# Selective solution-phase generation and oxidation reaction of $C_{60}{}^{n-}$ ($n = 1,2$) and formation of an aqueous colloidal solution of $C_{60}$

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**The facile chemical methods for the selective solution-phase generation of $C_{60}{}^{n-}$ ($n = 1,2$) and the preparation of an aqueous colloidal solution of $C_{60}$ are reported. When $C_{60}$ was treated with Al–Ni alloy or tin (or zinc powder or sodium hydrosulfite) in aqueous NaOH–THF or in aqueous NaOH–DMSO or DMF, $C_{60}{}^{-}$ or $C_{60}{}^{2-}$ was produced selectively with no need for control of stoichiometry. The reaction products were characterized by ESI–MS, VIS–NIR, EPR and $^{13}C$ NMR spectroscopies. It was found that $C_{60}{}^{n-}$ ($n = 1,2$) was inert to water, but very sensitive to oxygen. The oxidation reaction of $C_{60}{}^{2-}$ with oxygen follows the sequence: $C_{60}{}^{2-}\rightarrow C_{60}{}^{1-}\rightarrow C_{60}$, which is monitored by NIR absorption spectroscopy. When $C_{60}{}^{n-}$ ($n = 1,2$) is oxidized in aqueous solution the $C_{60}$ sol is formed, but in dry organic solvent black $C_{60}$ powder is deposited. It was proved that the sol was composed of $C_{60}$ by UV, FTIR and ESIMS. Transmission electron microscope analysis showed that the colloidal particles, *ca.* 10 nm in diameter, were non-crystalline and quite homogeneous.**

## Introduction

Since the discovery of superconductivity for $K_3C_{60}$,[1] the $C_{60}{}^{n-}$ anions have attracted considerable interest. Although all six anions of $C_{60}{}^{n-}$ ($n = 1–6$) have now been synthesized by electrochemical or chemical methods,[2–4] there are very few reports describing a facile and selective method for solution phased chemical generation[4] and isolation of a given $C_{60}{}^{n-}$ species associated with a variety of different counter-cations. The few routes to $C_{60}{}^{n-}$ reported[4] so far require the stoichiometric control of alkali metal or the use of liquid ammonia. Also, to our knowledge, there is no method for the generation of $C_{60}{}^{n-}$ in aqueous solution, which hinders the syntheses of a variety of metal fullerides in aqueous solution. It remains a challenge to explore a facile and selective method for the aqueous solution phase generation of $C_{60}{}^{n-}$.

Another of the challenges in fullerene chemistry is the production of anionic solutions in polar solvents, especially in water. It has been discovered that $C_{60}$ could convert oxygen from the triplet to the singlet state,[5] that functionalized $C_{60}$ derivatives cause photoinduced DNA scission[6] and that they can be incorporated into artificial lipid bilayers;[7] it has been suggested that these could present some potential health risks.[8] Recently it was reported that substituted fullerenes inhibit HIV-1 protease.[9,10] Investigating the biological properties of fullerenes is an interesting subject, but is difficult owing to their poor solubilities in polar solvents, although some attempts have been made to overcome this by synthesising more hydrophilic derivatives,[6] formation of host–guest inclusion complexes,[11] generation of sols stabilized by a dedicated additive or ultrasound, production of liposomes, micelles, vesicles *etc.*[12–15] In the present work, we have developed a method to produce an aqueous solution of fullerene in the absence of any additives and an aqueous solution of alkali metal fullerides.

## Experimental

$C_{60}$ was prepared and purified by the standard Kratschmer method,[16] followed by toluene extraction in a soxhlet apparatus. The solid fullerenes were washed with diethyl ether and purified by liquid chromatography in hexane on neutral alumina. Tetrahydrofuran (THF) and toluene were distilled from sodium–benzophenone in a Schlenk system. DMSO and water were distilled and bubbled with argon under reflux for 10 min before use. Al–Ni alloy, tin, zinc powder and NaOH are chemically pure and were used as purchased.

