

Identification of Chirality-Dependent Adsorption Kinetics in Single-Walled Carbon Nanotube Reaction Networks

Kejia Chen¹, Nitish Nair², Michael S. Strano², and Richard D. Braatz^{1,*}

¹University of Illinois at Urbana-Champaign, 293 Roger Adams Laboratory, Box C-3,
600 South Mathews Avenue, Urbana, IL 61801, USA

²Department of Chemical Engineering, Massachusetts Institute of Technology,
77 Massachusetts Avenue, Cambridge, MA 02139, USA

Single-walled carbon nanotubes (SWNTs) are carbon allotropes with electronic structures that vary with the diameter and helical wrapping of the constituent graphene sheet, which characterize the SWNT chirality. A computationally efficient numerical algorithm is derived for determining chirality-dependent adsorption rate constants in chemical reaction networks of SWNTs. A set of decoupled differential equations is derived for the total molar composition of vacant sites for the SWNTs of various chiralities, which requires no assumptions with regard to quasi-steady-state or the relative rates of adsorption and subsequent chemical reactions. Identifiability analysis indicates that quasi-steady-state operation results in the loss of information on the individual reactivity so that only the ratios of the adsorption rate constants can be estimated. Such SWNT reaction network models can be used to maximize sensitivity and selectivity in biosensors, manipulate the electronic properties of SWNTs in nanotube-based field effect transistors, and maximize the efficiency of electronic structure-based separations of SWNT mixtures.

Keywords: Nanobio, Biosensors, Nanobiosensors, Medical Sensing, Biomedical Sensing, Single-Walled Carbon Nanotubes, Carbon Nanotubes, Adsorption Kinetics, Chemical Reaction Networks.

1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are ideally suited for the transport of electrons in one dimension and have commercial potential as field emission displays,¹ nanoelectronic devices,² and nanochemical and nanobiosensors.^{3–6} Each SWNT consists of a single graphene sheet seamlessly rolled into the shape of a tube with diameter of nanometer dimension. Each possible rolling angle results in a SWNT of different chirality that is uniquely characterized by a pair of integers (n, m). SWNTs of different chiralities can have very different electronic structure, ranging from metallic to semi-metal to semiconducting. Methods for synthesis produce mixtures of SWNTs with varying chirality. Covalent chemistries have been developed in recent years that can selectively manipulate the electronic band structures of these SWNTs, thus increasing the flexibility of these materials in nanosensor and nanoelectronics applications as well as

producing additional variables to increase the efficiencies of processes developed to separate SWNTs of different chiralities.

For example, quantitative understanding of carbon nanotube chemistries is key to the design of improved carbon nanotube-based sensors for the quantitative detection of a wide variety of biomolecules including proteins,^{7–9} nucleic acids,^{4,10–12} pharmaceuticals,¹³ nerve agents,¹⁴ cholesterol,¹⁵ and glucose.^{16–18} Most SWNT-based sensors measure a change in electronic properties that occurs during the adsorption of molecules on the nanotube surface, either with or without subsequent covalent chemical reactions.^{3–5,16,17} Since molecular adsorption and covalent reaction depend on the electronic structure, the associated kinetic rates can be different for SWNTs of different chiralities. These different kinetic rates can affect the performance characteristics of SWNT-based nanosensors and other nanodevices.

This paper considers identification of chirality-dependent adsorption kinetics in SWNT reaction networks.

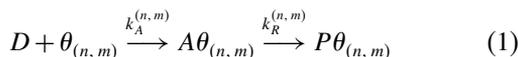
*Author to whom correspondence should be addressed.

Such a mathematical model of adsorption could be used in the design of the chirality of SWNTs to maximize sensitivity and selectivity for specific biosensor applications, to manipulate the electronic properties of SWNTs in nano-electromechanical systems, and to increase the efficiencies of processes developed to separate SWNTs of different chiralities¹⁹ as a key step in the manufacture of nanodevices with optimized chiralities.

