

Gold nanoparticles on nanodiamond for nanophotonic applications

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ABSTRACT

We present here some recent results of a research focused on the preparation of detonation nanodiamond/Au nanoparticles hybrid materials. Two different experimental routes are followed for the decoration of diamond nanoparticles by Au nanoparticles, that are in turn prepared by an innovative electroless approach.

Structure and morphology at the nanoscale level of the Au-on-nanodiamond deposits have been deeply investigated by electron microscopy (FE-SEM, HR-TEM) and diffraction (XRD) techniques.

Optical properties of these systems have been determined by performing scattering and UV-Vis absorption measurements, and by comparing the experimental data with simulated extinction spectra. The results highlighted very interesting plasmonic and scattering behaviors, mainly related to the high refractive index of diamond.

INTRODUCTION

Gold nanoparticles and nanodiamonds are two classes of materials that are receiving great attention in several emerging research areas, such as nanophotonics, nanomedicine and nano-biochemistry [1-7]. These and other connected research fields are presently converging toward common goals and their synergistic action is expected to offer practical solutions to technological problems related to optical labelling, imaging, molecular loading and biosensing.

In this context it is thought that the coupling of nanodiamonds with Au nanostructures and the investigation of the properties of these exciting hybrid systems could open a new fascinating scenario to the applied scientist community.

It is to be noted that, whereas a lot of scientific work has been devoted in the last years to the Au-nanoparticles / diamond systems [8-10], less attention has been given to the task of preparing and characterizing Au-nanoparticles/detonation nanodiamond materials. As regards the detonation nanodiamond [11], an exciting novel member of the nanocarbon family, up to now only in one case its coupling with Au nanoparticles [12] it has proposed.

In this paper we describe the decoration of detonation nanodiamond (ND) with Au nanoparticles (NP) and the investigations carried out to test the optical behaviour of the coupled nanostructures.

The generation and deposition of the Au nanoparticles is achieved by an electroless route, taking

advantage of an innovative Au(III)-aminoethyl imidazolium aurate salt [13], that is mixed with aqueous dispersions of nanodiamond.

EXPERIMENT

The Au(III)-aminoethyl imidazolium cationic complex $[\text{Cl}_3\text{AuNH}_2(\text{CH}_2)_2\text{ImMe}][\text{AuCl}_4]$ was prepared according to the procedure detailed in ref. 13.

A $7 \cdot 10^{-4}$ M solution of gold complex in water was prepared without the use of any supplementary additive and/or stabilizer.

As regards the diamond phase, both detonation nanodiamond powder (ITC standard Nanodiamond, purity $>98\%$, 4-5 nm primary particles size) and detonation nanodiamond dispersion (ITC Nanodiamond, 1%w in water, purity $>98\%$, 4-5 nm primary particles size, 30 nm average agglomerate size) were used. The powder was dispersed in water with the aid of an ultrasonic bath, and the final concentration was 0.1%w.

Agar gel was prepared starting from a 2% aqueous solution of highly purified Agar (Sigma Aldrich).

Two kinds of synthetic approaches were performed, the first one consisted in the mixing of 30 ml of a 0.1%w ND dispersion obtained from the powder with 90 ml of the $7 \cdot 10^{-4}$ M Au complex solution (*Route 1*).

Following this route several types of samples were prepared varying the reaction time.

In this paper we report about two samples collected after 15 minutes (AuND1) and 10 days (AuND2) from the starting of the reaction. Samples of AuND in powder form were obtained after several centrifugation and washing processes carried out in order to eliminate salts and unreacted species.

The second series of ND/Au samples were prepared using an innovative synthetic approach that utilizes Agar gel as medium for dispersion of nanodiamonds (*Route 2*). ND/Agar gel nanocomposites were obtained by mixing 5ml of 1% ND commercial dispersion in 45 ml of 2% Agar gel under agitation at 60°C. At this temperature the Agar is partially fluid but not yet melt. The next step was the addition of 20 ml of the Au complex solution. This operation was repeated at predefined times, and after each addition an amount of the composite was separated from the reaction bath and cooled.

Four samples collected after 15 min, 40 min, 60 min and 120 min, and named AuNDAg1, AuNDAg2, AuNDAg3, AuNDAg4, respectively, were treated with a 3M NaOH solution at 90 °C in order to eliminate the Agar, then washed and centrifugated many times up to neutrality. In every cases we did not use any additional additives and/or stabilizers or different reducing agent.

Optical spectra were recorded with a UV-1800 Shimadzu spectrophotometer in the spectral range 300-900 nm.