UV–NIR Spectra were recorded on a Shimadzu UV-3100 spectrometer. Analysis of metal in metal fulleride was completed on a Jarrell-Ash 1100 + 2000 Inductively Coupled Plasma Quantometer (ICP). NMR spectra were recorded at room temperature on a Bruker AM-500 MHz spectrometer and the shift was calibrated against internal solvent (THF). IR spectra were recorded on a Nicolet 170SX model FTIR spectrometer. Mass spectra were recorded on a Finnigan mat API SSQ-710 Mass Spectrometer. Electrochemical data were measured on BAS-100B electrochemical analyser. The one-compartment electrochemical cell was airtight with high-vacuum glass stopcocks connecting it to the Schlenk system. The working electrode consisted of a platinum microdisk or a mercury electrode [Hg(Pt)][17] sealed in glass. The counter electrode consisted of a platinum wire and the quasi-reference electrode was a silver wire standardized with ferrocene.

$E_{\frac{1}{2}}$ values correspond to $(E_{pc} - E_{pa})/2$ from cyclovoltammetry (CV) measurements. In some experiments an SCE reference electrode was used, separated from the working electrode compartment by a sintered glass frit. Transmission electron microscopic photographs were recorded on a JEOL JEM-200CX model electron microscope. Electrophoresis of the $C_{60}$ sol was done on a DV-3B model electrophoresis apparatus using 1% agarose gel as a substrate plate which was immersed in tris(acetic acid) buffer solution with 100 V and 60 mA.

### Solution of $C_{60}{}^{-}$ in THF

To a suspension of 34.0 mg $C_{60}$ powder (0.047 mmol), 150 mg Al–Ni alloy (3.49 mmol, excess) and 400 mg solid NaOH pellets (10 mmol) in 20 ml THF, 5 ml of degassed water was added to the Schlenk system. $C_{60}$ and Al–Ni alloy suspended in the interface between THF (upper layer) and aqueous NaOH (lower layer), while NaOH pellets dissolved in the water. As the reduction reaction proceeded, the red reaction products diffused into the THF layer, of which the colour turned to dark red–purple very quickly. In the present reaction system, the concentrated aqueous NaOH prevents the reaction product $C_{60}{}^{-}$ from dissolving in the water phase and causes it to enter into the THF phase. After 10 min, the dark red–purple solution of $C_{60}{}^{-}$ in THF was separated from colourless aqueous NaOH and used

