

Electronic Supplementary Information

Spontaneous Electron Transfer from C₆₀ to Au Ions: Oxidation of C₆₀ and Hole Doping

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Measurements of open circuit voltages

An additional evidence of the oxidation of C_{60} and the stability of oxidized C_{60} is provided by measuring open circuit voltage (E_{OCV}) of two samples: the C_{60} thin film and the C_{60} thin film immersed in $HAuCl_4$ solution. The E_{OVC} results for the oxidized C_{60} film are included in the main text, and the E_{OCV} results for the as-prepared C_{60} film are as follows:

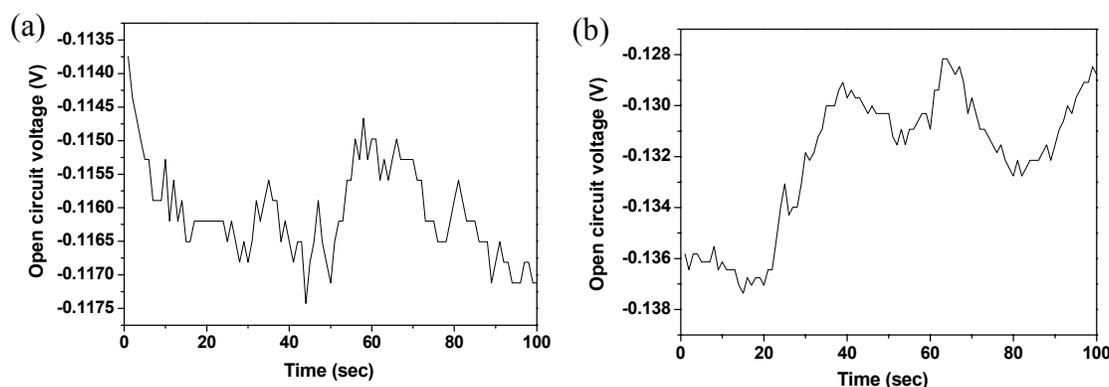
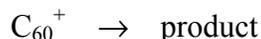


Figure S1. Change of open circuit voltage as a function of time: a) as-prepared C_{60} thin film, b) the C_{60} thin film after 30 min from the measurement in a).

The E_{OCV} values of C_{60} thin films in Figures S1a and b show marginal variation as a function of time. However, the E_{OCV} values of C_{60} thin film after immersing in $HAuCl_4$ solution in Figure 4a show large changes with gradual decay. This gradual decrease in the E_{OCV} values indicates that C_{60} radical cations generated after immersing in $HAuCl_4$ solution disappear gradually.

In order to receive a hint about the rate constant of consumption of C_{60} radical cation, the Nernst equation was modified with E_{OCV} in Figure 4a. The following result on the rate constant is based on the assumption of a first-order reaction.



$$E_{ocv}(t) = E^{\circ} - \frac{RT}{nF} \ln \frac{[product]}{[C_{60}^+]}$$

$$\ln \frac{[product]}{[C_{60}^+]} = -\frac{nF}{RT} (E_{ocv}(t) - E^{\circ})$$

$$\ln[C_{60}^+] = \frac{nF}{RT} (E_{ocv}(t) - E^{\circ}) + \ln[product]$$

Here, E_{ocv} is measured values in the experiment as a function of time. Thus, the concentration-time equation is obtained and the rate constant can be calculated from slope in plot of concentration of oxidized C_{60} with respect to time. The resulting rate constant is 0.00753 s^{-1} and the half-life ($t_{1/2} = 0.693/k$) is 92 seconds. These results are comparable with previously reported stability of oxidized C_{60} by other groups: Xie et al. reported that C_{60} radical cations generated electrochemically are relatively long-lived on the voltammetric time scale and the lifetime is estimated to be $\geq 0.5 \text{ min}$.¹ Reed et al. reported that C_{60}^+ is stable in the presence of equal molar amounts of a carborane anion for several hours.²