While the theoretical framework and many of the results of this paper apply to general SWNT reaction networks, for specificity we consider the identification of chirality-specific adsorption kinetics for semibatch reactions of SWNTs with 4-hydroxybenzene diazonium as a model electron acceptor.²⁰ After dynamic analysis of the reaction network involving SWNTs reacting with the diazonium, a computationally efficient numerical algorithm is provided to quantify the adsorption kinetics from changes in the photoabsorption spectra²¹ during adsorption and reaction. This is followed by a discussion of the identification of ratios of adsorption rate constants when the experimental conditions do not allow the identification of the absolute magnitudes of adsorption rate constants.

2. KINETIC ANALYSIS

The reaction of diazonium with SWNTs suspended in solution follows a two-step process:^{22, 23} an (n, m) -selective adsorption step followed by a covalent reaction step. The reaction network consists of a large number of parallel reactions in which each path in the network is associated with SWNTs of one chirality. For each (n, m) nanotube:



where D denotes the 4-hydroxybenzene diazonium molecule and $\theta_{(n, m)}$, $A\theta_{(n, m)}$, and $P\theta_{(n, m)}$ refer to the vacant sites on the nanotube, sites occupied by the adsorption intermediate, and sites occupied by the reaction product, respectively. The adsorption rate constant $k_A^{(n, m)}$ and reaction rate constant $k_R^{(n, m)}$ can be different for SWNTs of different chiralities due to the differences in electronic structure. Consider a semibatch operation in which diazonium is introduced at a known molar flow rate F_{D_0} (see Fig. 1). The molar conservation equations for 4-hydroxybenzene diazonium in solution (N_D) and for vacant sites on each nanotube ($N_{\theta_{(n, m)}}$) are

$$N_D = F_{D_0} t - \left(N_T - \sum_{(n, m)} N_{\theta_{(n, m)}} \right) \quad (2)$$

$$\frac{dN_{\theta_{(n, m)}}}{dt} = -k_A^{(n, m)} \frac{N_D}{V_R} N_{\theta_{(n, m)}} \quad (3)$$

where N_T is the total moles of sites on all the nanotubes in solution and V_R is the volume of solution. Taking ratios

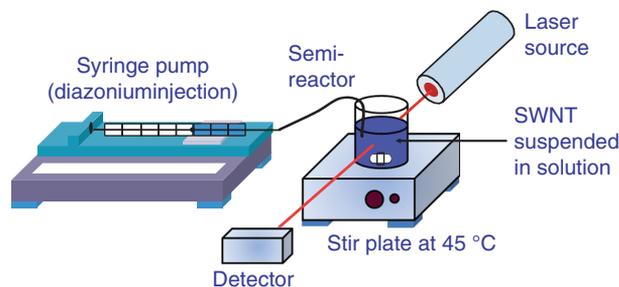


Fig. 1. Simplified diagram of reactor setup. For more details of a specific experimental system, see Ref. [22].

in Eq. (3) relates the coverages of nanotubes of different chiralities to each other:

$$\frac{dN_{\theta_{(n, m)}}}{dN_{\theta_{(\tilde{n}, \tilde{m})}}} = \frac{k_A^{(n, m)} N_{\theta_{(n, m)}}}{k_A^{(\tilde{n}, \tilde{m})} N_{\theta_{(\tilde{n}, \tilde{m})}}} \quad (4)$$

$$N_{\theta_{(n, m)}} = N_{\theta_{(\tilde{n}, \tilde{m})}} \left(\frac{N_{\theta_{(\tilde{n}, \tilde{m})}}}{N_{\theta_{(n, m)}}} \right)^{k_A^{(n, m)} / k_A^{(\tilde{n}, \tilde{m})}} \quad (5)$$

Inserting Eqs. (2) and (5) into Eq. (3) results in decoupled differential equations:

$$\begin{aligned} & \frac{dN_{\theta_{(\tilde{n}, \tilde{m})}}}{dt} \\ &= - \frac{k_A^{(\tilde{n}, \tilde{m})} N_{\theta_{(\tilde{n}, \tilde{m})}}}{V_R} \\ & \cdot \left(F_{D_0} t - N_T + \sum_{(n, m)} N_{\theta_{(n, m)}} \left(\frac{N_{\theta_{(\tilde{n}, \tilde{m})}}}{N_{\theta_{(n, m)}}} n \right)^{k_A^{(n, m)} / k_A^{(\tilde{n}, \tilde{m})}} \right) \quad (6) \end{aligned}$$

which can be simulated very efficiently by numerical integration for each (\tilde{n}, \tilde{m}) SWNT. Section 3 applies these equations to formulate computationally efficient algorithms for the identification of the adsorption rate constants $k_A^{(n, m)}$ from the measurement of the molar compositions of vacant sites on SWNTs of each chirality by the deconvolution of the photoabsorption spectrum of the SWNT solution.