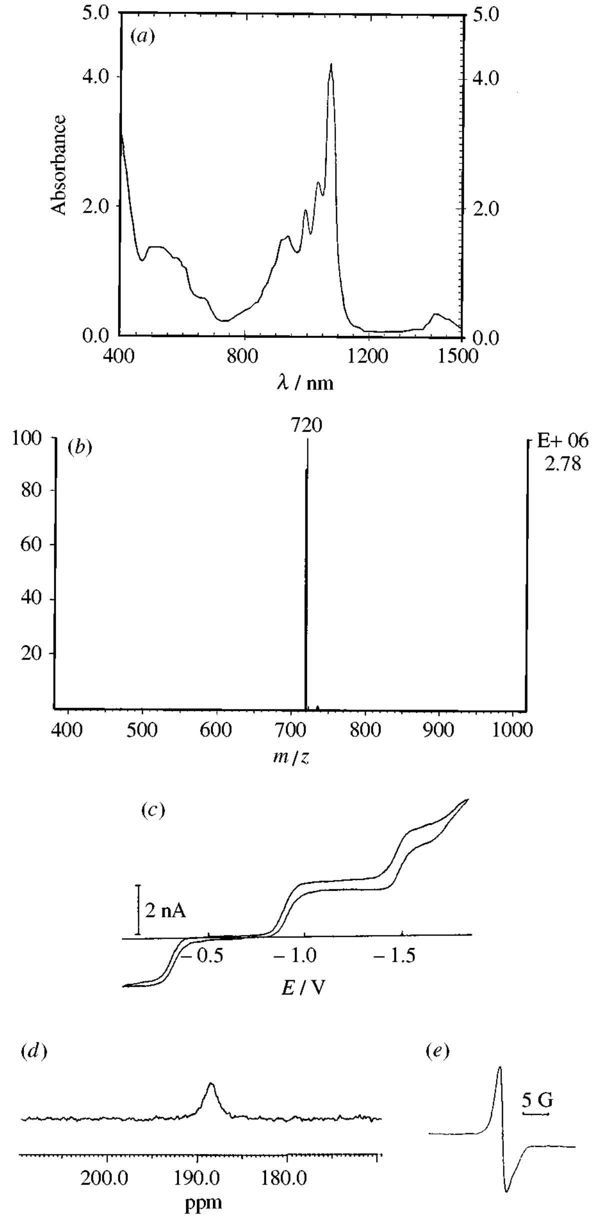

**Fig. 1** $C_{60}$ anions generated by reaction of $C_{60}$ and Al–Ni alloy in aqueous NaOH–THF (or DMSO). (*a*) NIR spectrum of $C_{60}^-$ in THF; (*b*) ESIMS; (*c*) cyclovoltammogram of $C_{60}^-$ in THF; (*d*) $^{13}$C-NMR spectrum; (*e*) EPR spectrum.

as a sample for electrospray ionization mass spectrometry (ESIMS), EPR and NIR spectroscopies. The results are shown in Fig. 1(*a*), (*b*) and (*e*). To 4 ml of the solution of $C_{60}^-$, 1 ml of degassed $D_2O$ was added and sealed under argon for $^{13}$C NMR analysis. The spectrum is shown in Fig. 1(*d*). To 20 ml of the solution of $C_{60}^-$ in THF, 10 ml of fresh distilled toluene was added to obtain a precipitate of $NaC_{60}$ which was isolated, dried under vacuum and used for measurements.

### Solution of $C_{60}^{2-}$ in DMSO

The procedure for generation of a $C_{60}^{2-}$ solution is the same as the preparation of the solution of $C_{60}^-$ in THF, except for use of DMSO as the solvent instead of THF.

### Aqueous colloidal solution of $C_{60}$

In a typical experiment, 20 ml of $C_{60}^-$ solution containing 80 mg of $C_{60}$ in THF was prepared following the method described above. Then the solution of $C_{60}^-$ in THF was added to 60 ml of undegassed distilled water dropwise and the aqueous colloidal solution of $C_{60}$ containing 1 mg ml$^{-1}$ $C_{60}$ was formed. The resulting transparent brightly coloured solution is slightly opalescent in reflected light.

## Results and discussion

### Selective generation and properties of $C_{60}^-$ and $C_{60}^{2-}$

Reduction of fullerenes is an important reaction. It was found that $C_{60}$ underwent Birch reduction to give $C_{60}H_{36}$ and $C_{60}H_{18}$[18*a*] and was reduced by Zn/H$^+$ to give $C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$.[18*b*] In contrast with these, the reduction reaction of fullerenes in aqueous NaOH solution using Zn, $Na_2S_2O_4$,[19] Sn or Al–Ni as reducing agents is quite different. The reduction products are fullerene anions instead of hydrogenated fullerenes. The VIS–NIR spectrum of the reduction products in the aqueous NaOH–THF shows two bands at 1075 and 994 nm [Fig. 1(*a*)], which is a very specific marker for the $C_{60}^-$ anion,[2*f*,4*c*,20] and the ESIMS [Fig. 1(*b*)] is very clean with only one strong peak at $m/z = 720$. There is no indication that modified fullerenes are formed. It is different from the electrochemical reduction, which leads to disruption of the $C_{60}$ framework[21*a*] or the coalescence reaction of fullerenes.[21*b*] The cyclovoltammogram of $C_{60}^-$ in THF [Fig. 1(*c*)] shows that there is an oxidation current when the potential is more positive than −0.35 V (*vs.* SCE), indicating that $C_{60}^-$ is oxidized, that there is a zero current near the potential −0.35 V (*vs.* SCE) which is the first redox potential of $C_{60}$, indicating there is no neutral $C_{60}$ in the THF solution and the reduction is complete. The $^{13}$C NMR spectra (298 K) of this solution shows only a single peak with a line-width of 3 ppm at $\delta$ 188.2 [Fig. 1(*d*)] which is 2 ppm different than the previous value.[4*g*] Using a different solvent and internal standard may account for this. The EPR spectrum shows a peak ($T = 110$ K) with $\Delta H = 2$ G at $g = 1.998$ [Fig. 1(*e*)]. The EPR spectra of $C_{60}^-$ are different from laboratory-to-laboratory. The sample prepared in various laboratories may have different sources of the sharp signals.[2*f*,4*b*,*c*,*e*,*f*] Radio-frequency Inductively Coupled Plasma (ICP) analysis data indicate that the counter-cation is Na$^+$, forming $Na^+C_{60}^-$ in THF solution. The sodium salt of the $C_{60}^-$ is soluble in THF, $CH_3CN$, DMSO, EtOH and $H_2O$.