Cyclic voltammogram of C_{60} film in aqueous environment

To confirm if C_{60} indeed undergoes electrochemical oxidation in water, we ran cyclic voltammetric experiments. The cyclic voltammogram (CV) recorded in a 0.10 M KCl solution at 100 mV s^{-1} is shown in Figure S2; the C_{60} film begins to get oxidized at about 0.10 V reaching a peak current at $\sim 0.25 \text{ V}$ with its cathodic peak showing up at $\sim 0.3 \text{ V}$ upon potential reversal. The formal potential of -0.007 V was estimated by averaging oxidation and reduction peaks. The sharp cathodic peak indicates that the reduction is a surface controlled reaction without complication. If the primary oxidation product, i.e.,

C_{60}^+ , underwent a following reaction during the anodic scan, resulting in incorporation of hydroxide or any other nucleophiles, the diffusion of its fission product such as OH^- from inside of the film to the solution would control the reaction during the cathodic scan³ and the cathodic current would decrease to a certain level according to the Cottrellian decay and form a plateau beyond the cathodic peak.

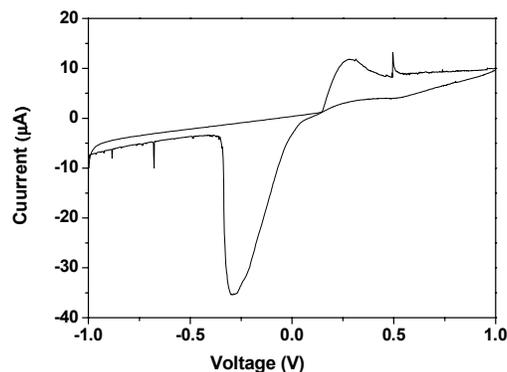


Figure S2. CV data of C_{60} film on Si in 0.1 M KCl solution.

Another aspect to note in this CV is that the oxidation potential is significantly lower than those reported in nonaqueous media. The oxidation potential reported in the literature was 1.26 V vs. Fc/Fc^+ in 1,1,2,2-tetrachloroethane (TCE), which corresponds to 1.42 V vs. $Ag|AgCl$ under our experimental conditions. The large negative shift in oxidation potential indicates that the radical cation feels at home to a great extent in a polar medium, i.e., water, with a dielectric constant of 78.3 in comparison to acetonitrile, which has a dielectric constant of 7.1. This is readily predicted from Born's theory of charged ion transfer from one medium to another.⁴

I- V_{DS} curves as a function of gate voltage

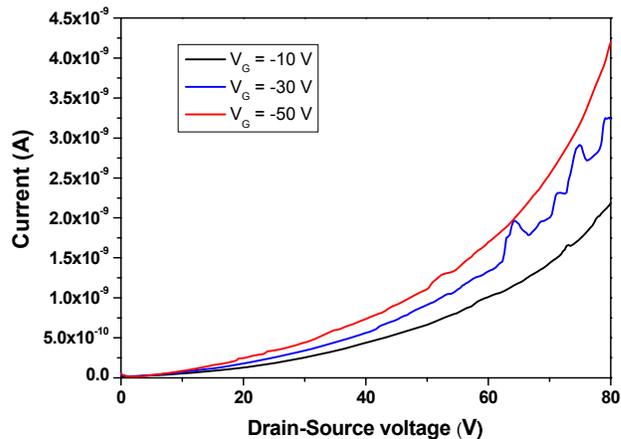


Figure S3. I- V_{DS} curves of Au-C₆₀ film FET device at different gate voltages of -10, -30, and -50 V.

References

1. Q. Xie, F. Arias and L. Echegoyen L, *J. Am. Chem. Soc.*, 1993, **115**, 9818-9819.
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3. C. Zhang and S.-M. Park, *J. Electrochem. Soc.*, 1987, **134**, 2966.
4. M. Z. Born, *Phys.*, 1920, **1**, 45.