TEM images and electron diffraction patterns were captured with a JEOL2010 @200 kV and HRTEM images and EDX analysis were performed by using a JEOL3000F @300 kV.

Scanning electron microscopy images were acquired using an Hitachi S4000 microscope.

XRD spectra were acquired by a Seifert 3003 diffractometer with a theta-2theta configuration, $K\alpha$ Cu $\lambda=1.54$ Å.

DISCUSSION

Samples obtained from synthetic route 1

When we mixed the ND water dispersion with the Au-complex solution under moderate agitation, the obtained dispersion became light-pink in about 5 minutes, indicating the formation of Au nanoparticles. The collected sample NDAu1 is a pink-brown powder easily redispersible in water. Sample AuND2, collected after 10 days, is characterized by an orange-brown color. UV-Vis absorption spectra of AuND1 and AuND2 water dispersions are reported in Fig. 1 together with the absorption spectrum of pure ND dispersion (in-set of Fig.1).

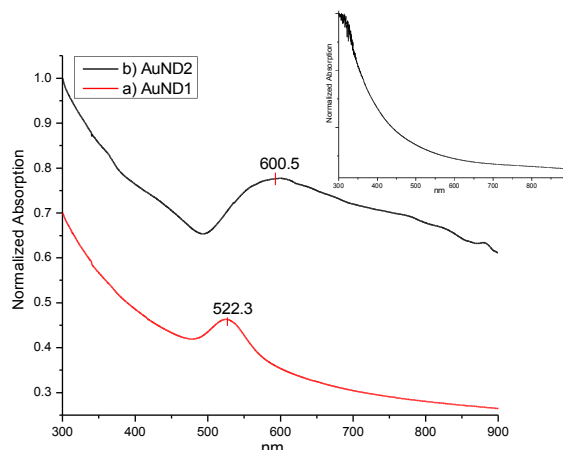


Fig. 1 UV-Vis normalized absorption spectra of aqueous dispersions: AuND1 a); AuND2 b) ; pure ND (in-set).

The spectrum of AuND1 is characterized by a strong absorption at about 522 nm, whereas the spectrum of AuND2 shows a larger and broad band at about 600 nm indicating the presence of larger Au particles. The spectrum of the pure ND dispersion does not exhibit any characteristic absorption but only a scattering line.

The TEM analysis of sample AuND1 evidenced the decoration of ND particles and aggregates with Au nanoparticles of about 5 nm in size. This last result is in accordance with the plasmonic band wavelength detected in UV-Vis spectrum and ascribed to small (4-6 nm) quasi-spherical Au particles [1,2]. A TEM image of the AuND1 sample is reported in Fig. 2.

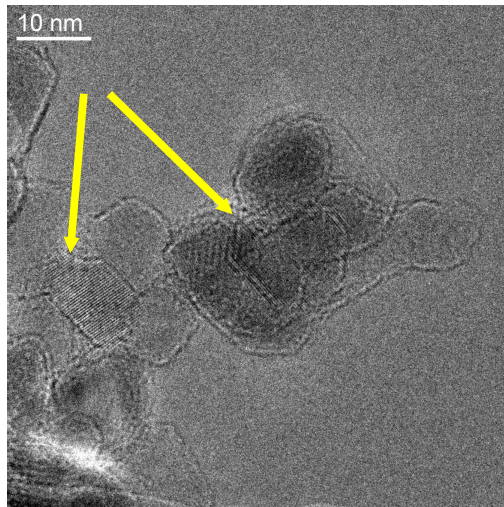


Fig.2 TEM image of AuND1 sample, the arrows indicated the AuNPs on ND aggregates.

FE- SEM images of AuND2 sample are reported in fig. 3. Also in this case the Au particles are strongly combined to NDs and are not aggregated to each other.