Before attempting to identify parameters from experimental data, an important consideration is whether the rate constants are *identifiable*, that is, whether it is possible to uniquely determine their values. None of the chemical rate constants ($k_R^{(n, m)}$) are identifiable from measurement of $N_{\theta_{(\tilde{n}, \tilde{m})}}$, as they do not appear in Eq. (6). All of the adsorption rate constants $k_A^{(n, m)}$ in a chirality-selective SWNT reaction network are identifiable if and only if the sensitivity matrix $\nabla_{k_A} N_{\theta}$ between the adsorption rate parameters and the measured variables is full rank,²⁴ where N_{θ} is the vector of open-site coverages, k_A is the vector of adsorption rate constants over all (n, m) nanotubes, and

$$\frac{\partial N_{\theta_{(n, m)}}}{\partial k_A^{(\tilde{n}, \tilde{m})}} \quad (7)$$

is the element in the (n, m) row and the (\tilde{n}, \tilde{m}) column of $\nabla_{k_A} N_\theta$. With SWNTs of chirality (n', m') arbitrarily selected as a reference to which the coverages of nanotubes of other chiralities will be related, apply the chain rule to Eq. (5) with (n', m') in place of (\tilde{n}, \tilde{m}) to give the elements of the sensitivity matrix as²⁵

$$\frac{\partial N_{\theta_{(n,m)}}}{\partial k_A^{(n,m)}} = \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{k_A^{(n',m')} N_{\theta_{(n',m')}}} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(n,m)}} + \frac{N_{\theta_{(n,m)}}}{k_A^{(n',m')}} \ln \frac{N_{\theta_{(n',m')}}}{N_{\theta_{0(n',m')}}}, \quad (n, m) \neq (n', m') \quad (8)$$

$$\frac{\partial N_{\theta_{(n,m)}}}{\partial k_A^{(\tilde{n}, \tilde{m})}} = \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{k_A^{(n',m')} N_{\theta_{(n',m')}}} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(\tilde{n}, \tilde{m})}}, \quad (n, m) \neq (\tilde{n}, \tilde{m}) \neq (n', m') \quad (9)$$

$$\frac{\partial N_{\theta_{(n,m)}}}{\partial k_A^{(n',m')}} = \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{k_A^{(n',m')} N_{\theta_{(n',m')}}} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(n',m')}} - \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{(k_A^{(n',m')})^2} \ln \frac{N_{\theta_{(n',m')}}}{N_{\theta_{0(n',m')}}} \quad (10)$$

where SWNTs of chirality (n', m') is arbitrarily chosen as a reference to which the coverages of nanotubes of other chiralities are related. Applying elementary row and column operations^{26,27} to the sensitivity matrix results in Ref. [28]

$$\text{diag} \left(1, \dots, 1, \sum_{(n,m)} k_A^{(n,m)} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(n,m)}} \right) \quad (11)$$

which indicates that the sensitivity matrix is full rank if and only if²⁹

$$\sum_{(n,m)} k_A^{(n,m)} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(n,m)}} \neq 0 \quad (12)$$

This identifiability condition can be interpreted in terms of the response of the measured variables to a relative change in the adsorption rate constants, $\delta k_A = \gamma k_A$ for scalar $\gamma > 0$:

$$\begin{aligned} \delta N_{\theta_{(n,m)}} &= (\nabla_{k_A} N_{\theta_{(n,m)}}) \gamma k_A \\ &= \gamma \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{k_A^{(n',m')} N_{\theta_{(n',m')}}} \sum_{(n,m)} k_A^{(n,m)} \frac{\partial N_{\theta_{(n',m')}}}{\partial k_A^{(n,m)}} \end{aligned} \quad (13)$$

