometer-spaced electrodes and (ii) the precise placement of the nanoparticles between the electrodes. Several techniques have been developed for the fabrication of SETs using metal nanoparticles.

![Figure 1](image.png)

**Figure 1.** (a) Schematics design of a single nanoparticle between two metal electrodes. (b) Equivalent electrical circuit of a single electron transistor.

3. Nanojunction fabrication

There are mainly two approaches for connecting nanocrystals between electrodes. The first one is to make top-contact junctions, which includes scanning tunnelling microscopy (STM) [6-14] and conducting atomic force microscopy (AFM)) [15, 16]. Although very useful for fundamental investigations, this strategy is, however, far from practical applications and makes difficult to introduce a third gate electrode. The second approach which overcomes these limitations is to fabricate devices based on nanogap electrodes [17], a strategy potentially downscalable opening the way to realize integrated circuits. In the last two decades, prominent efforts has been made to develop
novel fabricating techniques for nanodevice realization. Several effective and novel methods of fabricating nanogap electrodes with controlled spacing have been reported, including electron-beam lithography [24-26], electromigration [27-29], mechanical break junctions [30, 31], electrochemical plating [32], focused ion beam lithography [33], shadow mask evaporation [34], scanning probe and atomic force microscopy lithography [35], on-wire lithography [36, 37], etc. Different methods are frequently combined as well to obtain a desired nanocircuit arrangement.

3.1 Mechanical Controllable Break Junctions (MCBJ)

This method was first adopted by Reed et al. [31] to fabricate nanogap electrodes, which yielded electrodes with a separation of few nanometers. In this process, a notched metallic wire is generally glued to an elastic substrate (Fig.2 (a)), which serves as the bending beam. The substrate is bent by pushing its centre with a driving rod and consequently the notched wire is fractured, after which an adjustable tunnelling gap can be established. The surfaces can be brought together again, and the distance can be controlled by a piezoelectric element. The breaking process is mostly conducted under low temperature and high vacuum conditions, and this guarantees two atomically clean surfaces. The MCBJ technique is very stable and the contact separation can be continuously adjusted under the control of an ultrafine piezoelectric component without polluting the junction [38-40]. Although the MCBJ method is really useful for fundamental investigation, it is not facile to fabricate highly integrated nanojunction arrays because of the constraint of the piezoelectric components, and it is difficult to build devices with three or even more electrodes or electrodes with larger separation.

3.2 Electrochemical Deposition for Nanogap Electrodes

Electrochemical deposition methods, combined with standard lithography techniques, provide a simple, accurate, and more reproducible way for the fabrication of the nanogap electrodes [41-45]. The initial electrodes with a relatively large gap are fabricated by conventional lithography techniques on substrates. The gap is then narrowed down to few nanometers by electrochemically depositing specific atoms from a solution onto the lithographically defined electrodes (Fig 2(b)). This method can conveniently prepare gaps that range from several angstroms to 10 nm. Another advantage is the ability to fabricate asymmetric nanogap electrodes [46, 47]. Chen et al. have recently reported a method for fabricating heterometallic nanogaps, which are made of two different metal nanorods separated by a nanometer-sized gap [48].

3.3 Oblique Angle Shadow Evaporation

The oblique angle shadow evaporation method is often combined with optical and electron-beam lithography to define metal leads [49, 34, 50, 51]. By suspending the mask above the substrate and controlling the direction of the deposition angle with respect to the surface normal, features with sizes smaller than those of the masks can be obtained (Fig. 2(c)). Gap electrode separations smaller than 10 nm can be reproducibly fabricated in this way [51]. Moreover, the gap size could also be adjusted by changing stepwise the tilt angle. Sun and coworkers [50] have achieved the fabrication of large nanojunction arrays with gaps as small as 3 nm and successfully applied them to electrical studies on nanocrystals.

3.4 Electromigration and Electrical Breakdown Methods

Electromigration has also been utilized successfully to fabricate nanogap electrodes for nanodevices [52, 27-29, 53-55]. The flow of a large current density or application of a dc voltage to a thin metal wire predefined by electron-beam lithography causes the electromigration of metal atoms and eventual breakage of the nanowire [54]. This process can yield a stable electrode separation of 1 nm with high efficiency (Fig 2(d)) and is especially advantageous to prepare three-terminal devices and electrode arrays [29]. Recently, Xiang and co-workers [53] have reported the fabrication of sub-5 nm
reconnectable nanogaps by a reproducible and automated, feed-back controlled electromigration process. By applying a simple voltage ramp, nanogaps were electrically reconnected many times. Ittah et al. have [56] reported fabrication of metal quantum point contacts (MQPCs), with dimensions comparable to the de Broglie wavelength of conducting electrons, revealing ballistic transport of electrons and quantized conductance values in the range of $1-4G_0$ ($G_0 = 2e^2/h$), with a contact stability of hours at room temperature. The contacts can be deterministically switched between conductance values, or reform in case they break, using voltage pulses. However the electromigrated nanojunctions have to face two major issues. The first one is the role of temperature in the breaking of a nanowire. The other major problem is the possible metal debris left behind in the gap after fabrication, which can interfere with the introduction and the following studies of transport through metal nanoislands (or other nanosystems of interest) [57].