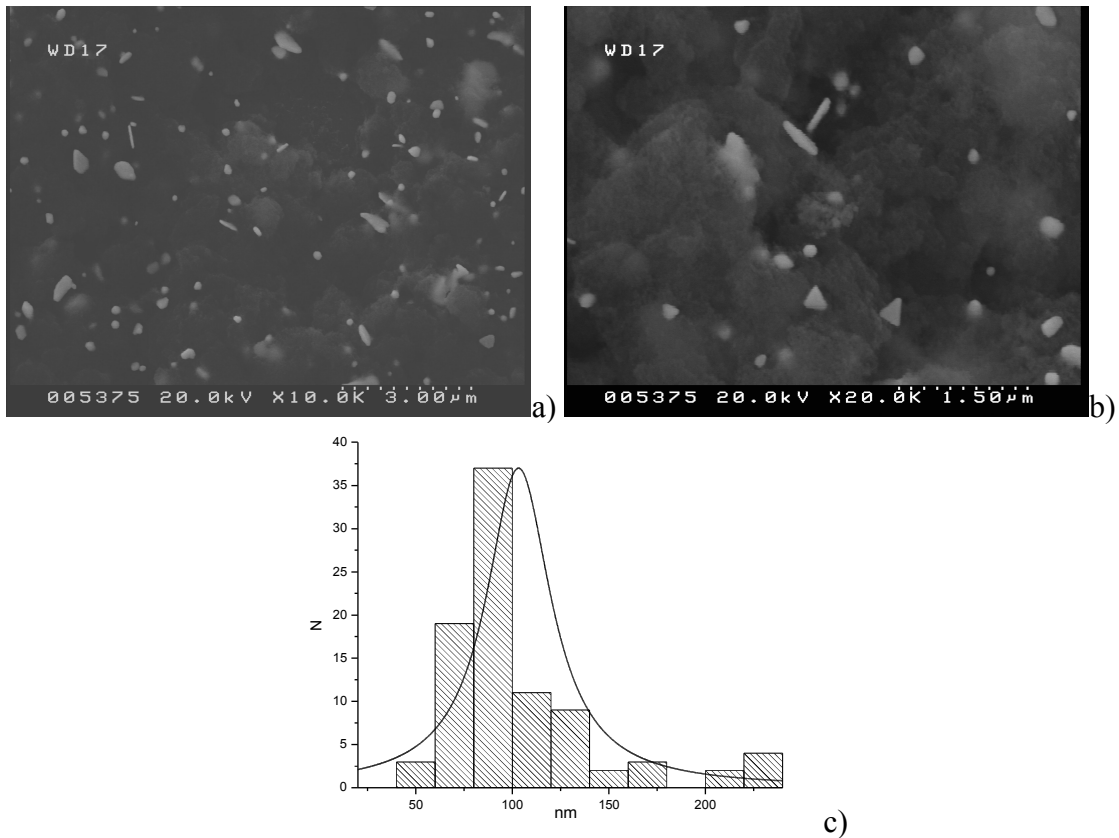


Fig. 3 SEM images of sample AuND2; a general view of the sample a); quasi-spherical, rods and triangular nanostructure b); histogram distribution of quasi-spherical Au nanoparticles c)

It is interesting to note that quasi-spherical, rod-like and triangular Au nanostructures are present in the samples. The distribution of the quasi-spherical particles is centered at about 80 nm. The aspect ratio of the rods is 3.3 ± 0.7 . The population of rods and triangular nanostructures is about 18% and 4%, respectively. The presence of rods could be rationalized by the ability of the amine-terminated liquid ionic complex to act as a capping and as a stabilizing agent during the Au growth [14-16].

In Fig. 4 the XRD spectra of pure ND powder (Fig.4 a)) and of sample AuND2 (Fig. 4 b)) are reported.

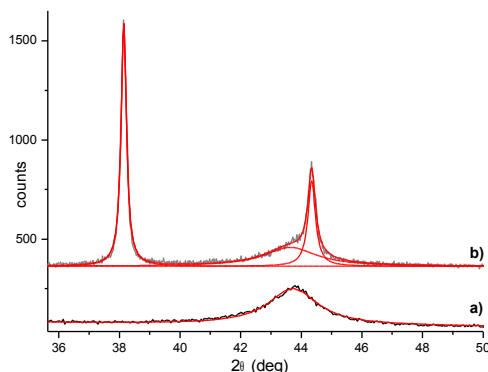


Fig. 4 XRD spectra of: pure ND powder a); of sample AuND2 b).

The XRD curve for the AuND2 sample clearly shows the main two reflections for the Au cubic phase (s.g.: Fm3m) at 38.14° and 44.34° [17]. The peak at 44.34° is superimposed to the ND signal centered at 43.7° . The fit reveals that both the position and the FWHM of diamond signals are unchanged, thus indicating that the structure of the ND is not affected by Au decoration. The dimensions of the AuNPs crystallites, evaluated by the Scherrer formula, are about 42 nm. In summary the *route 1* synthetic approach has highlighted that Au complex is directly and fast reduced on the ND surface. The AuNPs nanostructures are well dispersed on the ND surfaces and are not aggregated, thus allowing to preserve their properties over time.

Samples obtained from synthetic route 2

In the case of Agar-based composites, the Au complex reacts very efficiently and the final gels appear dark-pink colored. After Agar dissolution and neutralization a rather stable dispersion was obtained.