Equation (13) indicates that the identifiability condition (12) must hold for it to be possible to determine the magnitude of any adsorption rate constant. Provided that all of the molar concentrations of vacant sites can be measured, the magnitude of each adsorption rate constant is the only

information that is lost when the identifiability condition is not satisfied, as the matrix in Eq. (11) always has rank at least $n - 1$.²⁷ In particular, the ratios of the adsorption rate constants are identifiable regardless of whether the identifiability condition (12) holds. Further, the ratio

$$\frac{\delta N_{\theta_{(n,m)}}}{\delta N_{\theta_{(\tilde{n}, \tilde{m})}}} = \frac{k_A^{(n,m)} N_{\theta_{(n,m)}}}{k_A^{(\tilde{n}, \tilde{m})} N_{\theta_{(\tilde{n}, \tilde{m})}}} \quad (14)$$

indicates that the SWNTs with the largest adsorption rate constants and the most accurate measurement of the number of vacant sites are the easiest to accurately identify from experimental data, which is to be expected.

The above analysis, which derived exact analytical expressions for $\theta_{(n,m)}$ rather than writing balances on the molar concentrations of sites occupied by adsorbate or product, $A\theta_{(n,m)}$ and $P\theta_{(n,m)}$, requires no assumptions regarding whether or not the adsorption step is rate limiting. The measurement of $\theta_{(n,m)}$ provides no information on the chemical rate constants, and so any assumptions with respect to the chemical kinetics do not simplify the analysis. The identification of the chemical rate constants would require measurement of either the molar concentrations of sites occupied by adsorbate or product.

3. IDENTIFICATION OF ADSORPTION RATE CONSTANTS

This section applies the kinetic analysis to formulate computationally efficient algorithms for determining chirality-specific adsorption rate constants in SWNT reaction networks. The least-squares estimates of the adsorption rate parameters from dynamic data are solutions to the optimization

$$\inf_{k_A^{(n,m)}} \sum_j \sum_{(n,m)} (N_{\theta_{(n,m)}}^{\text{model}}(t_j) - N_{\theta_{(n,m)}}^{\text{exp}}(t_j))^2 \quad (15)$$

which can be numerically solved by coupling a generic optimizer with a differential equation solver for Eq. (6). Since the differential equation for the concentration of SWNT for each chirality is independent of the other differential equations, the solver can simulate each equation independently, for an overall computational cost that is proportional to the square of the number of different chiralities. This inexpensive evaluation of the objective function in Eq. (15) enables the use of optimizers such as simulated annealing³⁰ that have a very high probability of converging to a global solution. The fast numerical solution also enables the very accurate quantification of the probability distributions for the adsorption rate parameters by application of Markov Chain Monte Carlo (MCMC) simulation.^{31,32}

The least-squares objective (15) should be modified if the experimental data include molar concentrations of vacant sites that have low accuracy, for example, due

to a high degree of peak overlap in the photoabsorption spectrum.²¹ When this happens, a large number of adsorption rate parameters result in similar values for the least-squares objective (15), and faster and more reliable convergence is obtained by addition of a regularization term³³

$$\inf_{k_A^{(n,m)}} \sum_j \sum_{(n,m)} (N_{\theta_{(n,m)}}^{\text{model}}(t_j) - N_{\theta_{(n,m)}}^{\text{exp}}(t_j))^2 + \delta \sum_{(n,m)} (k_{A_{(n,m)}})^2 \quad (16)$$

where δ is a small number.

An alternative formulation to the optimization (15) is useful when the identifiability condition (12) does not hold, in which case an infinite number of solutions exist for the optimization (15). The analysis in Section 2 indicated that in this case the magnitude of the adsorption rate constants cannot be identified. Such a loss in identifiability can occur in seemingly reasonable experimental systems. For example, consider the experimental setup in which the diazonium concentration is not allowed to accumulate (see Fig. 1). In this case, Eqs. (2) and (3) give that²³

$$\frac{dN_D}{dt} = F_{D_0} - \frac{N_D}{V_R} \sum_{(n,m)} k_A^{(n,m)} N_{\theta_{(n,m)}} \approx 0 \Rightarrow N_D \approx \frac{F_{D_0} V_R}{\sum_{(n,m)} k_A^{(n,m)} N_{\theta_{(n,m)}}} \quad (17)$$