3.5 Template-based methods

Haztor and co-workers [58] had presented a method of constructing 30-nanometer structures in close proximity with precise spacings that uses the step-by-step application of organic molecules and metal ions as size-controlled resist on predetermined patterns, such as those formed by electron-beam lithography. The organic molecules serve as a ruler for scaling down a larger “parent” structure. After metal deposition and lift-off of the organic multilayer resist, an isolated smaller structure remains on the surface. This approach was first used to form thin parallel wires (15 to 70 nanometers in width and 1 micrometer long) of controlled thickness and spacing. Since then this method has been readily developed further and has been in use for the realization of nanogap electrodes [59-61].

3.6 Large scale nanojunction arrays by optical lithography and wet etching

Fabrication of large arrays of nanojunctions by optical lithography and wet etching of an AlGaAs/GaAs quantum-well (QW) structure was first reported by Krähne et al. [62]. The main advantage in this method is that the thickness of the quantum well and of the deposited metal layer controls the nanogap size with sub-nanometer precision, without the need of expensive e-beam systems [63, 64]. However, this innovative approach to nanoscale electronics had some intrinsic drawbacks: because of the bulk leakage currents through the semiconductor substrate under ambient conditions, such nanojunctions could be only potentially employed at cryogenic temperatures and in the dark. Later Maruccio et al. [65-67] significantly improved this method by means of selective oxidation of the two AlGaAs barriers above and below the QW in order to reduce the leakage current through the semiconductor layers and thus extended the functionality of these nanoscaled devices to room temperature [Fig 2 (e)]. Typical molecular/nanocrystal features, such as Coulomb blockade, Coulomb staircase, rectification, negative differential resistance (NDR) and other magnetoelectrical behaviour were successfully studied on these systems [62, 65]. This method provides a simple, highly reproducible, and economical way of fabricating metallic electrodes separated on the nanoscale and it is especially promising for the construction of large arrays of nanojunctions.

3.7 Other fabrication methods

Recently there has been a hunt for other fabrication methods to produce nanogap devices like focused ion beam (FIB) lithography [33]. Because the minimum diameter of a FIB is relatively small (approx. 5–20 nm) and the proximity effects are much less than for electron beam lithography, a FIB could be a reliable way to prepare nanogap electrodes with the advantages of maskless nanostructuring, good reproducibility and high speed of the nanogap cutting. Similar to the FIB technique, oxidative plasma can also be utilized for elaborate ablation of pre-patterned nanowires to form nanogap electrodes [68, 69]. Other methods include scanning probe lithography (SPL) where a microscopic or nanoscopic stylus is moved mechanically across a surface to form a pattern [70]. Because the sharp tips of a scanning probe microscope with a radius smaller than 10 nm can be neatly and controllably manipulated across the substrate, SPL can be utilized to construct nanogap electrodes [71].
Positioning the nanoparticles

A prerequisite for future applications using nanoparticles as functional entities is control of their arrangement, since they typically require to be located at appropriate substrate locations in order to be connected among themselves and to the outside world. This is still an extremely challenging goal and different approaches are possible to accomplish the controlled positioning.

Molecular, physical, or electrostatic templates can be used for precise positioning of the active nanomaterials. Self-assembled monolayers (SAMs) are ordered assembly of organic molecules that spontaneously form on the surface of metals, metal oxides, and semiconductors. The surface properties of SAMs can be modulated by selecting appropriate tail groups or modifying them with various techniques [72-74]. Then, the substrate surface functionalized with localized patterns of SAMs can serve as template onto which nanoscale or microscale building blocks are selectively attached (Fig 3 (a,b,f)). Physical templates includes holes and ditches that can be fabricated on a substrate surface using lithography and etching/lift-off techniques [75]. The general methods are capillary force driven placement into physical templates, where the capillary force is exploited to place individual nanoscale materials blocks into trenches or holes (Fig. 3c) [75]. Another example of the attaching strategy is dip-pen nanolithography (DPN), which was pioneered by Mirkin and co-workers [76, 77] and uses an atomic force microscope (AFM) tip to transport adsorbed molecules to precise substrate locations with resolution as high as a few tens of nanometers. Electrostatic interactions between a charged substrate and nanoscale building blocks can be also employed for controlled positioning by letting the building blocks interact with electrostatic templates created using microcontact printing, electron beams, ion beams and scanning probe microscopes [76, 77]. Placement via dielectrophoresis exploits another completely different approach, consisting of
motion of uncharged objects in a liquid dielectric medium under a non-uniform electric field [78-81], which can be successfully controlled by a suitable design. Recently [81], a lot of efforts has been made to utilize dielectrophoresis for controlled positioning of nanomaterials for realization of nanoelectronic devices or sensors (Fig. 3 (d,e)). This process is also suitable for placement of the building blocks onto addressable locations on a large scale.