The $C_{60}$ monoanion is inert to degassed distilled water. In a typical example, the $^{13}$C NMR, NIR and ESIMS spectra of the solution of the sodium salt of $C_{60}^-$ in THF containing 20% degassed water, which was sealed under argon for two weeks, showed no changes.

Although the reducing agents used in our experiments were in excess, only $C_{60}^-$ was generated in aqueous NaOH–THF. The method described here has some advantages: the reducing agents, Al–Ni alloy, tin, zinc powder and sodium hydrosulfite are readily available, cheap and stable in air. There is no need for stoichiometric control, which makes handling more convenient.

Using DMSO or DMF as a solvent instead of THF, following a similar method used for $C_{60}^-$ generation, we obtained a dark red–brown solution of the fullerene dianion. The VIS–NIR absorption spectra of the dark red–brown solution show that there are no characteristic bands (1075 and 994 nm) of $C_{60}^-$ and that new bands appear at 945 and 836 nm (Fig. 2), which are characteristic of dianion $C_{60}^{2-}$.[2*f*,4*c*,20*b*,*d*] This indicates that there is no $C_{60}^-$ in solution, which is 'pure' by NIR criteria. As indicated in ref. 22 EPR spectroscopy is particularly sensitive to traces of $C_{60}^-$. The EPR spectrum of the frozen ($T = 110$ K) dark red–brown solution consists of a sharp peak ($g = 2.0000$, $H = 3$ G) superimposed on a pair of shoulders with a separation of 9.2 G, which is in accord with that previously reported for the dianion $C_{60}^{2-}$ formed in solution.[2*f*,4*g*] There is no evidence of $C_{60}^-$ contamination of the $C_{60}^{2-}$ sample.

The redox potentials of various $C_{60}$ anions in several solvents are shown in Table 1. $E_{\frac{1}{2}}$ of $C_{60}^{0/-}$ and $C_{60}^{-/2-}$ couples in DMSO are −0.16 and −0.66 V (*vs.* SCE) which are more positive than in THF, so the redox potentials of Al–Ni alloy and Sn, Zn or $Na_2S_2O_4$ in solution with high concentration of OH$^-$ are sufficiently negative to reduce $C_{60}$ to $C_{60}^{2-}$.

