Catalytic and Optical Behavior of Polymer Embedded Metal Nanoparticles

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Summary: Very small metal aggregates (nanoaggregates) embedded in an inert polymer matrix, which simply stabilizes the nanodispersion, show unique catalytic and optical behaviour.

Indeed Ru-nanoparticles in vinyl-aromatic polymers or polyphosphazenes display an enhanced reactivity for hydrogenation of different groups, such as aromatic rings, keto and nitro groups, oximes and nitriles which are converted into the corresponding saturated derivatives under mild conditions.

The optical properties of terthiophenethiol-coated gold nanoparticles in UHMWPE (concentration lower than 4 wt.%) are characterized by poor dichroism due to their centrosymmetric structure. High dichroism ($R = 30$ at 400 nm, $DR = 30$) is on the contrary recorded for the terthiophene band showing the chromophores to be sensitive to mechanical orientation also when complexed with gold. On the other hand, nanocomposites based on polymers containing vinyl alcohol units and dispersed gold nanoparticles with average diameter ranging from 3 to 20 nm have been efficiently prepared by an UV photo-reduction process. Uniaxial drawing of the irradiated Au/polymer nanocomposites favours the anisotropic distribution of packed assemblies of gold particles, providing oriented films with polarization-dependent tunable optical properties.

Keywords: catalysis; metal clusters; nanocomposites; optical dichroism

Introduction

Very small metal aggregates (nanoaggregates) embedded in an inert polymer matrix which simply stabilizes the nanodispersion show an enhanced and innovative catalytic activity as the external metal atoms of the aggregate can be considered as coordinatively unsaturated species. On the other side the high efficiency of the above nanodispersion allows to provide the polymer matrix with unique optical properties without altering the thermoplastic behaviour.

As far as the former aspect is concerned, macromolecular systems containing transition metal nanoparticles trapped into macromolecules are of great interest in catalysis[1] and can be easily prepared by the gentle decomposition of organometallics in the presence of an appropriate polymer[2] having the capacity of a weak coordinative interaction with metal atoms located on the nanoparticles surface.

Suitable organometallics for this goal are transition metal mononuclear or cluster compounds containing organic ligands which can be easily removed from the metal under mild conditions, such as zerovalent olefin transition metal complexes[3]

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or solvated metal atoms obtained by reactions of metal vapor with weakly stabilizing organic ligands.[4] As far as polymeric substrates are concerned, a variety of different macromolecules (e.g. polystyrene,[5] or polyvinylpirrolidone[6] and others) have been exploited. Very recently also poly(organophosphazenes)[7] were successfully used[8] as they combine the versatily and processability of organic macromolecules with an improved thermal stability typical of inorganic polymers[9]. Moreover the nitrogen atoms along the polyphoshazene chain can be protonated or form coordination complexes with metal salts.[10]

Also, noble metal nanoparticles represent an important class of nanostructured materials due to their optical properties easily tunable as a function of size, morphology and aggregation behaviour[11,12]. Differently from smooth metal surfaces or metal powders, gold, silver or copper clusters assume a real and natural colour due to the absorption of visible light at the surface plasmon resonance frequency. The combination of the optical characteristics of metal clusters with the mechanical properties of thermoplastic materials in polymer nanocomposites has recently received remarkable attention[13–15].

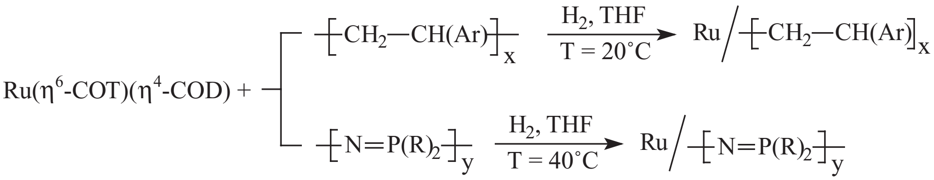
A complete overview of the two systems is out of the scope of the present paper which rather will present specific examples derived from the authors laboratory in an attempt to provide reliable evidence about the potentiality of the nanocomposites derived from the dispersion of metal clusters into an appropriate polymer matrix. Broad and updated information about preparation, properties and both catalytic and optical applications of polymer embedded nanoparticles can be found in the references of the present paper.