Figure 3. (a) AFM images of nanoscale gaps after nanoparticle self-assembly. Reproduced with permission from Chu et al., J. Am. Chem. Soc., 129 (2007) 2287 Copyright © 2007 ACS (b) SEM image of a nanodevice with immobilized nanoparticles. Reproduced with permission from Kuemmeth et al., Nano Lett., 8 (2008) 4506 Copyright © 2008 ACS. (c) Low-magnification and high-magnification SEM images of single 50-nm Au nanoparticles organized between nanojunctions. Reproduced with permission from Cui et al. Nano Lett., 4 (2004) 1093 Copyright © 2004 ACS. (d, e) Typical DEP assembled gold nanoparticle structures between different electrodes. Fused or melted nanoparticle interconnect and half-melted/unmelted nanoparticle interconnect. Reproduced with permission from Xiong et al., Appl. Phys. Lett. 91 (2007) 063101 Copyright © 2007 AIP. (f) Mesa nanojunctions with immobilized DNA probes after hybridization with gold NPs functionalized with complimentary DNA strands: a number of nanoparticles immobilized on the electrodes and close to the gap are visible. Reproduced with permission from Maruccio et al., Analyst 134 (2009) 2458 Copyright © 2009 The Royal Society of Chemistry.

5. Transport and magnetotransport through metal and magnetic nanoparticles

The focus of this review is the transport behaviour of nanocrystals or quantum dots, which are quasi-zero-dimensional nanostructure systems and whose electronic states are completely quantized. The confinement of carrier motion in these structures is imposed in all three spatial directions, resulting in a discrete spectrum of energy levels as in an atom or molecule. This analogy is further reinforced by the presence of atom-like wavefunction in semiconductor quantum dots and nanocrystals [10-12]. In these systems the introduction of even a single electron is sufficient to dramatically change the transport properties due to the charging energy associated with this extra electron. One of the main consequences is to give rise to Coulomb blockade of transport, where conductance oscillations are found on addition or subtraction of a single electron from a quantum dot [4, 5]. In metal nanoparticles, the resulting transport behaviour can be analyzed purely in terms of classical charging. On the other hand, the study of single-electron tunnelling in semiconductor quantum dots and nanoparticles allows the observation of new phenomena, not observable in their metallic counterparts, which arise from the fact that strong quantum confinement in the low-density limit leads to quantized energy levels whose energy scales can be comparable to the Coulomb charging energy [5-12, 82, 83].
5.1 Basic Principle

The equivalent electrical circuit which reveals the properties of single-electron tunnelling comprises of only one Coulomb island and two leads/electrodes (Figure 1). A third gate electrode, capacitatively coupled to the island, may be added to this double tunnel junction system [84, 5]. Applying a bias voltage between the electrodes, may cause either sequential transfer of electrons into and out of the central island or no charge transport at all. The result depends on the drain-source voltage $V_{ds}$ (or $V$) as well as on the voltage $V_g$ applied to the gate electrode. The total energy change of the system $\Delta E$ while one electron is tunnelling in one of the junctions consists of the charging energy of the island itself as well as of the work done by the voltage source i.e. $\Delta E = e^2/(2C) \pm eV/2$. This means that for $-e/C \leq V \leq e/C$ the change of energy is positive. Hence, electron tunnelling would only increase the energy of the system, and this transition does not occur if the system cannot take some energy from its environment, i.e., when the temperature is assumed to be low enough. Therefore there is a Coulomb blockade state in the single-electron transistor when the voltage $V$ is within the interval given previously and $V_g$ is zero. Outside this range, the device conducts current by means of sequential tunnelling of electrons. If a finite gate voltage $V_g$ is applied, an additional term has to be included in the energy, because of additional polarization of the island capacitively/electrostatically induced by the gate. The result of this consideration is illustrated in Figure 4(a), where the $V$ vs $V_g$ diagram is shown with its typical CB diamonds. The behaviour of the transistor outside the Coulomb blockade region also shows the single-electron peculiarities, especially for the case of a highly asymmetrical junction, where $R_1 >> R_2$, and $C_1 >> C_2$. In Figure 4(b), one can see the I(V) characteristics with a step-like structure fading with decrease of $V$. This so-called Coulomb “staircase” results from the fact that an increase in the total energy increases the number of channels for tunnelling in a step-like manner, allowing an increasingly larger number of electrons to be present on the island. Another demonstration of charging effects in the SET is the offset of the linear asymptotes by $e/C$. The dependence of the transistor current on the gate voltage opens up the opportunity to fabricate a sensitive device which measures either directly an electric charge on the island or the charge induced on the island by the charges collected to the gate, i.e. a highly sensitive electrometer. The sensitivity of such an electrometer, which has already been reached in practice, is of the order of parts of electronic charge, exceeding by far the charge sensitivity of conventional devices [85-87].

