

In situ synthesis of gold-cross-linked poly(ethylene glycol) nanocomposites by photoinduced electron transfer and free radical polymerization processes†

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Gold-cross-linked poly(ethylene glycol) nanocomposites were prepared by simultaneous photoinduced electron transfer and free radical polymerization processes.

Nanocomposite materials containing noble metal nanoparticles dispersed into a polymer matrix may exhibit novel physical and chemical properties that are of high scientific and technological importance.¹ The combination of the physical properties of small size metal nanoparticles with those of polymeric materials yields hybrid materials with unique and versatile properties. Advanced optoelectronic and sensor devices can be fabricated with these materials.^{2–5} In particular gold–polymer hybrid nanocomposites are the subject of increasing attention because they have high potential for applications in many technologies and for electron or energy storage.⁶ In such applications, the homogeneous dispersion of these thermodynamically unstable nanoparticles is a key challenge due to their easy agglomeration arising from their high surface free energy. In order to produce stable nanoparticles, these nanoparticles must be detained during the preparation by adding protecting agents or setting them in an inert environment. Their synthesis has been performed under a variety of conditions, including citrate reduction,⁷ thiol stabilization⁸ and several thermal and photochemical techniques using thiols,⁹ amines,¹⁰ micelles,¹¹ dendrimers¹² and polymers¹³ as protective agents to aid in their stabilization in aqueous or organic media. Among them, photochemical methods involving light induced reduction of metal ions such as Ag and Au complexes are of particular interest as they find a wide range of applications including synthesis of metallic colloids, and metallization and patterning of films. A common strategy employed for the preparation of nanoparticles by photochemical means is direct excitation of metal ions and complexes by hard UV photons below 300 nm.^{14,15} Despite the many potential applications, direct excitation has several

serious drawbacks that limit their use. For example, some transparency to high-energy radiation and stability against extensive photochemical degradation is often difficult to achieve.¹⁵ To circumvent existing problems associated with the absorption characteristics, metal complexes that absorb light at wavelengths above 300 nm were used. However, there exists only a limited number of metallic species absorbing at long wavelengths and undergoing efficient photoreduction. Several other procedures involving photoreactions of aromatic carbonyl compounds to initiate the formation of nanoparticles have been developed. Photolysis of aromatic ketones leads to the formation of electron donor radicals capable of reducing Ag, Au and Cu complexes to metal particles. Both cleavage (type I) and H-abstraction type (type II) photoinitiators were successfully used for the photochemical generation of reducing radicals.¹⁶ The synthesized polymer–metal nano-composites usually have a linear structure and thus exhibit limited thermal and mechanical properties, which are an important issue for the fabrication of optoelectronic and sensor devices. One way to increase thermomechanical stability of the nanocomposites is cross-linking of the polymer matrix. However, consideration needs to be given to diffusion of the nanoparticles in the preformed network, crosslinking agent blends, temperature and time, and kinds of crosslinker *etc.* Post cross-linking of linear polymer nanocomposites is a demanding process, as the polymer should possess additional functional sites in the structure capable of forming insoluble networks. *In situ* UV-curing technology has many obvious advantages, including low temperature conditions and a very fast polymerization rate. Quite recently, we have reported a novel approach for the preparation of silver-polymer nanocomposites, in which nanoparticle formation and UV crosslinking process were accomplished in one pot by simply irradiating appropriate formulations, obtaining the homogeneous distribution of the nanoparticles within the polymer network without any macroscopic agglomeration. Silver nanoparticles and cationic reactive species were formed in a single redox process.¹⁷

In this communication, we report simultaneous UV induced radical polymerization of a typical acrylic resin and gold nanoparticle formation by the reduction of HAuCl₄. In the presence of a suitable photoinitiator, the UV generated radicals can start the polyaddition reaction of the acrylic resin, and at the same time, they are capable of reducing Au³⁺ to Au⁰. Thus, gold nanoparticles are formed *in situ* during the polymer network formation.

For our studies we chose 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959) to serve as

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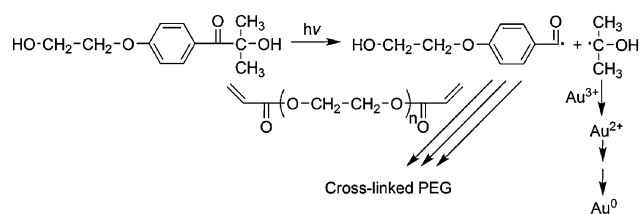
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† Electronic supplementary information (ESI) available: Experimental procedures, figure showing real time FT-IR curves for UV-curing of the formulations, and table showing properties of the cured films. See DOI: 10.1039/b803279c

photoinitiator to generate both reducing and initiating radicals and HAuCl_4 as the nanoparticle precursor. Poly(ethylene glycol diacrylate) (PEGDA) was selected as a photocurable acrylic resin to construct the nanocomposite in one pot. PEGDA can ultimately form cross-linked networks due to the two acrylate double bonds present in the structure. Because the PEG segment is biocompatible, this method also has the potential of application to biomedicine utilizing nanoparticles as drugs with sizes similar to or smaller than that of cellular components, for dealing with a variety of diseases.¹⁸

Thus, simple irradiation of Irgacure 2959 in PEGDA in the presence of HAuCl_4 leads to its reduction with rapid generation of both metallic gold and initiating radicals without any undesirable side reactions. The formation of the gold nanoparticles during the polymerization is confirmed by a gradual change of solution color from yellow to purple.¹⁹ The overall process is represented in Scheme 1. While electron donating ketyl radicals function as reducing agent, either or both radicals may initiate the polymerization. In this connection we refer the work of Pappas *et al.*²⁰ who demonstrated that both radicals are equally effective initiating species for the polymerization of (meth)acrylates.

Real-time FT-IR studies revealed that polymerization proceeds quite rapidly and an almost complete acrylic double bond conversion is achieved within less than one minute of UV irradiation (ESI† Fig. S1). It is also evident that by increasing HAuCl_4 content, double bond conversion decreases. In this case, a higher amount of ketyl radicals are required for the reduction of HAuCl_4 and their participation in the initiation process is avoided. The morphology of the cured systems was further investigated by TEM analyses. In Fig. 1 the bright-field TEM micrographs for the cured films containing various amount of the metal precursor are reported. As can be seen, the nanoparticles were well dispersed and no macroscopic aggregation occurred. Expectedly, the gold nanoparticles dimensions increase by increasing concentration of the precursor salt in the photocurable formulations. It should be pointed out that some aggregation was noted at high HAuCl_4 concentrations but the particle size always remained in the nanometer range. Fig. 2 shows the UV-Vis absorption spectrum of the cured films that indicates a maximum absorbance at around 600 nm, which is close to the reported surface plasmon resonance of gold nanoparticles.²¹ Thermal analysis (DSC) showed a slight decrease on T_g values for cured films by increasing the HAuCl_4 content (ESI† Table S1). This is an obvious consequence of the decrease of double bond conversion, and accordingly crosslink density. In all cases, however, high gel content values (above 90%) are obtained, indicating the formation of a highly cross-linked polymer network.



Scheme 1 *In situ* synthesis of gold-cross-linked poly(ethylene glycol) nanocomposite.

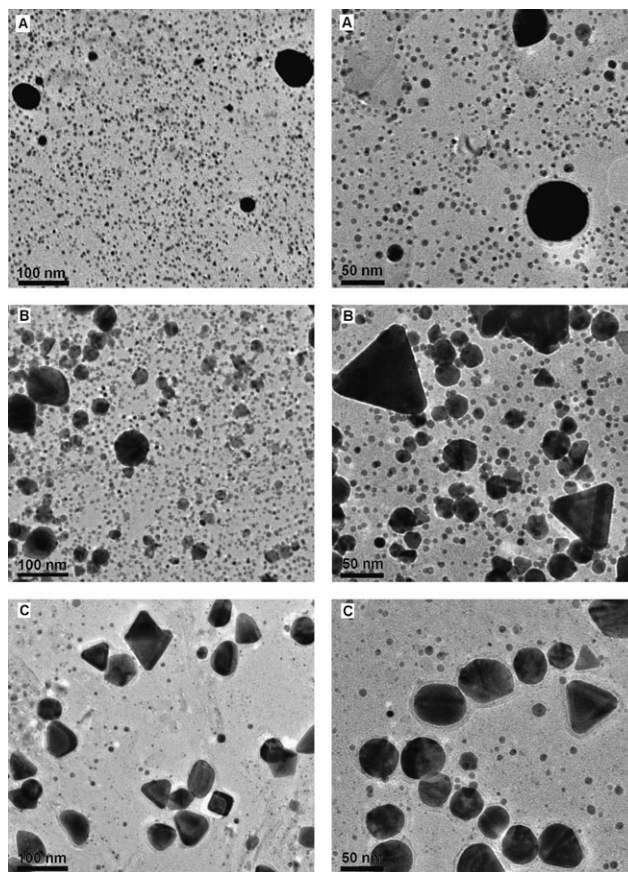


Fig. 1 Bright field TEM images of the UV cured films obtained by irradiation of poly(ethylene glycol) diacrylate containing different concentrations of HAuCl_4 and Irgacure 2959 (4 wt%). 1 wt% HAuCl_4 (A), 3 wt% HAuCl_4 (B), and 5 wt% HAuCl_4 (C).

In summary, gold PEG network composites have been prepared by simultaneous free radical polymerization and electron transfer processes. Simply irradiating the mixture containing PEG with polymerizable acrylate groups and HAuCl_4 in the presence of a photoinitiator, without necessity of an external reducing agent, leads to the formation of desired composites. Compared to chemical cross-linking²² of gold nanoparticle decorated polymer matrices, the method described here is quite attractive since it allows for simultaneous gold nanoparticle and network formation which secures the

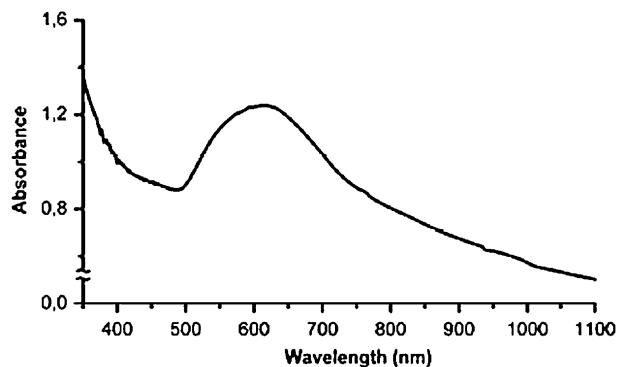


Fig. 2 UV-Vis absorption spectrum of gold-crosslinked PEG nanocomposite film.

resulting structure, and permits long-term stability. The morphology of the cured systems, investigated by TEM analysis, demonstrated that the nanoparticles are homogeneously distributed in the network without macroscopic agglomeration.

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