**Table 1** $E_{\frac{1}{2}}$ of various $C_{60}$ anions in several solvents

| | $E_{\frac{1}{2}}$/V (*vs.* SCE) | | | | |
|---|---|---|---|---|---|
| Solvent | $C_{60}/C_{60}^{-}$ | $C_{60}^{-}/C_{60}^{2-}$ | $C_{60}^{2-}/C_{60}^{3-}$ | $C_{60}^{3-}/C_{60}^{4-}$ | Reference |
| THF | −0.33 | −0.92 | −1.49 | −1.99 | 23*a* |
| THF | −0.35 | −0.94 | −1.50 | −1.99 | 23*b* |
| THF | −0.35 | −0.93 | −1.43 | −2.01 | This work[a] |
| DMF | −0.26 | −0.72 | −1.31 | −1.85 | 23*a* |
| DMSO | −0.16 | −0.66 | — | — | This work[a] |

[a] Concentration of $C_{60}$ anions is $2.5 \times 10^{-3}$ mmol ml$^{-1}$, containing 0.1 M (TBA)ClO$_4$ under argon, sweep rate: 0.05 V s$^{-1}$, working electrode: Pt, T = 298 K.

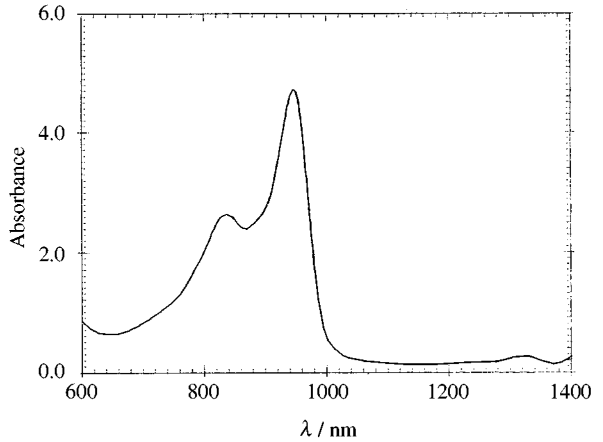

**Fig. 2** NIR spectrum of $C_{60}^{2-}$ ($10^{-3}$ mmol ml$^{-1}$) in DMSO at 298 K

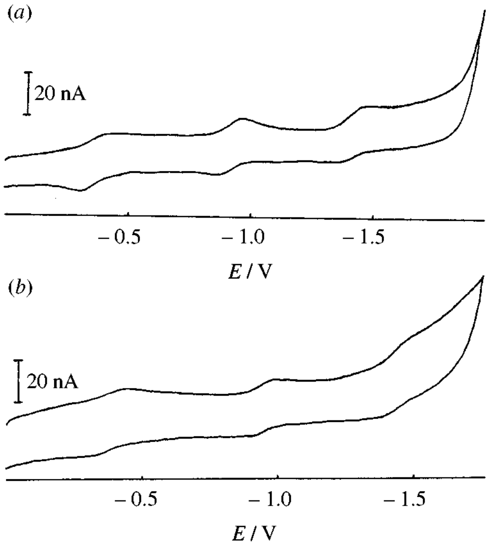

**Fig. 3** Cyclovoltammogram of $C_{60}^{-}$ ($1.5 \times 10^{-3}$ mmol ml$^{-1}$) in THF containing degassed water (*a*) 5 µl, (*b*) 15 µl; 0.1 M (TBA)ClO$_4$ under argon, sweep rate 0.54 V s$^{-1}$, working electrode Pt, $T$ = 298 K

Fig. 3 presents the effect of water on the cyclic voltammagram of $C_{60}^{-}$ in THF. There was no obvious change when 5 µl degassed water was added to the solution of $C_{60}^{-}$ in THF. After addition of 15 µl of degassed water, the first and second redox peaks still show no clear change, except the current increases rapidly near the third redox peak, which corresponds to the redox reaction of water. It indicates that the redox potential of water is more negative than $C_{60}^{n-}$ ($n$ = 1,2) so, the water cannot oxidize $C_{60}^{n-}$ ($n$ = 1,2) at all. The result is in agreement with the acidity of fullerene anions[24] and does not support the previous conclusion.[2f,21a]

Protonation of $C_{60}^{2-}$ and $C_{60}^{-}$ in *ortho*-dichlorobenzene, dimethyl sulfoxide and acetonitrile has recently been studied by several groups.[24] $C_{60}H$ and $C_{60}H_2$ are types of weak acids with $pK_{a,1} = 4.7$ and $pK_{a,2} = 16$ for $C_{60}H_2$ and $pK_a = 9$ for $C_{60}H$. The fullerene anion and dianion will accept one or two protons to form hydrogenated fullerene in acid medium, but will be stable in basic solution. Water is an even weaker acid than $C_{60}H$ and $C_{60}H_2$, so $C_{60}^{-}$ and $C_{60}^{2-}$ cannot accept the protons from the water molecule and are stable in oxygen-free pure water.

