



Low temperature plasma treatment of rice husk derived hybrid silica/carbon biochar using different gas sources

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ABSTRACT

Hybrid silica/carbon particles were synthesized from rice husk as sustainable precursor material. Synthesized material was subjected to low temperature plasma treatments in presence of different gas sources like Argon, Oxygen and Sulphur Hexafluoride. Effects of plasma treatments were characterized using various techniques. It was found that plasma treatments were effective in altering surface properties like surface binding energies, functionalities and morphology. Plasma treatments did not have any substantial effects on bulk properties of rice husk biochar. However, in case of oxygen plasma treatments it was found to be effective in surface level etching resulting in increased nanoporous structure.

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1. Introduction

Nanomaterials with high surface area, superior reactivity and improved thermal, mechanical and electrical properties are very desirable in the various fields of engineering for energy, environment and structural applications [1,2]. However, synthesis of such materials using fossil fuel sources require very sophisticated procedures and has serious environmental concerns. Instead, there are many sustainable agricultural materials which have huge potential to be used as precursors for developing advanced materials with high performance and multifunctionality [3]. Among such natural precursors, rice husk is of particular importance due to presence of silica (SiO_2) making it a naturally occurring organic-inorganic composite material. Rice husk typically contains of cellulose (35–40 wt%), hemicellulose (15–20 wt%), lignin (20–25 wt%) and silica (15–28%) [4].

Carbon derived from sustainable sources is of limited use mainly due to inactive surface functionalities and reduced surface area. Activation of such materials is typically achieved through wet chemical processes. The objective of activation is to increase surface area and/or to introduce active functional groups. There are many approaches to fine tune surface properties like covalent, non-covalent and defect functionalization. But these approaches tend to deteriorate desirable properties of carbon sometimes. To overcome these problems researchers are

exploring new methods to improve the surface properties of carbon materials without affecting their bulk properties. Nowadays, plasma technology is being regarded as a highly efficient tool for material preparation or modification [5,6]. Usually, plasma technology is a low energy, cost effective process. It also does not yield any harmful chemical waste making it a sustainable route for material modifications. Low-temperature plasmas (LTPs) are a unique state of matter due to the presence of neutral atoms and molecules, radicals, excited states, ions, and electrons [7]. During a typical plasma material modification process, the energetic radicals attack the surface of material and then a series of physical and chemical reactions occur during the energy exchange, the redundant reactants then are removed from the material surface and thus change the physical and chemical properties of the material [8–11]. Valentini et al. functionalized Carbon nanotubes (CNT) and Graphene sheets using CF_4 gas to activate surface through covalent C-F bonds and induce structural disorder due to impregnation of fluorine atoms within graphitic structure [12,13]. Edge-rich and dopant-free metal-free electrocatalysts of graphene and CNT's with superior performance were developed using Argon RF plasma. Plasma treatments were effective in increasing defect sites by generating holes and edges [14]. The objective of current work is to implement low temperature plasma process in presence of various gases to modify surface functionalities and morphology of rice husk derived silica/carbon hybrid particles. To best of our knowledge, this is the first time effects of plasma treatments on biochar derived from agricultural products is being reported.

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2. Experimental

Rice husk (RH) provided by three H's LLC was washed with distilled water to remove surface impurities, it was dried in oven overnight at 100 °C to remove moisture contents and then ball milled for 3 h to reduce size. Then the powder was sieved using 45 μ mesh to exclude bigger particles and achieve uniform powder. Thus, obtained RH powder was pyrolyzed at a heating rate of 10 °C/min upto a temperature of 1000 °C and held for 2 h under autogenic pressure using high-pressure/temperature reactor to obtain Rice Husk Ash (RHA). Plasma treatment of RHA was done using PE-100 Plasma Etch setup equipped with a rotating circular drum to ensure uniform functionalization of the powder. RHA was plasma treated in presence of Argon (Ar), Oxygen (O₂) and Sulphur Hexafluoride (SF₆) gas individually at a chamber pressure of 0.2 Torr and constant flow of 30 ccm. Radiofrequency (RF) power of 150 W generated at a standard frequency of 13.5 MHz was used to treat samples for a duration of 30 min each. Plasma treated samples were then characterized using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) for surface energy and functional changes. Transmission electron microscope (TEM), Field emission scanning electron microscope (FE-SEM)/ Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) techniques were used to study morphological changes due to plasma treatment.