![Figure 4](image)

**Figure 4.** (a) Idealized periodic rhombic pattern showing the Coulomb blockade region on the plane of voltages $V$ and $V_g$. A transistor conducts only outside the rhombic-shaped regions. $n$ is the number of extra electrons in blocked state trapped in the island. (b) The dependence of the time-averaged current $I$ vs $V$ for an asymmetrical single-electron transistor ($R_1 >> R_2$, and $C_1 >> C_2$).
5.2 Experiments on Single-Electron Tunnelling in Nanoparticles

The theoretical background of SET has found its first experimental manifestation in lithographically fabricated capacitors, having typically capacitances in the pF range [17, 25, 37]. Because of their extremely low charging energies, they needed to be cooled down to very low temperatures for single-electron operation. Furthermore, such a capacitor is typically driven at an operating voltage of 10–100 mV, which leads to the storage of a few tens of thousands of electrons per charging. The utilization of SET events for applications up to the range of room temperature leads to the necessity of decreasing the junction capacitance, at least by two orders of magnitude. As already discussed in above sections, this can be realized by the use of ligand-colloidal metal nanoparticles in a size range of few nanometers. These nanoparticles are stabilized by organic molecules, which surround the metal cores and play the role of an insulating layer in contacts with neighbouring clusters as well as with conducting objects.

5.2.1 Au nanoparticles

Most of the studies in existing literature on SET incorporating single nanoparticles or island involve gold nanocrystals [80, 88-98, 23, 99-103]. Ralph [104] and co-workers observed well-defined electronic states in a Au nanoparticle using tunnel junctions formed from SAMs at low voltages and mK temperatures. Sato et al. [91] found that a sub-monolayer of gold colloidal particles deposited by using an aminosilane adhesion agent (i.e., 3-2-aminoethylamino propyltrimethoxysilane) transform themselves into chains consisting of a few gold colloidal particles probably linked by alkane chains derived from the employed dithiol molecules. These particle chains were formed on SiO2 substrates with source, drain, and gate metal electrodes defined by electron beam lithography in order to bridge the source-drain gap with a multi-tunnel junction (with the chain itself). The electron conduction through the chain exhibited a clear Coulomb staircase and periodic conductance oscillations as a function of gate voltage (Fig. 5). These measurement results corresponded closely to simulations based on the orthodox theory [103]. Kim et al. [102] have recently observed Coulomb blockade in the field-emission current of a metallic island between two electrodes freely suspended by thin tunnelling barriers with a third electrode serving as a gating contact to trace the Coulomb staircase of the device. The results were in very good agreement with a theoretical model based on orthodox Coulomb blockade and field emission theory. Similarly, in most of the nanojunctions with metal nanoparticles, Coulomb blockade has been observed with the orthodox theory being the tool to understand the inter-component contribution to the SET [23, 105, 93, 98].

However there are reports [105, 100, 101] where the results could not be explained completely with the orthodox theory. Khosousi et al. [100] fabricated single-electron devices by alkanedithiol assisted self-assembly and found a fivefold discrepancy in single-electron charging energies contrary to predictions of the orthodox model for double tunnel junction devices, determined by Coulomb blockade (CB) voltage thresholds in current-voltage measurements versus those determined by an Arrhenius analysis of conductance in the CB region. The energies do, however, scale with particle sizes, consistent with single-electron charging phenomena. They have suggested that the discrepancy is caused by a multibarrier junction potential that leads to a voltage divider effect. Temperature and voltage dependent conductance measurements performed outside the blockade region are consistent with this picture. Kuemmeth et. al. [105] instead have explained their discrete energy levels of individual gold nanoparticles in a SET with monolayers of organic molecules serving as tunnel barriers by means of random-matrix-theory [106]. In particular, they have shown that the nanoparticles are non-magnetic and have spectra in good agreement with predictions taking into account strong spin-orbit coupling. Also recently, Govor and co-workers [101] have bridged a pair of gold electrodes with a single nanoparticle stabilized with citrate molecules. The device exhibited pronounced linear current–voltage characteristics with switching of the current at a fixed bias voltage ascribed to conformational changes in the citrate molecules induced by charge transfer to the molecules.
5.2.2 Other metallic, magnetic and semiconducting nanoparticles