### Oxidation of $C_{60}^{n-}$ ($n$ = 1,2)

It is well known that $C_{60}^{-}$ is sensitive to oxygen and the rate of oxidation of $C_{60}^{-}$ in dry THF solution is dependent upon the nature of the cation by the mechanism involving superoxide ion $O_2^{-}$.[22] Considering that the redox potential of the electrode reaction (1) is much more positive than that of $C_{60}^{n-}$ ($n$ = 1,2),

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^- \quad E_{\frac{1}{2}} = +0.15\ \mathrm{V}\ (vs.\ \mathrm{SCE}) \quad (1)$$

this reaction may be responsible for the oxidation of $C_{60}^{n-}$ ($n$ = 1,2). The oxidation of $C_{60}^{n-}$ proceeds very rapidly to give a black precipitate of $C_{60}$ or a dark red–brown $C_{60}$ sol, depending on whether the solvent contains water or not. When $C_{60}^{n-}$ ($n$ = 1,2) in a dry organic solvent is exposed to air, the $C_{60}$ black powder is precipitated as the oxidation proceeds. However, the dark red–brown sol is formed if the DMSO–H$_2$O solution of $C_{60}^{2-}$ and THF–H$_2$O solution of $C_{60}^{-}$ are open to air. The oxidation process was monitored by NIR spectroscopy (Fig. 4).

As the oxidation reaction proceeds, the absorption band at 945 nm, which is characteristic of $C_{60}^{2-}$, decreases gradually and a new band appears at 1075 nm which is characteristic of $C_{60}^{-}$. This means that $C_{60}^{-}$ is an intermediate species of the oxidation of $C_{60}^{2-}$. $C_{60}^{-}$ is sensitive to oxygen also and takes a further reaction to form the neutral fullerene $C_{60}$. Hence the band at 1075 nm increases first and then decreases after reaching a maximum. The oxidation of $C_{60}^{2-}$ follows the sequence: $C_{60}^{2-} \rightarrow C_{60}^{-} \rightarrow C_{60}$.

### Aqueous sol of $C_{60}$

THF solution of $C_{60}^{-}$ was added to undegassed water dropwise to give a dark red–brown aqueous colloidal solution of $C_{60}$. Using this method, various concentrations of the sol may be prepared conveniently. The sol, even at a concentration as high as 1 mg ml$^{-1}$, is very stable for six months at least. The aqueous sol with proper dilution was used as a sample for electrospray ionization mass spectrometry without being precharged. The ESIMS of the sol shows only one strong peak at *m*/*z* 720 which indicates that there is no indication of modified fullerenes being formed, that the sol is composed of $C_{60}$ and that the species detected are $C_{60}^{-}$ or $(C_{60})_n^{n-}$. The results of electrophoresis of the $C_{60}$ sol show that the particles of the $C_{60}$ sol carry a negative charge. Like usual aqueous sols, the $C_{60}$ sol precipitated when an electrolyte such as NaOH, HCl, NaCl or BaCl$_2$ was added. The IR spectrum (KBr pellets) of the precipitates is the same as that for $C_{60}$ with four characteristic bands at 1428, 1183, 573 and 527 cm$^{-1}$. The UV spectrum of the precipitates in toluene is also the same as $C_{60}$. The oxidation process is given by eqn. (2).

$$4C_{60}^{-} + O_2 + 2H_2O \longrightarrow 4C_{60}(\mathrm{Sol}) + 4OH^- \quad (2)$$