3. Results and discussion

The RHA (60% yields) obtained after pyrolysis contained of about 52% CO₂ and 48% SiO₂ confirmed by TGA analysis in presence of oxygen. TEM micrographs (Fig. 1a) of RHA revealed that the silica particles are highly crystalline and with nanoporous structure. The amorphous carbon particles are randomly oriented along with embedded silica particles. The silica particles appear to have very small sizes between 10 and 20 nm. These nanoporous nature of the particles can facilitate better interactions when treated with plasma gases. The elemental composition of RHA using SEM/EDS spectroscopy revealed that the samples contained carbon (67.07%), Oxygen (24.33%) and Silicon (20.56%) in its atomic form as shown in Fig. 1(b–f).

XPS survey of untreated and plasma treated RHA using various gases have shown changes in surface energies due to plasma induced changes during treatment. The surface atomic composition data shows that for all the treatments C content (C1s) decreased from 80.5% to 76.0, 71.2 and 50.8% for Ar, O₂ and SF₆ plasma treatments respectively shown in table 1. However, oxygen content (O1s) was highest for oxygen plasma treatment which was 23.9% compared to 15.6% for untreated samples. In case of SF₆ treated samples there was additional fluorine content (F1s) of about 22.7% due to fluorine atoms from the gas reacting with surface carbon of RHA show in Fig. 2(e). Deconvoluted graphs of C1s XPS (Fig. 2(a–d) and Table 1) gave further insights into surface level energies of carbon content due to plasma treatments. Ar plasma treatments improved the carbon surface energies (~285.0 eV) which was primarily due to presence of reactive species in plasma during treatment. In case of oxygen plasma treatments, it was found that there was decrease in surface energy of atomic carbon from 51.42 to 37.64% but also there was drastic increase in surface energy due to C–O (~286.0 eV) from 40.32% to 55.40% due to reactive oxygen ions reacting with surface carbon of RHA during plasma treatment process. Finally, with SF₆ plasma treatment it was found that C–O surface energies decreased upto a value of 16.17%. However, the C=O (~288–289 eV) energies increased from 8.26% to 20.54% and there was additional 14.15% energy related to CF₂/CF₃ (~292–293 eV) which was unique only to SF₆ treatments. Thus, plasma treatments were effective in increasing surface energies corresponding to fluorine related reactions. FTIR graphs for untreated and plasma treated samples further confirmed the effectiveness of plasma treatments on improved surface functionalities shown in Fig. 2(f). The intensities corresponding to Si–O–Si stretching at 1100–1000 cm^{−1} decreased for Ar and SF₆ treatments. For Ar treatments there was slight increase in intensity at 1640–1680 cm^{−1} corresponding to alkene (C=C) and at 3000 cm^{−1} corresponding to C–H. In case of SF₆ plasma treatment there was a peak observed at 700–600 cm^{−1} corresponding alkyl halide of C–F.