Catalytic Activity of Ruthenium Nanoparticles in Aromatic Polymers

Preparation and Structural Characterization

Ruthenium metal cluster can be embedded in various organic polymers starting with organotransition metal complexes containing weakly bonded ligands. Indeed these compounds are able to release the metal under mild conditions which do not affect the structure of the macromolecular support. In this work the ruthenium complex with cycloocta -1,3,5-triene and cycloocta-1,5-diene [Ru(η^6-COT) (η^4-COD)] was used as starting compounds. Indeed, the above complex in THF at temperature of 20–40 °C gives in hydrogen atmosphere metallic Ruthenium small clusters which are stabilized by the interaction with the arene side chains of aromatic polymers such as polystyrene[5,16] or with the various donating groups of poly(aryl/alkyphosphazenes)[8]. (Scheme 1).

The complex obtained according the route of Scheme 1 with polystyrene shows after examination by EXAFS the presence of Ru-atoms each bonded to a single phenyl ring thus excluding the formation of a bis-arene complex. Indeed the Ru-C distance (from six carbon atoms) of 2.05 Å is very close the typical Ru-C distance detected in homogeneous monomeric Ru/arene complexes. However, EXAFS data indicate that ruthenium atoms can be found in the



Scheme 1.

Reaction of a weakly coordinated Ru-complex with Aromatic vinyl polymers or polyphosphazenes.

Table 1.
EXAFS analysis of Polystyrene/Ruthenium System (Phenyl/Ru = 2)

Ru–C	2.05 ± 0.05Å
Coordination number (C per Ru)	6 ± 1
Ru–Ru	2.88 ± 0.1Å
Coordination number (Ru per Ru)	2 ± 2

second shell of the coordination sphere, being the observed Ru-Ru distance (2.88Å) similar to that found for small ruthenium clusters. These results suggest a structure where small ruthenium clusters are coordinated to the aromatic rings of polystyrene side chains through the external Ru-atoms. The formation of an insoluble polymeric complex[5] during the reaction between Ru(η^6-COT) (η^4-COD), and 1,3-diphenylpropane (DPP) in the presence of hydrogen is in agreement with these results. The above insoluble product has a composition corresponding to (DPP)Ru_2 which is in agreement with the prevalent structure of small Ru cluster bridged by DPP. EXAFS results were similar as observed for the polystyrene system by varying the composition thus indicating that the structure is substantially independent of metal loading. The average information derived from EXAFS is reported in Table 1.

TEM analysis shows the contemporary presence of amorphous and diffraction domains typical of polymeric materials (the polystyrene was atactic). The presence of domains able to diffract the electron beam on the other side is an evident indication of a substantial degree of organization which must involve ruthenium species (Figure 1).

Moreover, diffraction parameters differ markedly from those observed for mechanical mixtures of atactic polystyrene and metallic ruthenium. This is confirmed by FTIR analysis showing a progressive background change of the spectrum towards semiconductor features with the appearance of the vibronic band when increasing the ruthenium content. In addition, the permanence of the typical absorption of the monosubstituted phenyl ring at 660 and 800 cm^{-1} is a clear evidence that several phenyl rings of the polystyrene chains are not involved in the Ru coordination as it can be observed in the proposed structure (Figure 1).

The HR-TEM micrograph shows that the metal particles are well dispersed in the polymer matrix with nano-dimension distribution in the range 1–3 nm (average diameter = 1.55 ± 0.5 nm).

Catalytic Behaviour

Thanks to the high dispersion granting, to the large overall ruthenium surface and to the presence in the nanoparticles of coordinatively unsaturated ruthenium atoms, the prepared nanocomposites display a very high catalytic activity for hydrogenation with significant chemical and shape selectivity.

Catalytic hydrogenation[5,8] of carbon-carbon and carbon-oxygen double bond can be obtained at room temperature and pressure in case of olefins, substituted olefins and ketones. Benzene is hydrogenated to cyclohexane and the same easily occurs for alkylated benzene derivatives. Some negative steric effect is observed with bulky substituents; thus hexamethylbenzene and polystyrene do not react. The hydrogenation of the aromatic ring is also possible when substituents such as –OH in phenol, –CN in benzonitrile, $–NO_2$ in nitrobenzene, $–COCH_3$ in acetophenone, and $–C(CH_3)=NOH$ in its oxime are present.