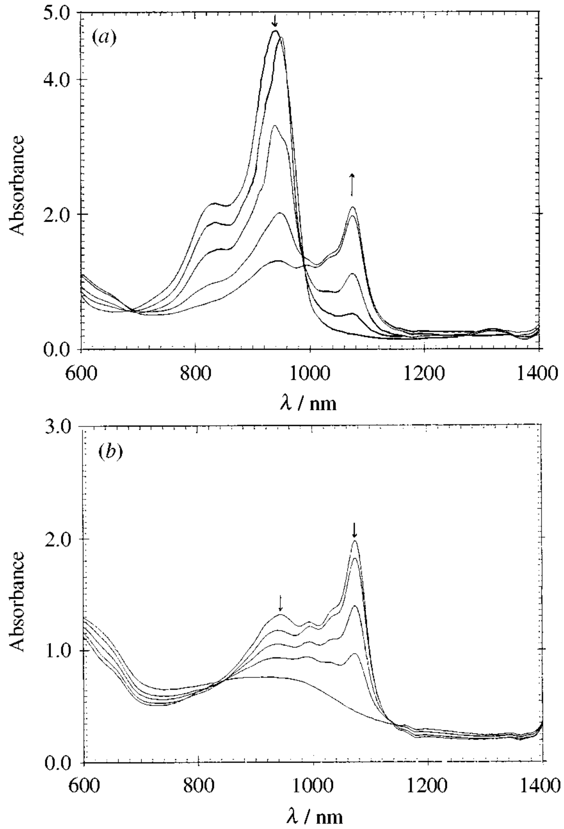

**Fig. 4** NIR spectra of the oxidation process of $C_{60}^{2-}$ in DMSO–$H_2O$. Each scan was recorded every 5 min. (*a*) Characteristic band of $C_{60}^{2-}$ at 945 nm decreases and of $C_{60}^{-}$ at 1075 nm increases as the reaction proceeds. (*b*) After reaching a maximum, the 1075 nm peak decreases as the reaction proceeds. (*a*) and (*b*) are recorded in the same experiment, but are separated for clarity.

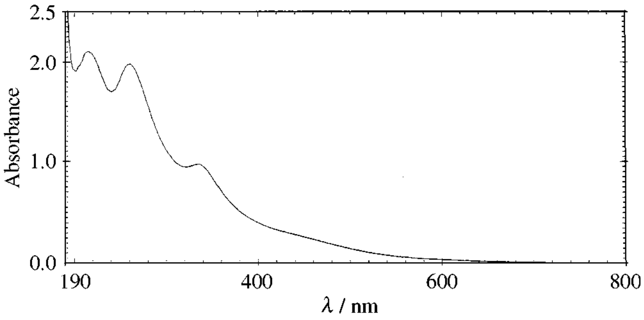

**Fig. 5** UV spectrum of the $C_{60}$ sol (0.05 mg ml$^{-1}$, $T = 298$ K, $H_2O$ as blank)

The $C_{60}$ sol is stable. No substantial reverse extraction of the fullerenes by toluene from the colloidal dispersion was observed. The precipitates deposited by electrolytes do not dissolve in $H_2O$ or THF again, but will dissolve in toluene. This can be rationalized by considering the role of a charged bilayer of the $C_{60}$ sol particles. The precipitates of the $C_{60}$ sol can be dispersed in water again by ultrasound and the sol formed is stable for a long period, but the size of sol particles is bigger than the original.

The UV spectrum of the $C_{60}$ sol is shown in Fig. 5. There are three broad absorption bands at 340, 260 and 220 nm. It indicates that the aggregation state of $C_{60}$ presents in the sol. The colours of the $C_{60}$ sol vary with the concentrations: 1 mg ml$^{-1}$, dark brown–red; 0.33 mg ml$^{-1}$, brown–red; 0.11 mg ml$^{-1}$, pale red and 0.04 mg ml$^{-1}$, pale yellow. It might be an indication of the particle size changing with the concentration of the sol.