Once surface level changes were confirmed further investigations to study bulk property changes were done using XRD analysis. It was found that the sharp diffraction peak at 22.4° is ascribed to the peak of crystalline cristobalite, SiO₂ which is corresponds to the (101) plane with an interlayer spacing of about 0.40 nm as shown in Fig. 3(a). The particle sizes were estimated from XRD data

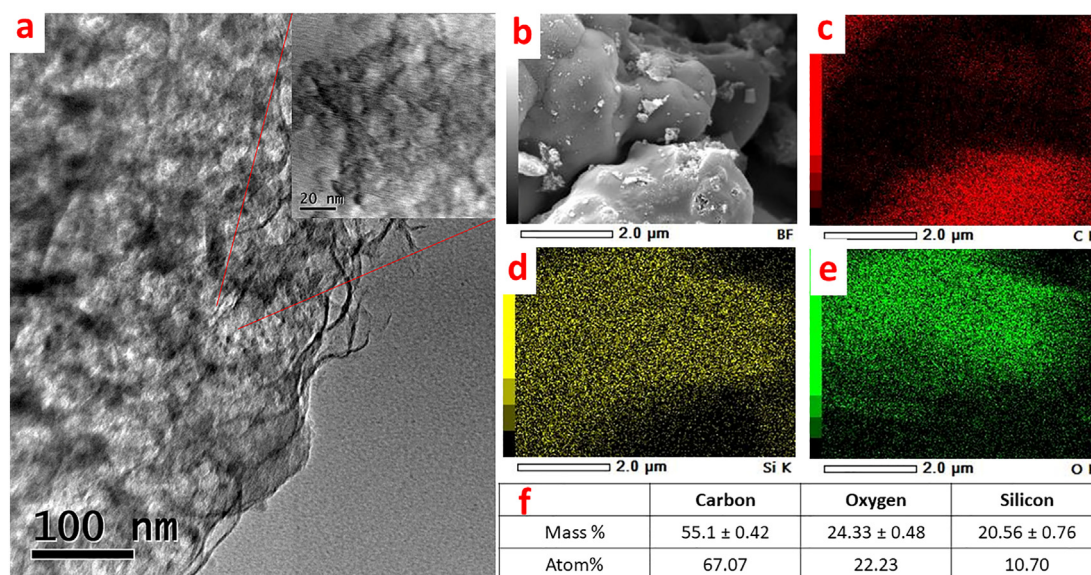
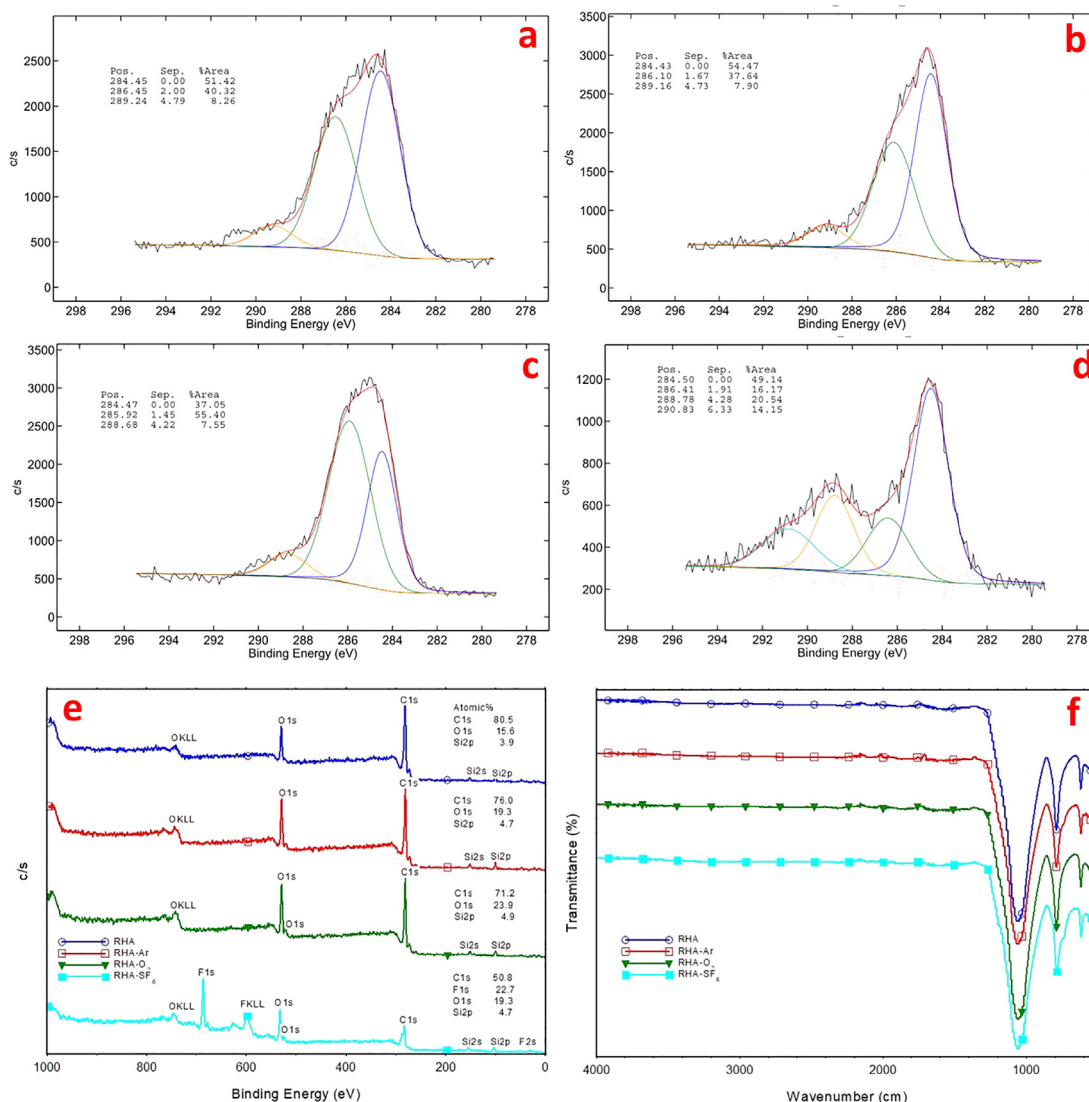