Although the majority of the existing literature deals with studies of Coulomb blockade and SET operation with gold nanoparticles, there is also a considerable attention to other systems like other metallic nanoparticles [107-110], magnetic nanocrystals [111-114] and semiconducting quantum dots [115-121]. Ralph et al. [107] investigated the spectrum of discrete electronic states in single, nm-scale Al particles incorporated into a new kind of tunnelling transistor. The addition of the gate allowed (i) measurements for different numbers of electrons in the same particle, (ii) a greatly improved resolution and qualitatively new results for spectra within superconducting particles, and (iii) detailed studies of the gate-voltage dependence of the resonance level widths, which have directly demonstrated the effects of non-equilibrium excitations. Wolf and co-workers [115] have instead very recently described an approach to fabricate single-electron devices consisting of a silicon quantum dot (QD) between metallic leads. The devices showed Coulomb blockade corresponding to a charging energy of 19.4 meV and could be switched from a non-conducting to a conducting state giving rise to Coulomb diamonds. The behaviour was found to be well reproduced by a numerical orthodox theory calculation similar to metallic systems. Recently, Hai and co-workers [116] have reported that spin relaxation can be strongly suppressed for extra electrons confined in a ferromagnetic-metal nanoparticle, resulting in a very long spin-relaxation time of up to 10 µs (Fig. 6). They have suggested that such a long spin-relaxation time could be useful in nanoscale metallic spintronic devices, such as spin memory and single electron spin transistors.

**Figure 5.** (a) Drain current $I_D$ vs source-drain voltage $V_{SD}$ characteristics at various gate voltages $V_G$ and (b) $I_D-V_G$ characteristics at various source-drain voltages $V_{SD}$ of a three-dot gold colloidal particle transistor measured at 4.2 K. Reproduced with permission from Sato et al., J. Appl. Phys. 82 (1997) 696 Copyright © 1997 AIP.

**Figure 6.** (a) Schematic of a device structure with a MnAs nanoparticle as a ferromagnetic island. (b) TMR = $(R_{H=0} - R_{H=10\, \text{Ko}})/R_{H=10\, \text{Ko}}$ as a function of $V_{dd}$. TMR oscillation was observed up to 0.6 V. Reproduced with permission from Hai et al., Nat. Nano, 5 (2010) 593 Copyright © 2010 Macmillan Publishers Limited.
The use of magnetic nanoparticles or ferromagnetic leads with metal nanoparticles is stimulating a new field of research, often referred as nanospintronics, since the SET characteristics exhibits even more interesting and potential phenomena with magnetic interactions due to the interplay between spin polarized and single electron tunnelling [122, 123]. Magnetotransport through NPs has been investigated both in vertical structures within granular systems prepared by sputtering or physical evaporation methods [124, 125] and within superlattices made of self-assembled colloidal NCs [126-129]. In 2000, Black et al. reported spin-dependent electron transport in periodic arrays of cobalt nanocrystals with 10% magnetoresistance [130]. An enhanced spin accumulation and magnetoresistance oscillations with periodical sign changes as a function of bias voltage were instead observed in magnetic nanoparticles by Yakushiji et al. [125] as shown in Fig 7 (a-b). Recently Bernard-Mantel and co-workers [131] have found anisotropic magneto-Coulomb effects and magnetic single-electron-transistor action in a single nanoparticle bridging magnetic electrodes. They have demonstrated that a significant magneto-Coulomb effect can be induced by conventional magnetic electrodes and mimic spin-valve magnetoresistance (Fig. 7c-d). They also suggested that the magnetic electrode could act as the gate electrode leading to a ferromagnetic single-electron transistor with only two terminals. On the other hand, Birk et al.[132] demonstrated a spin-accumulation mechanism of magnetoresistance in an Al nanoparticle with a single ferromagnetic contact. The angle between the accumulated magnetic moment and the magnetization changes with the applied magnetic field, causing magnetoresistance. They concluded that this mechanism needs to be considered when interpreting results in spintronics involving discrete energy levels.

**Figure 7.** (a) Current–voltage curves and (b) V dependence of the tunnel magnetoresistance, showing oscillation with alternate sign change with applied bias voltage. Reproduced with permission from Yakushiji et al., Nat. Mat., 4 (2005) 57 Copyright © 2005 Macmillan Publishers Limited. (c) Schematic representation of a structure containing a 2D assembly of nanoparticles embedded in a tunnel barrier and connected to top/bottom Co electrodes. (d) Low-bias I–V characteristics at T=1.5 K for the high-resistance state at 500 Oe (red), the low-resistance state at −100 Oe (black) and the corresponding simulations. The inset represents the resistance versus magnetic field measured at a voltage of 14mV. Reproduced with permission from Bernard-Mantel et al., Nat. Phys. 5 (2009) 920 Copyright © 2009 Macmillan Publishers Limited.
Conclusion

Irrespective of their type, nanoparticles generally result in interesting phenomena because of quantum confinement and unique electronic properties which are the basis for future device applications. However the final outcome of this exploration depends on the environment the nanoparticles are experiencing in the nanodevices e.g. the contacts, the protective layer and the assembly. Development in the synthesis of metal nanoclusters and colloidal nanoparticles has resulted in impressive progress in this direction. Chemical processes are also very useful to scale up for industrial purposes. Self-assembly techniques in particular have been so much improved that nowadays semiconductor as well as metal or magnetic nanoparticles can be arranged in perfectly ordered assemblies of remarkable extensions [133]. Much advancement has been accomplished in understanding charge transport phenomena through these nanostructures. The electrical properties of metal nanoparticles are mainly determined by the Coulomb charging energy, and the phenomena can, in general, be understood in terms of single electron tunnelling on the basis of the orthodox theory. It appears that engineered metal nanoparticles in SETs could be a potential approach to further developments of nanoelectronics beyond CMOS technologies in the future. The use of magnetic nanoparticles or ferromagnetic leads then provides advance opportunities in the emerging field of nanospintronics.

Acknowledgements

This work was financially supported by the SpiDME European project (6th Framework Program, NEST, Project No. 029002) and by the Italian Ministry for Foreign Affairs through the bilateral project “Spintronic devices for mass-scale electronics” between Italy and India.

References

[1] Bratton D, Yang D, Dai J and Ober C K 2006 Polymers for Advanced Technologies 17 94
[2] Li T, Hu W P and Zhu D B 2010 Adv. Mater. 22 286-300
[3] Maruccio G and Bramanti A 2009 Nanobioelectronics – for Electronics, Biology, and Medicine, ed A Offenhäusser and R Rinaldi: Springer New York) pp 139-66
[4] Likharev K K 1999 Proceedings of the IEEE 87 606-32
[5] Maruccio G and Wiesendanger R 2010 Quantum Materials, Lateral Semiconductor Nanostructures, Hybrid Systems and Nanocrystals, ed D Heitmann: Springer Berlin Heidelberg) pp 183-216
[6] Banin U, Cao Y W, Katz D and Millo O 1999 Nature 400 542-4
[7] Liljeroth P, van Emmichoven P A Z, Hickey S G, Weller H, Grandidier B, Allan G and Vanmaekelbergh D 2005 Physical Review Letters 95 086801
[8] Grandidier B, Niquet Y M, Legrand B, Nys J P, Priester C, Stiévenard D, Gérard J M and Thierry-Mieg V 2000 Physical Review Letters 85 1068
[9] Millo O, Katz D, Cao Y W and Banin U 2001 Physical Review Letters 86 5751-4
[10] Maltezopoulos T, Bolz A, Meyer C, Heyn C, Hansen W, Morgenstern M and Wiesendanger R 2003 Phys. Rev. Lett. 91 196804
[11] Maruccio G, Janson M, Schramm A, Meyer C, Matsui T, Heyn C, Hansen W, Wiesendanger R, Rontani M and Molinari E 2007 Nano Lett 7 2701-6
[12] Maruccio G, Meyer C, Matsui T, Talapin D V, Hickey S G, Weller H and Wiesendanger R 2009 Small 5 808-12
[13] Ohnishi H, Kondo Y and Takayanagi K 1998 Nature 395 780-3
[14] Fallahi P, Bleszynski A C, Westervelt R M, Huang J, Walls J D, Heller E J, Hanson M and Gossard A C 2005 Nano Lett. 5 223-6
[15] Agrait N, Yeyati A L and van Ruitenbeek J M 2003 Physics Reports-Review Section of Physics Letters 377 81-279
[16] Morita T and Lindsay S 2007 Journal of the American Chemical Society 129 7262
[17] Li T, Hu W P and Zhu D B Advanced Materials 22 286-300
[18] Lu W and Lieber C M 2007 Nature Materials 6 841-50
[19] Fulton T A and Dolan G J 1987 Phys. Rev. Lett. 59 109
[20] Devoret M H, Esteve D and Urbina C 1992 Nature 360 547-53
[21] Devoret M and Glattli C 1998 Physics World 11 29-33
[22] L. Feldheim D and D. Keating C 1998 Chemical Society Reviews 27 1-12
[23] Ray V, Subramanian R, Bhadrachalam P, Ma L-C, Kim C-U and Koh S J 2008 Nat Nano 3 603-8
[24] Fischbein M D and Drndic M 2006 Appl. Phys. Lett. 88 063116-3
[25] Fischbein M D and Drndic M 2007 Nano Lett. 7 1329-37
[26] Maruccio G, Visconti P, D'Amico S, Calogiuri P, D'Amone E, Cingolani R and Rinaldi R 2003 Microelectron. Eng. 67-8 838-44
[27] Strachan D R, Smith D E, Johnston D E, Park T H, Therien M J, Bonnell D A and Johnson A T 2005 Appl. Phys. Lett. 86 043109
[28] Esen G and Fuhrer M S 2005 Appl. Phys. Lett. 87 263101
[29] Johnston D E, Strachan D R and Johnson A T C 2007 Nano Lett. 7 2774-7
[30] Muller C J, van Ruitenbeek J M and de Jongh L J 1992 Physica C: Superconductivity 191 485-504
[31] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 Science 278 252-4
[32] Morpurgo A F, Marcus C M and Robinson D B 1999 Appl. Phys. Lett. 74 2084-6
[33] Tseng A A 2005 Small 1 924-39
[34] Egger S, Ilić A, Fu Y T, Chongsthathien J, Kang D J and Welland M E 2005 Nano Lett. 5 15-20
[35] Notargiacomo A, Foglietti V, Cianci E, Capellini G, Adami M, Faraci P, Evangelisti F and Nicolini C 1999 Nanotechnology 10 458-63
[36] Qin L D, Park S, Huang L and Mirkin C A 2005 Science 309 113-5
[37] Qin L D, Jang J W, Huang L and Mirkin C A 2007 Small 3 86-90
[38] van Ruitenbeek J M, Alvarez A, Pineyro I, Grahnmann C, Joyce P, Devoret M H, Esteve D and Urbina C 1996 Review of Scientific Instruments 67 108-11
[39] Champagne A R, Pasupathy A N and Ralph D C 2005 Nano Lett. 5 305-8
[40] Christian A M and et al. 2008 New Journal of Physics 10 065008
[41] Kervennic Y V, Van der Zant H S J, Morpurgo A F, Gurevich L and Kouwenhoven L P 2002 Appl. Phys. Lett. 80 321-3
[42] Kervennic Y-V and Kubatkin S 2009 Small 5 2541-4
[43] Boussaad S and Tao N J 2002 Appl. Phys. Lett. 80 2398-400
[44] Qing Q, Chen F, Li P, Tang W, Wu Z and Liu Z 2005 Angewandte Chemie International Edition 44 7771-5
[45] Jemmy S and et al. 2010 Journal of Micromechanics and Microengineering 20 045016
[46] Kashimura Y, Nakashima H, Furukawa K and Torimitsu K 2003 Thin Solid Films 438-439 317-21
[47] Luis De Los Santos V and et al. 2010 Nanotechnology 21 445304
[48] Chen X, Yeganeh S, Qin L, Li S, Xue C, Braunschweig A B, Schatz G C, Ratner M A and Mirkin C A 2009 Nano Lett. 9 3974-9
[49] Yoiichi O and et al. 2004 Nanotechnology 15 1639
[50] Sun L F and et al. 2005 Nanotechnology 16 631
[51] Philipp G, Weimann T, Hinz P, Burghard M and Weis J 1999 Microelectronic Engineering 46 157-60