**Fig. 6** Electron diffraction photograph of $C_{60}$ sol; 0.11 mg ml$^{-1}$ $C_{60}$ sol was spread on a collodion film substrate with graphite powder

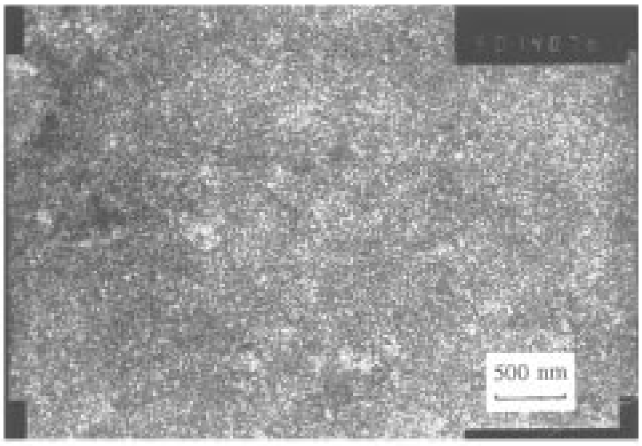

**Fig. 7** Transmission electron microscope photograph of the $C_{60}$ sol (0.11 mg ml$^{-1}$)

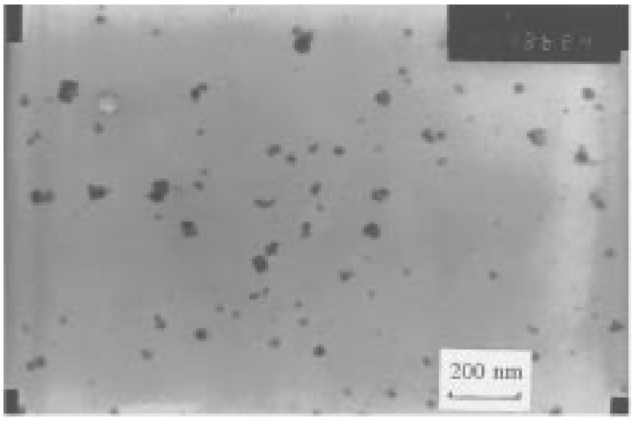

**Fig. 8** Transmission electron spectroscopy photograph of the $C_{60}$ sol, which was generated by spreading the precipitates again with ultrasonic vibration

## Transmission electron microscopy

The $C_{60}$ sol was spread on a collodion film substrate with graphite powder. The electron diffraction photograph and the transmission electron microscope photograph are shown in Figs. 6 and 7, respectively. There are wide rings and no spread dots there. This indicates that the sol particles are non-crystalline. Fig. 7 shows that the $C_{60}$ sol particles are quite homogeneous with a size of *ca.* 10 nm. Fig. 8 shows that the $C_{60}$ sol particles, which were formed by dispersing the precipitates with ultrasound, are bigger than the original sol. The size of the sol particles is in the range of 20–100 nm.

## Conclusions

Owing to the redox potentials of $C_{60}$ being quite different in the solvents of different polarity, the selective solution phase generation of $C_{60}{}^{n-}$ ($n = 1,2$) was reached in THF and DMSO using common reducing agents such as Al–Ni alloy, tin, zinc powder and sodium hydrosulfite. $C_{60}$ is reduced to only $C_{60}{}^{-}$ in aqueous NaOH–THF, but to $C_{60}{}^{2-}$ in aqueous NaOH–DMSO or DMF without the stoichiometric control. The $C_{60}{}^{n-}$ ($n = 1,2$) is inert to water, but very sensitive to oxygen. The $C_{60}{}^{2-}$ is oxidized to form $C_{60}$ *via* the sequence $C_{60}{}^{2-} \rightarrow C_{60}{}^{-} \rightarrow C_{60}$, obtaining $C_{60}$ as a black powder in dry organic solvent, but generating $C_{60}$ sol in aqueous solution. The sol particles are non-crystalline with a size of *ca.* 10 nm. The sol is stable for a long period.

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