Fig. 1. (a) TEM image of RHA. (b–f) EDS analysis of RHA.

Table 1

Elemental compositions and relative area (%) corresponding to different chemical bonds from XPS data.

	Atom (%)				Area (%)			
	C1s	O1s	Si2p	F1s	C-C/C-H	C-O	C=O	CF2/CF3
RHA	80.5	15.6	3.9	–	51.42	40.32	8.26	–
Ar-RHA	76.0	19.3	4.7	–	54.47	37.64	7.90	–
O2-RHA	71.2	23.9	4.9	–	37.05	55.40	7.55	–
SF6-RHA	50.8	19.3	4.7	22.7	49.14	16.17	20.54	14.15

**Fig. 2.** Deconvoluted C1s XPS graph of (a) Untreated RHA (b) Ar Plasma treated RHA (c) O₂ Plasma treated RHA (d) SF₆ Plasma treated RHA. (e) XPS graph of untreated and plasma treated RHA. (f) FTIR graph of untreated and plasma treated RHA.

using Debye-Scherrer's equation. The full width at half maxima of 100% peak is measured as 0.0099 rad. The particles sizes estimated from this equation are ~ 15 nm which was also confirmed from TEM images. It was found that plasma treatments did not have any major effect in altering crystal lattice structure of RHA, confirming that plasma induced changes were confined only to surface level changes. SEM analysis was performed to study surface level morphological changes on RHA particles due to plasma treatments. It was found that there was no noticeable change in surface morphology of Ar plasma treated samples (Fig. 3c). In case of SF₆ plasma treated samples shown in Fig. 3e, there was evidence of some surface level etching. However, in case of oxygen plasma

treatment maximum etching effects were observed primarily due to oxidation of surface during reactive ion bombardments as shown in Fig. 3d. These micro/nano porous structures can be very useful for applications involving surface area reactions.