[52] Strachan D R, Smith D E, Fischbein M D, Johnston D E, Guiton B S, Drndić M, Bonnell D A and Johnson A T 2006 Nano Lett. 6 441-4
[53] Xiang C, Kim J Y and Penner R M 2009 Nano Lett. 9 2133-8
[54] Heersche H B, Lentsch nig G, O'Neill K, van der Zant H S J and Zandbergen H W 2007 Appl. Phys. Lett. 91 072107-3
[55] Park H, Lim A K L, Alivisatos A P, Park J and McEuen P L 1999 Appl. Phys. Lett. 75 301-3
[90] Yamaguchi H, Terui T, Noguchi Y, Ueda R, Nasu K, Otomo A and Matsuda K 2010 Appl. Phys. Lett. 96 103117-3
[91] Sato T, Ahmed H, Brown D and Johnson B F G 1997 Journal of Applied Physics 82 696-701
[92] Novembre C, Guerin D, Lmimouni K, Gamrat C and Vuillaume D 2008 Appl. Phys. Lett. 92 103314-3
[93] Negishi R, Hasegawa T, Terabe K, Aono M, Tanaka H, Ogawa T and Ozawa H 2007 Appl. Phys. Lett. 90 223112-3
[94] Azuma Y, Yasutake Y, Kono K, Kanehara M, Teranishi T and Majima Y 2010 Japanese Journal of Applied Physics 49 3
[95] Nishino T and et al. 2010 Nanotechnology 21 225301
[96] Wu C S, Chen C D, Shih S M and Su W F 2002 Appl. Phys. Lett. 81 4595-7
[97] Huang S, Tsutsui G, Sakaue H, Shingubara S and Takahagi T 2000 Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures 18 2653-7
[98] Persson S H M, Olofsson L and Gunnarsson L 1999 Appl. Phys. Lett. 74 2546-8
[99] Gao B and et al. 2009 Nanotechnology 20 415207
[100] Zabet-Khosousi A, Suganuma Y, Loputa K, Trudeau P-E, Dhirani A-A and Statt B 2005 Phys. Rev. Lett. 94 096801
[101] Govor L V, Bauer G H, Lüdtke T, Haug R J and Parisi J 2010 Physics Letters A 374 3328-31
[102] Kim C, Kim H S, Qin H and Blick R H 2010 Nano Lett. 10 615-9
[103] Hanna A E and Tinkham M 1991 Physical Review B 44 5919
[104] Petta J R, Salinas D G and Ralph D C 2000 Appl. Phys. Lett. 77 4419-21
[105] Kuemmeth F, Boltolin K I, Shi S-F and Ralph D C 2005 Nano Lett. 5 4506-12
[106] Beenakker C W J 1997 Rev. Mod. Phys. 69 731-808
[107] Ralph D C, Black C T and Tinkham M 1997 Phys. Rev. Lett. 78 4087
[108] Wang B, Wang K, Lu W, Yang J and Hou J G 2004 Physical Review B 70 205411
[109] Wang B, Wang K, Lu W, Wang H, Li Z, Yang J and Hou J G 2005 Appl. Phys. Lett. 82 3767-9
[110] Bezryadin A and Dekker C 1997 Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures 15 793-9
[111] Gu, eacute, ron S, Deshmukh M M, Myers E B and Ralph D C 1999 Phys. Rev. Lett. 83 4148
[112] Deshmukh M M, Kleff S, Gu, eacute, ron S, Bonet E, Pasupathy A N, von Delft J and Ralph D C 2001 Phys. Rev. Lett. 87 226801
[113] Aleksandrovic V, Greshnykh D, Randjelovic I, Frol’msdorf A, Kornowski A, Roth S V, Klinke C and Weller H 2008 ACS Nano 2 1123-30
[114] Petit C, Cren T, Roditchev D, Sacks W, Klein J and Pileni M P 1999 Advanced Materials 11 1198-202
[115] Wolf C R, Thonke K and Sauer R 2010 Appl. Phys. Lett. 96 142108-3
[116] Hai P N, Ohya S and Tanaka M 2010 Nat Nano 5 593-6
[117] van der Wiel W G, De Franceschi S, Elzerman J M, Fujisawa T, Tarucha S and Kouwenhoven L P 2003 Rev. Mod. Phys. 75 1-22
[118] De Franceschi S, van Dam J A, Bakkers E, Feiner L F, Gurevich L and Kouwenhoven L P 2003 Appl. Phys. Lett. 83 344-6
[119] van Kouwen M P, Reimer M E, Hidma A W, van Weert M H M, Algra R E, Bakkers E, Kouwenhoven L P and Zwijler V 2010 Nano Lett. 10 1817-22
[120] Nagamune Y, Sakaki H, Kouwenhoven L P, Mur L C, Harmans C, Motohisa J and Noge H 1994 Appl. Phys. Lett. 64 2375-81
[121] Waugh R, Berry M J, Mar D J, Westervelt R M, Campman K L and Gossard A C 1995 Phys. Rev. Lett. 75 705-8
[122] Yakushiji K, Mitani S, Ernult F, Takanashi K and Fujimori H 2007 Phys. Rep.-Rev. Sec. Phys. Lett. 451 1-35
[123] Seneor P, Bernand-Mantel A and Petroff F 2007 Journal Of Physics:Condensed Matter 19
[124] Schelp L F, Fert A, Fettar F, Holody P, Lee S F, Maurice J L, Petroff F and Vaurès A 1997 Physical Review B 56 R5747
[125] Yakushiji K, Ernult F, Imamura H, Yamane K, Mitani S, Takanashi K, Takahashi S, Maekawa S and Fujimori H 2005 Nat. Mater. 4 57-61
[126] Tan R P, Carrey J, Desvaux C, Grisolia J, Renaud P, Chaudret B and Respaud M 2007 Physical Review Letters 99 176805
[127] Tan R P, Carrey J, Respaud M, Desvaux C, Renaud P and Chaudret B 2008 Journal Of Magnetism And Magnetic Materials 320 L55-L9
[128] Poddar P, Fried T and Markovich G 2002 Physical Review B 65
[129] Lekshmi I C, Buonsanti R, Nobile C, Rinaldi R, Cozzoli P D and Maruccio G 2011 Acs Nano 5 1731-8
[130] Black C T, Murray C B, Sandstrom R L and Sun S H 2000 Science 290 1131-4
[131] Bernand-Mantel A, Seneor P, Bouzehouane K, Fusil S, Deranlot C, Petroff F and Fert A 2009 Nat Phys 5 920-4
[132] Birk F T and Davidovic D 2010 Physical Review B 81 241402
[133] Pileni M P 2008 Journal Of Physics D-Applied Physics 41