Inserting Eq. (17) into Eq. (3) for the (n, m) nanotube gives

$$\frac{dN_{\theta_{(n,m)}}}{dt} \approx - \frac{F_{D_0} N_{\theta_{(n,m)}}}{\sum_{(\tilde{n}, \tilde{m})} k_A^{(\tilde{n}, \tilde{m})} / k_A^{(n,m)} N_{\theta_{(\tilde{n}, \tilde{m})}}} \quad (18)$$

which indicates that the number of vacant sites on the nanotubes of each chirality is only a function of the ratios of adsorption rate constants. It is not possible to estimate the absolute magnitude of the adsorption rate constants with the seemingly reasonable experimental setup in Figure 1. The scaling of all the kinetic constants by an arbitrary number does not affect the number of vacant sites on the nanotubes, and only the relative rate constants can be estimated from the experimental data. For problems in which the identifiability condition (12) does not hold, it is better to reformulate the least-squares optimization as

$$\inf_{k_A^{(n,m)}/k_A^{(n',m')}} \sum_j \sum_{(n,m)} (N_{\theta_{(n,m)}}^{\text{model}}(t_j) - N_{\theta_{(n,m)}}^{\text{exp}}(t_j))^2 \quad (19)$$

subject to Eq. (6) with $k_A^{(n',m')}$ set to a fixed constant, or subject to a simplified model equation such as (18) in which only the ratios appear. A regularization term as in Eq. (16) should be introduced for experiments in which some of the molar compositions of vacant sites are measured with low accuracy.

It is straightforward to generalize the expressions and algorithms to weighted least-squares, minimum variance, maximum likelihood, and maximum a posteriori parameter estimation in which more sophisticated assumptions are made on the noise and prior knowledge, and to the case of multiple experimental data sets.²⁴

4. CONCLUSIONS

A dynamic analysis of SWNT reaction networks was provided that included (i) an efficient numerical algorithm for computing the molar concentration of vacant sites on SWNTs of varying chirality, (ii) efficient numerical algorithms for the identification of adsorption rate constants from experimental data on the molar concentration of vacant sites for each (n,m) -SWNT, and (iii) an analysis of the identifiability of both absolute magnitudes and ratios of adsorption rate constants. The analyses required no assumptions with regard to the relative rates of adsorption and covalent chemical reactions for the SWNTs. Sensitivity analysis shows that quasi-steady-state operation of the system results in the loss of information on the individual reactivity, so that only the relative adsorption rate constants can be estimated.

For specificity the paper considered semibatch reactions of SWNTs with 4-hydroxybenzene diazonium, however, the analysis and algorithms apply to other multi-step adsorption/reaction mechanisms with minor modifications. For example, the mechanism underlying most SWNT-based biosensors concerns the indirect measurement of the rates of adsorption of biomolecules on the surface of SWNTs by tracking changes in spectra, conductance, capacitance, etc., and the identification of the adsorption kinetics can be used to determine chirality distributions in SWNT-based biosensors to maximize selectivity or sensitivity.

Acknowledgment: Support from the National Science Foundation (grant #0426328) is acknowledged.

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25. Without loss in generality, it is assumed that $k_A^{(n', m')} \neq 0$.
26. Diag is matrix with its arguments placed on the diagonal.
27. Elementary row and column operations do not change the rank of the matrix, e.g., see S. Roman, *Advanced Linear Algebra*, second edition, Springer Verlag, Lemma 1.15, page 48 (2005).
28. Provided that all of the (n, m) SWNTs are present in the system, so that the number of vacant sizes for each chirality is nonzero.
29. Inserting a rearrangement of Eq. (9) into Eq. (12) results in an equivalent identifiability condition $\sum_{(n, m)} k_A^{(n, m)} \partial N_{\theta_{(n'', m'')}} / \partial k_A^{(n, m)} \neq 0$, provided that the adsorption rate constant for the (n'', m'') SWNTs is nonzero. That is, any SWNT can be used as the reference for comparisons of adsorption rate constants among SWNTs of different chirality.
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Received: 24 July 2009. Accepted: 30 October 2009.