The presence of two unsaturated functions in the same substrate arises the problem of selectivity and competitive reactivity. The benzoic acid free carboxylic group is not affected at room temperature but the hydrogenation of the aromatic ring takes place with the formation of cyclohexanecarboxylic acid. In the case of ethylacetoacetate the carbonyl group is selectively converted into the corresponding alchol while the ester is not affected, whereas the cinnamic acid is converted into 3-cyclohexylpropanoic acid and the α-acetamidocinnamic acid into N-acetylcyclohexylalanine.

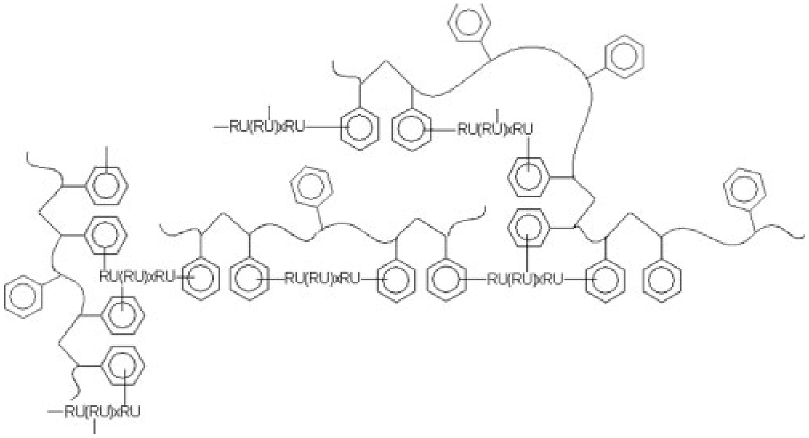
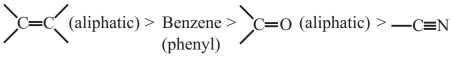


Figure 1.
Proposed Structure of the Polystyrene/Ru nanocomposite.

The following order of hydrogenation seems to be operative:



$$\mathrm{>C{=}C<}\ \text{(aliphatic)} > \underset{\text{(phenyl)}}{\text{Benzene}} > \mathrm{>C{=}O}\ \text{(aliphatic)} > \mathrm{-C{\equiv}N}$$

The available data allow also to propose this tentative order of ability to assist hydrogenation of the phenyl ring:

$$-\mathrm{OH} > -\mathrm{COOH} > -\mathrm{NO_2}$$
$$\cong -\mathrm{C(O)} - \mathrm{CH_3} > -\mathrm{C} \equiv \mathrm{N}$$

The dependence of catalytic properties on the nature of the aromatic polymer ligand, metal loading, and substrate structure, as well as reaction stereochemistry, can be explained by taking into account the substrate activation by coordination and steric effects at the molecular level of homogeneous ruthenium and rhodium complexes that are active for arene hydrogenation.[17]

With polystyrene and poly-1-vinylnaphathalene very modest differences are observed,[5,16] whereas the activity of the deposited metal nanoparticles is markedly affected by the structure of the side chains in the Ru/poly[bis(aryloxy)]phosphazene system. As an example, the hydrogenation rate of methylbenzoate and of *p*-aminomethyl-benzoic acid with the system Ru/–[N=P(OAr)$_2$]$_n$ decreases in the order Ar=Ph (*m*–or *p*–OMe] > Ph > Ph (*p*–COPh). The modification of the ligand allows on the other side to obtain either high swellable or completely heterogeneous systems, and the use of enviromentally friendly solvent such as alcohols and water. In general, the Ru/polymer catalyst exhibits very good stability against agglomeration under reaction conditions as shown by HR-TEM analysis.

Optical Properties of Gold Nanoparticles in Ethylene Polymers

Preparation and Structural Characterization

Gold particles have been prepared by $HAuCl_4$ reduction in toluene solution in the presence of an aliphatic (dodecyl mercaptane: $C_{12}H_{25}SH$) and/or an heteroaromatic thiol (5″-thiooctadecyl-2,2′:5′,2″terthiophene-5- thiol, $C_{18}S$–TT–SH). Two nanoparticle systems with overall 30 wt.% thiol content have been obtained. The former ***DT***, contains only dodecyl mercaptane (Au/thiol = 2.4 molar ratio), and the latter ***TT***, a dodecyl mercaptane/heteroaromatic thiol mixture, both 15 wt.% (Au/thiol = 3.1 molar ratio). The supposedly weak binding of the terthiophene sulphur atoms to gold leaves the size of the nanoparticles almost solely dependent on the number of –SH groups, which therefore determines***TT*** particles to be bigger than ***DT*** ones,[18] according to the Au/thiol molar ratio. The gold nanoparticles have then been dispersed in a UHMWPE 4 wt.% *p*-xylene solution at 130 °C and the corresponding films, obtained by casting, uniaxially stretched at 125 °C, as reported previously.[13]

With another synthetic approach gold nanoparticles dispersions in vinyl alcohol based polymers have been prepared by the bottom-up approach directly inside the polymer matrix by a photochemical method. The polymers used, poly(vinyl alcohol) (PVA) and poly(vinyl alcohol)-co-(ethylene) (EVAl), acts in this case both as protective agents against particles agglomeration and as polymeric support for the nanometric additive.

The polymers and the hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4$, the Au(III) precursor, 4 wt.%) have been dissolved in deionised water or in dimethylsulphoxide with 30 wt.% of ethylene glycol (EG). The film obtained after casting and solvent evaporation is irradiated for different times by a 400 W high pressure Hg UV lamp, to promote the reduction of the Au(III) precursor and the formation of Au(0) clusters.

The photo-generated gold particles are efficiently stabilized by the presence of electron-donor hydroxyl groups of the polymer matrix that prevents particles agglomeration and formation of micro-sized phase separated metal aggregates.

Bright-field TEM pictures ***DT*** and ***TT*** nanoparticles from colloidal dispersions shows for both systems an approximately spherical shape, more regular for the former and slightly elongated for the latter. ***DT*** nanoparticles appear to exhibit a bimodal distribution in the size ranging from 1 to 3–4 nm for the smallest, with the largest particles, forming approximately the 15% of the total amount, in the size range 7–18 nm.

On the contrary, in spite of the higher Au/sulphur molar ratio initially assumed as leading to larger dimensions, a monomodal distribution is observed for ***TT*** nanoparticles characterized by a mean size less than 2 nm, indicating the higher gold binding ability of the chromophoric thiol with respect to the aliphatic one. This is probably due to the increased electronic density on the –SH group directly linked to the heteroaromatic terthiophene nuclei and the possibility of taking advantage of the existence of a secondary binding site at the alkyl functionalized 5″ sulphur atom. The size of ***DT*** nanoparticles result particularly influenced by the mixing process with UHMWPE. Actually, the ***DT*** particles embedded in the polyethylene matrix show an increased size of the smallest distribution of about 2–3 nm while ***TT*** nanoparticles appear much less influenced by the mixing process displaying a particles distribution in the polymer matrix similar to the unmixed ones.

After PE stretching, the gold nanoparticles result oriented along the drawing direction and assumed an anisotropic distribution; the size and size distribution are not modified suggesting a scarce aggregation of the particles during the polymer thermo-mechanical elongation.

In the case of vinyl alcohol based polymer matrices, the bright-field TEM picture of the Au/PVA film irradiated for 5 minutes (Au/PVA 5 min.) evidences the formation of nanoparticles with approximately spherical shape characterized by a mean size of 12 ± 6 nm and a quite broad monomodal distribution. The presence of Au(0) in the colloidal particles composition is confirmed by electron diffraction analysis. After a prolonged irradiation time, the generation of much smaller gold nanoparticles is observed, by providing Au/PVA nanocomposites with average particle size of 5 ± 3 nm with respect to the value of 12 ± 6 nm that characterizes the same film but just after 5 minutes of UV illumination. Further exposition to UV lamp up to 2 hours (Au/PVA 120 min.) seems just to promote the agglomeration of the previously formed gold particles by coalescence phenomenon leading to Au/PVA nanocomposites with an average size of the dispersed gold colloids around 10 ± 5 nm.

Analogously to Au/PVA composites, the photo-reduction process performed on EVAl based films provides gold nanoparticles stabilized by the –OH groups composing the polymer matrix. Also in these cases, the Au/EVAl films change quickly their absorption behaviour from pale yellow to homogeneously purple with UV irradiation. However, the lower –OH content of EVAl copolymers with respect to PVA generates Au(0) colloids with larger size. This phenomenon is particularly evident for the Au/EVAl composites at the early stages of the photo-reduction process, while increasing the irradiation time, the particles' size actually decreases from 23 ± 12 nm for Au/EVAl$_{27}$ 5 min. film to 4 ± 3 nm for Au/EVAl$_{27}$ 30 min. film due to the formation of a large number of very small gold nanoparticles (Ø ~ 2–3 nm).

Optical Properties

The optical behavior of gold nanoparticles in UHMWPE dispersion is described both in absorption and in emission.

In the former case both **DT** and ***TT*** particles show the gold plasmon band located at about 550 nm. Due to the small dimension of the nanoparticles, this band results weak, as suggested by other literature reports[19]. Compared to the pure C$_{18}$S–TT–SH chromophore, the terthiophene absorption of ***TT*** particles in xylene dispersion is about 10 nm red-shifted (380 → 390 nm). This probably reflects an alteration of its electronic properties, likely due to the interactions of the chromophore with the noble metal nanoparticles. The gold plasmon absorption (550 nm) is characterized by poor dichroism, as shown by small-sized gold nanoparticles[14]. High dichroism (dichroic ratios between 14 and 30 recorded at 400 nm, depending on the drawing ratio) is on the contrary recorded for the terthiophene band of ***TT*** nanoparticles, indicating a sensitivity of the chromophores to mechanical orientation also when at the gold nanoparticle interface.

Fluorescence emission is observed only for ***TT*** particles in *p*-xylene dispersion, similar to that of pure C$_{18}$S–TT–SH by exciting at 390 nm (emission max. = 460 nm), but with lower emission intensity. This phenomenon may be attributed to a partial quenching by the gold. Even for ***TT*** nanosystem, no emission behaviour was recorded exciting in a band associated to gold, precisely at 288 nm. Differently from *p*-xylene colloidal dispersions, the UHMWPE nanocomposites exhibit luminescence, also without the presence of aromatic groups. Interestingly, this emission, pointed at 435 nm, is recorded upon excitation at 288 nm, in a band associated to gold and not to the chromophore. This phenomenon is attributed to the radiative emission of small metal aggregates connected to excitation of electrons from occupied *d* bands into unoccupied sp states above the Fermi level.[20]

In our case, the photoluminescence of ***TT*** nanocomposites results greatly enhanced with respect to ***DT*** nanoparticles dispersed in UHMWPE (Figure 2). Very probably, the introduction of terthiophene based thiol as capping agent may modify the electronic levels of the gold[27,28]and even more important, ***TT*** nanoparticles show when dispersed in polyethylene smaller dimensions (about 2 nm) than ***DT*** system (about 4–5 nm). It is indeed well known that very small metal particles (Ø less than 5 nm) provide high emission intensities, due to a more efficient coupling of the incident radiation to their surface plasmon.[12]

On the other hand, when exciting ***TT*** nanocomposites at the chromophore excitation wavelength (390 nm), the typical terthiophene fluorescence, centred at 470 nm as observed in polyethylene dispersions without gold, completely disappears due to the quenching process promoted by the noble metal. The terthiophene based chromophores in ***TT*** nanocomposites are therefore present and oriented as evidenced by the UV-vis absorption, but likely all in a gold-bound form that changes their emission behaviour.

Even more interestingly, ***TT*** nanocomposites show very high emission dichroism in the gold excitation and sensitivity to the drawing extent of the polyethylene matrix:

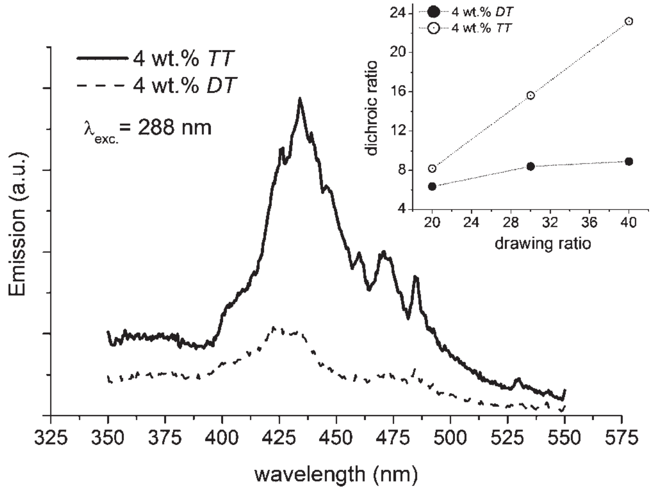


Figure 2.
Emission of ***TT*** and ***DT*** nanocomposites and dichroic ratio values calculated as a function of the drawing ratio UHMWPE films.

e.g. emission dichroic ratios of 9 for ***DT*** and 23 for ***TT*** nanocomposites (Figure 2). The emission dichroism of gold nanoparticles anisotropically distributed along the UHMWPE fibres can be probably addressed to a sort of electromagnetic energy transport between plasmon-polarization modes of closely spaced oriented particles.[12,13]

The optical behavior of the oriented Au/polymer nanocomposite with PVA and EVAl prepared photochemically is characterized by an absorption strongly dependent on the polarization direction of the incident light.

Differently from very small isolated gold clusters embedded into a polymer matrix, the anisotropic interacting gold particles show bathochromically (i.e., red-) shifted absorption band when the polarization vector of the photons is aligned with the stretching direction of the film, and, on the

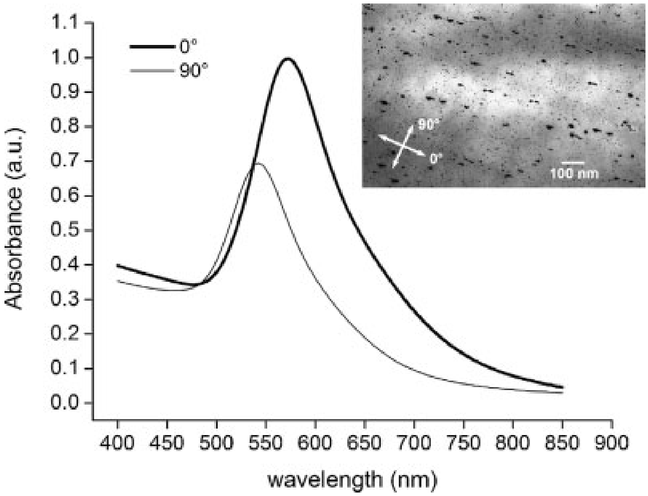


Figure 3.
UV-vis spectra of Au/EVAl27 30 min. oriented film (Dr = 6) as a function of the angle (φ) between the polarization of light and the drawing direction of the film, and transmission electron micrograph of the same film.

contrary, hypsochromic (blue-) shift for cross-polarized absorption (Figure 3).[12,14] For all the oriented nanocomposites, the shift in wavelength between the absorption at 0° and 90° ($\Delta\lambda$) has been evaluated and a very high dichroic behaviour recorded for almost all Au/polymer oriented composites with $\Delta\lambda$ maximum values higher than 40 nm, especially for films irradiated for just 5–15 minutes.

Probably, the UV exposure above 15–30 minutes generates for all the Au/polymer films very small gold particles ($\text{Ø} \leq 3$–4 nm, according to TEM measurements) that resulted scarcely interacting after uniaxial orientation, as similarly reported for small gold particles ($\text{Ø} \sim 3$–4 nm) embedded into ultra high molecular weight polyethylene composites.

This lack of particles interaction leads to an absorption behaviour very modestly sensitive to the polarization direction of the incident light, thus obtaining composite film with decreased $\Delta\lambda$ values. On the contrary, for low irradiation times (5–15 min.), Au/polymer oriented nanocomposites show a very pronounced dichroic behaviour. Oriented Au/PVA 30 min. ($Dr = 5$), the larger particles ($\text{Ø} \sim 7$–8 nm) prepared during the first photo-reduction steps, resulted well packed along the drawing direction and joined together in very close assemblies.

In addition, the shift in wavelength of the surface plasmon resonance of the aligned gold nanoparticles recorded from the $\varphi = 0^\circ$ (parallel) to the $\varphi = 90^\circ$ (perpendicular) positions is associated with a change in colour of the Au/polymer nanocomposites from blue to purple respectively. The alignment of the packed together gold particles assemblies is thus macroscopically reflected in a well-defined colour change of the nanocomposite film as a function of the polarization direction of the incident light.

Final Remarks

Two very evident examples are described regarding the potentiality of the combination of polymers with metal aggregates for the preparation of versatile nanocomposites where the polymer acts on one side as stabilizers of the nanoparticles produced by chemical reactions, photochemical conversion and metal vaporization. Also, the nature and processing of the polymeric material allows to shape the macroscopic form of the nanocomposite according to the application objective from powder to films. Finally, it is demonstrated that novel catalytic and optical properties can be obtained by various routes.

Even if the examples here are limited to two metals (Ru and Au) and few polymers, they suffice to show clearly the enormous potentiality of this approach which has acquired a very broad scientific and technical interest.

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