UV-Vis absorption spectra taken from the aqueous dispersions of samples AuNDAg1, AuNDAg2, AuNDAg3 and AuNDAg4 are reported in fig. 5

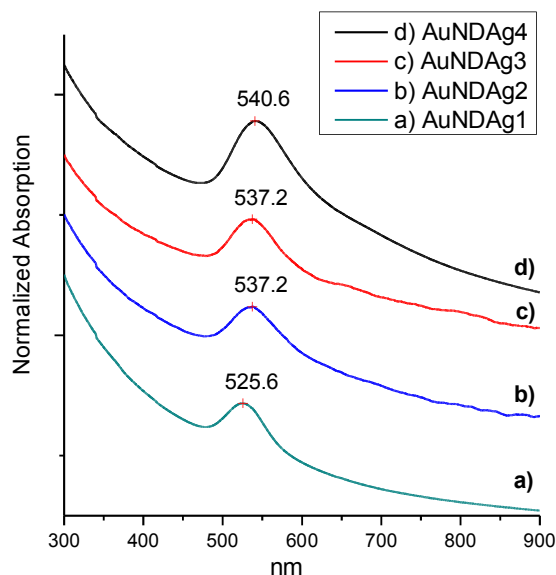


Fig.5 UV-Vis absorption spectra of water dispersion taken from samples: AuNDAg1 a); AuNDAg2 b); AuNDAg3 c); AuNDAg4 d).

In all the spectra a strong absorption peak in the green region is detected. The band position shifts continuously, from 525.6 nm for sample AuNDAg1 to 540.6 nm for sample AuNDAg4 , indicating an increasing of the AuNPs size. The FE-SEM images of Fig 6 highlight the presence of larger particles for the sample collected after 2,3 and 4 additions of Au complex, as an example, sample AuNDAg2 exhibits AuNPs of about 20 nm whereas AuNDAg4 shows particles of about 50 nm (Fig. 6).

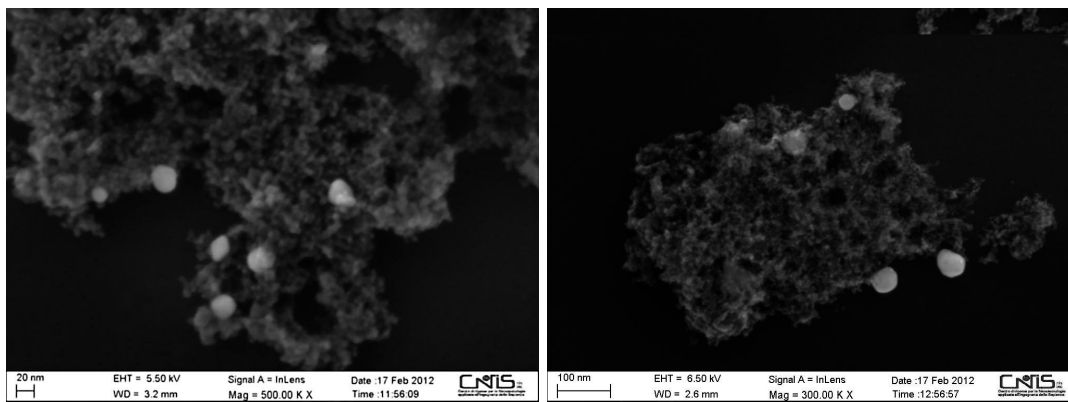


Fig 6 FE-SEM images of samples: AuNDAg3 a); and AuNDAg4 b).

Also in this case the AuNPs are dispersed and disaggregated on ND surface or/and on ND assemblies, resulting in very stable plasmonic systems.

CONCLUSIONS

The preliminary results of the present research establish the first rules on which to base future designs of more complex nanoAu/ND systems. The relevance of the topic is ultimately related to the exciting new fields of research opened by the use of hybrid materials with advantageous functional properties.

Our synthetic approaches present several interesting aspects. With respect to the conventional preparation of Au nanoparticles for decoration purposes, it is to be noted that the process is carried out in the absence of any reducing agent or heat treatment. Moreover the process allows us to modulate both size and shape of the Au nanoparticles as well as the features of the coating in terms of particles density and coverage degree of the diamond phase, thus allowing to selectively produce hybrid systems with different chemical and optical properties.

As regards the use of Agar as a medium for the dispersion of nanodiamond nanoparticles, this is certainly an innovative approach, that goes in the direction of a sustainable chemistry.

Overall the Au/ND materials prepared following our synthetic routes exhibit a remarkable biocompatibility and, beyond being of paramount interest for basic photonic research, could also easily find applications in bio-related research areas. We are presently exploring a series of Au-on-nanodiamond systems as platforms for sensors and biosensors and as novel nanosources for light amplification.

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