4. Conclusions

In summary, from the observations made it can be established that plasma treatment process can be applied to alter surface energies of silica/carbon particles derived from rice husk. Oxygen plasma treatments in particular has potential for surface level

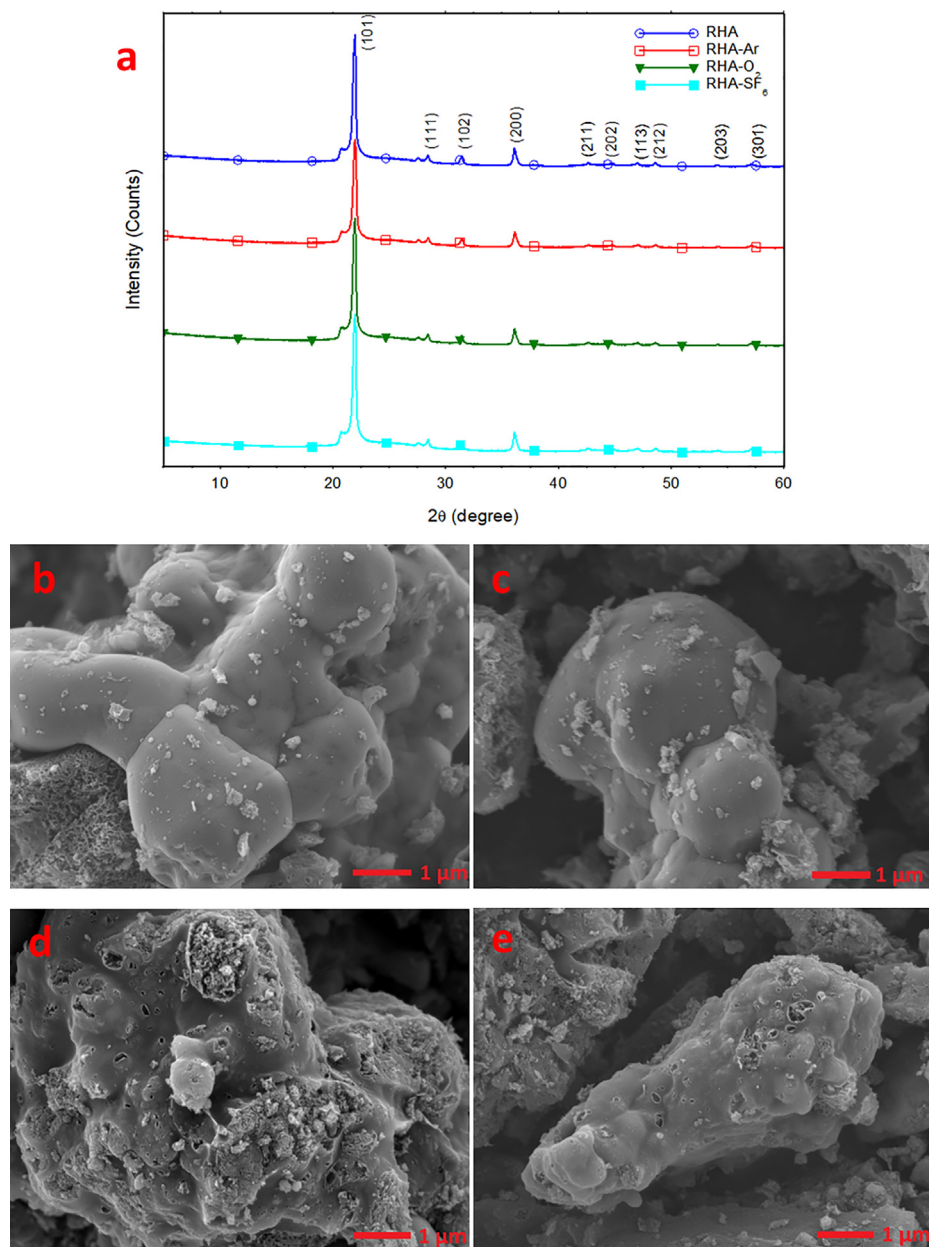


Fig. 3. (a) XRD graph of untreated and plasma treated RHA. SEM image of (b) Untreated RHA (c) Ar Plasma treated RHA (d) O₂ Plasma treated RHA (e) SF₆ Plasma treated RHA.

etching of carbonaceous materials. Upon further optimization of parameters like power, gas composition and treatment duration desired results can be obtained. Properties like wettability, surface area, surface energy, pore size and surface conductivity can be altered. Materials thus obtained has great potential in the areas of composites, energy, environment and structural applications.

CRediT authorship contribution statement

Zaheeruddin Mohammed: Writing - original draft. **Shaik Jeelani:** Supervision. **Vijaya Rangari:** Conceptualization, Writing-review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] M.S. Mauter, M. Elimelech, Environmental applications of carbon-based nanomaterials, *Environ. Sci. Technol.* 42 (16) (2008) 5843–5859, <https://doi.org/10.1021/es8006904>.
- [2] C. Sanchez, K.J. Shea, S. Kitagawa, U. Schubert, Hybrid materials themed issue Cluster-based inorganic – organic hybrid materials, *Chem. Soc. Rev.* 40 (2011) 453–1152, <https://doi.org/10.1039/c0cs00009d>.
- [3] R. Kumar, R.K. Singh, D.P. Singh, Natural and waste hydrocarbon precursors for the synthesis of carbon based nanomaterials: graphene and CNTs, *Renew. Sustain. Energy Rev.* 58 (2016) 976–1006, <https://doi.org/10.1016/j.rser.2015.12.120>.
- [4] S.-S. Huang, M.T. Tung, C.D. Huynh, B.-J. Hwang, P.M. Bieker, C.-C. Fang, N.-L. Wu, Engineering rice husk into a high-performance electrode material through

- an ecofriendly process and assessing its application for lithium-ion sulfur batteries, *ACS Sustain. Chem. Eng.* 7 (8) (2019) 7851–7861, <https://doi.org/10.1021/acssuschemeng.9b00092>.
- [5] M.V. Naseh, A.A. Khodadadi, Y. Mortazavi, F. Pourfayaz, O. Alizadeh, M. Maghrebi, Fast and clean functionalization of carbon nanotubes by dielectric barrier discharge plasma in air compared to acid treatment, *Carbon N. Y.* 48 (5) (2010) 1369–1379, <https://doi.org/10.1016/j.carbon.2009.12.027>.
- [6] Z. Mohammed, S. Jeelani, V. Rangari, Effect of low-temperature plasma treatment on surface modification of polycaprolactone pellets and thermal properties of extruded filaments, *JOM.* 72 (4) (2020) 1523–1532, <https://doi.org/10.1007/s11837-020-04004-y>.
- [7] H.P. Li, K. (Ken) Ostrikov, W. Sun, The energy tree: Non-equilibrium energy transfer in collision-dominated plasmas, *Phys. Rep.* 770–772 (2018) 1–45, <https://doi.org/10.1016/j.physrep.2018.08.002>.
- [8] Shuo Dou, Li Tao, Ruilun Wang, Samir El Hankari, Ru Chen, Shuangyin Wang, Plasma-assisted synthesis and surface modification of electrode materials for renewable energy, *Adv. Mater.* 30 (21) (2018) 1705850, <https://doi.org/10.1002/adma.v30.2110.1002/adma.201705850>.
- [9] D.L. Sun, R.Y. Hong, F. Wang, J.Y. Liu, M. Rajesh Kumar, Synthesis and modification of carbon nanomaterials via AC arc and dielectric barrier discharge plasma, *Chem. Eng. J.* 283 (2016) 9–20, <https://doi.org/10.1016/j.cej.2015.07.023>.
- [10] F. Khodadadei, H. Ghourchian, M. Soltanieh, M. Hosseinalipour, Y. