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Fullerene-mediated electrosynthesis of Ag–C_{60} nanocomposite in a water-organic two-phase system

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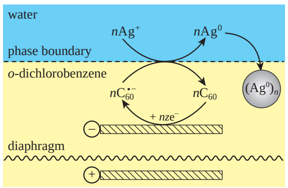
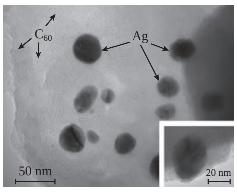
By example of fullerene-mediated electrosynthesis of Ag–C_{60} nanocomposite in water–*o*-dichlorobenzene, the possibility of using a liquid–liquid two-phase system for the electrosynthesis of metal nanoparticles has been demonstrated for the first time.





The chemical reduction of metal ions (complexes) in water-organic two-phase systems known as the Brust–Schiffrin method[1,2] is among the efficient methods for synthesizing ultra-small monodispersed metal nanoparticles (M-NPs). Faraday[3] was the first to use a two-phase system to obtain Au-NP (colloidal gold) by reduction of a gold salt in aqueous solution with elementary phosphorus in carbon disulfide. A distinctive feature of the method is that both the reducing agent and the metal ion are initially located in different liquid phases, while the M-NPs are stabilized in one of the phases. This method was used to obtain ultra-small NPs of gold,[1,4–7] silver,[5,7–10] palladium[10,11] and copper.[5,7,12–14]

The electrochemical methods for synthesizing M-NPs in the solution bulk are commonly based on the reduction of metal ions directly on the electrode, *e.g*. the pulse sonochemistry method[15–17] and the Reetz method.[18–22] However, these methods do not allow one to employ this efficient approach in a two-phase system in full measure, since, by definition, cathode and metal ion should be located in two different phases. On the other hand, the use of two-phase system may be quite helpful in mediated electrosynthesis of M-NPs[23–33] for both synthesizing ultra-small NPs and expanding the method capabilities, in particular, improving the process efficiency.

A two-phase system would make it possible to use metal salts (complexes) soluble in water (organic phase) but insoluble in an organic phase (water), and mediator compounds soluble in an organic phase (water) but insoluble in water (organic phase), within the same experiment. This feature prevents the reduction of the metal ions directly on the electrode and metal deposition on it, which is the main problem that limits the electrochemical reduction of metal ions during the preparation of M-NPs in the solution bulk. M-NP electrosynthesis with large ratios between metal ion and mediator can be accomplished in two-phase system, even if the metal salt is partially soluble in the organic phase and the metal ion is reduced directly on the electrode more easily than the mediator. Furthermore, the oxidation of the M-NPs generated on the anode, which is possible in the course of the electrolysis in an undivided cell, is totally prevented.

Hypothetically, it seems that a few versions of mediated electrosynthesis in a two-phase system can be implemented. This communication presents the first example of the M-NP electrosynthesis version in a water-organic two-phase system (Figure 1), *viz*., the C_{60} fullerene mediated electrosynthesis of Ag-NPs in a water–*o*-dichlorobenzene (DCB) performed in a divided cell.

In this case, the fullerene is attractive as a mediator for the following reasons: (i) it is soluble in DCB and insoluble in water;[34] (ii) it can reversibly accept up to six electrons per molecule in a stepwise manner,[35–37] and hence it can act as a mediator transferring one or more electrons from the electrode to the substrate;[38–43] (iii) radical anions and dianions are not protonated by such proton donors as water or phenol,[44–47] *i.e*. these species would not be consumed in side reactions in contact with aqueous phase under the conditions of their generation; (iv) by analogy with the C_{60}-mediated electrosynthesis of the Au–C_{60} nanocomposite in DCB–DMF medium,[31] one may believe that the fullerene would serve as not only a mediator at potentials of the $C_{60}/C_{60}^{\bullet-}$ redox couple, but also as a stabilizer of the generated Ag-NPs, eventually giving the Ag–C_{60} nanocomposite. Such silver-based nanomaterials are very promising for applications in biology and, particularly, for surface-enhanced Raman spectroscopy in medical diagnostics.[48,49]

Initially, the organic phase (12 ml), hosting a glass-carbon cathode (S = 5.6 cm^2), contains the fullerene (2.0 mM) and Bu_4NBF_4 (0.1 M) as the supporting electrolyte, while the aqueous phase (4 ml) contains $AgNO_3$ (1.5 mM) and $NaBF_4$ (0.1 M). Upon stirring the solution, the fullerene is not transferred to the

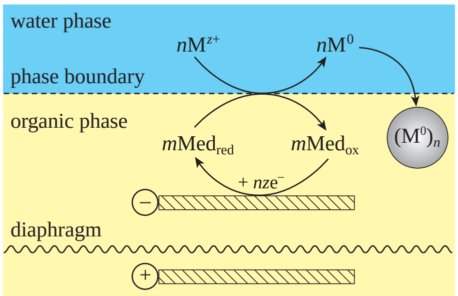


Figure 1 The mediated electrosynthesis of M-NPs in a water-organic two-phase system performed in a divided cell.

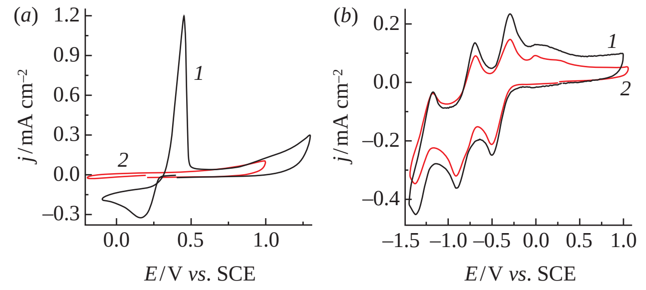


Figure 2 CV curves of (*a*) water phase containing $AgNO_3$ and $NaBF_4$; (*b*) DCB phase containing C_{60} fullerene and Bu_4NBF_4 in the two-phase water–organic system (*1*) before and (*2*) after the electrolysis, v = 100 mV s^{-1}.

water layer and completely remains in DCB, as indicated by the absence of maroon coloring of the aqueous phase typical of the fullerene (Figure S1, see Online Supplementary Materials). Accordingly, cyclic voltammetry (CV) of the organic layer reveals three reversible one-electron peaks corresponding to the fullerene reduction to produce the $C_{60}^{\bullet -}$ radical anion, C_{60}^{2-} dianion and $C_{60}^{\bullet 3-}$ radical trianion, respectively, whereas the aqueous layer gives no fullerene signals (Figure 2). Conversely, the reduction peak of Ag^+ ions and the corresponding reoxidation peak of metallic silver deposited on the electrode are observed on the CV curves of the aqueous layer and are missing on the CV curves of the organic layer (see Figure 2). This means that Ag^+ ions reside almost completely in the aqueous layer. Meanwhile, the distribution of supporting electrolyte cations between the phases remains unknown, but it may be assumed that with time, they would only partially be transferred to the other phases.

The preparative electrolysis (sample 1) was performed in potentiostatic mode at the potential of the first peak of fullerene reduction to the radical anion (up to E = –0.38 V *vs*. SCE). The amount of electricity Q = 0.6 C (1 F), which is theoretically required for the quantitative reduction of Ag^+ ions, was passed during the electrolysis (21 min). In this case, the organic layer remained homogeneous and the solution color changed from violet to brownish-maroon, whereas the aqueous layer remained colorless (Figure S1). After the electrolysis, the CV curves of the aqueous layer contained no Ag^+ reduction and reoxidation peaks, while the CV curves of the organic layer showed only the fullerene reduction and reoxidation peaks with a slightly decreased intensity (Figure 2). Note that no additional peaks, that would correspond to the reduction of other Ag^I derivatives and oxidation of Ag^0, were recorded in any of the phases. The results obtained signify that the fullerene is nearly not consumed during the electrolysis, while fullerene-mediated reduction of Ag^+ ions occurs. The resulting metal nanoparticles are bound and stabilized in the organic phase. They are neither adsorbed (deposited), nor oxidized on the glass-carbon electrode, which is due to their incapsulation in a matrix well solvated by DCB.

The nanoparticles obtained by electrolysis were studied by UV-VIS spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM), and X-ray powder diffraction (XRPD).

In the NP dispersion in ethanol,[†] the DLS method identifies only large, nearly micrometre-sized particles with a mean hydrodynamic diameter of 817 nm (the polydispersity index PdI = = 0.344±0.041) [Figure S2(*a*)]. One can see from TEM image and energy-dispersive spectrum (Figure 3) that the resulting particles are aggregates of spherical silver nanoparticles with a mean size of 36 ± 13 nm, dispersed in the organic matrix. The UV–VIS spectrum of the ethanolic solution contains absorption bands typical of C_{60} fullerene solutions[34] [Figure S2(*b*)]. Due to the solution turbidity, light scattering occurs in the entire visible spectrum and, thus, we failed to record the absorption bands corresponding to the surface plasmon resonance of Ag-NPs[50–52] and the usually observed bands at 410–430 nm. Apparently, the electrolysis results in the Ag–C_{60} nanocomposite with the Ag-NPs stabilized by C_{60} fullerene shell. The fullerene is insoluble in ethanol,[34] therefore the Ag–C_{60} nanocomposite exists as large aggregates rather than as individual particles in this medium.

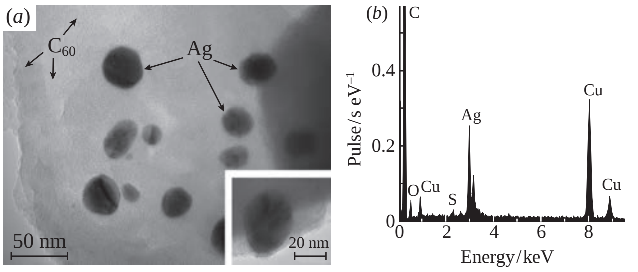


Figure 3 (*a*) TEM image and (*b*) energy-dispersive spectrum of the Ag–C_{60} nanocomposite.

The XRPD has shown that the deposit isolated from the ethanolic solution consists of a few crystal phases and a small fraction of an amorphous component. Comparison of the diffraction data with the powder diffractometry database (ICDD PDF-2) allowed us to ascertain that the sample contained crystalline silver, Ag (syn, code #01-087-0720), and silver chloride, AgCl (syn, code #01-085-1355) (Figure 4). The sample studied also contained a small amount of an unknown crystalline component with a few diffraction peaks in the range of 2θ = 20–35°. Identification of this phase does not seem possible due to the small number of diffraction peaks.

It is of note that the presence of identifiable amounts of crystalline AgCl in the sample was totally unexpected. The electrolysis was repeated (sample 2) with thorough control of the experiment purity and XRPD was performed again using the nanocomposites isolated and dispersed into ethanol. However, the new sample still contained two crystalline phases, *viz*., silver and silver chloride crystallites (Figure 4). Analysis of the calculated sizes of Ag^0 and AgCl crystallites (Tables S1–S4, Figures S3, S4) indicates that the silver crystallites are somewhat larger in the case of the second electrolysis, whereas the silver chloride crystallites have the same sizes in both cases. In total, the silver crystallites are characterized by a platelet shape with minimum sizes in the range of 6–19 nm, whereas the silver chloride particles are more liable to form spherical particles with a mean size in the range of 38–90 nm.

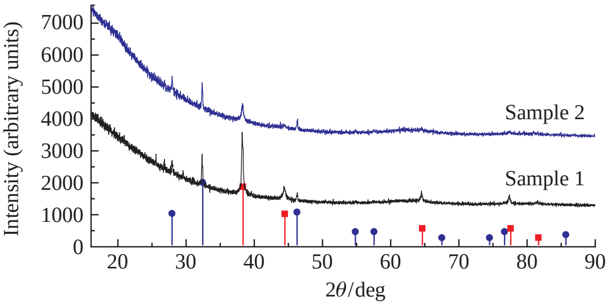


Figure 4 XRPD patterns of the samples 1 and 2. The interference peaks corresponding to the crystalline form of Ag (syn., code #01-087-0720) are shown by vertical dashes marked with squares, to the crystalline form of AgCl (syn., code #01-085-1355) – by vertical dashes marked with circles.

[†] The nanoparticles were deposited from the organic layer by means of centrifugation (15 000 rpm, 1 h) and washed with toluene, water, and two times with ethanol by sonication of the deposit in a solvent, followed by centrifugation (14 500 rpm, 30 min). Using this technique, we purified the NPs from the non-bound fullerene and supporting electrolyte.[31] After that, the precipitate was dispersed into ethanol by sonication.

Obviously, according to the data obtained, AgCl was formed upon reductive dechlorination of DCB. Four reversible fullerene reduction peaks were recorded in DCB,[35] *i.e.* not only the fullerene radical anion, but even its tetraanion failed to reduce DCB at a noticeable rate during the time required for recording a CV curve (seconds). No inappropriate consumption of fullerene radical anions was observed in the C_{60} mediated electrosynthesis of the Au–C_{60} nanocomposite in DCB–DMF medium (2 : 1 v/v).[31] Based on these data, fullerene mediated electroreduction of DCB is quite unlikely to occur at potentials of the $C_{60}/C_{60}^{\bullet-}$ redox couple. On the other hand, it was shown previously[53] that metal(0) particles generated *in situ* in a mediated process demonstrated high catalytic activity in the electroreduction of organohalogen compounds. Most likely, slow reduction of DCB by silver nanoparticles and clusters also proceeds in this case. This process involving Ag-NPs occurs not only upon electrolysis, but also during subsequent NP isolation, until DCB has been removed completely.

During a TEM study, the irradiated AgCl particles were decomposed to metal particles. Therefore, the TEM image (see Figure 3) provides the overall picture of metal nanoparticles obtained both during the electrolysis and under irradiation.

Thus, the application of DCB as the organic phase in a two-phase water-organic system allowed us to demonstrate that it is possible in principle to use two-phase system and C_{60} fullerene as a mediator in the electrochemical synthesis of the Ag–C_{60} nanocomposite. However, this is not an optimal solvent in terms of electrosynthesis efficiency, since the target process is accompanied by reductive dechlorination of DCB to give AgCl.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.11.013.

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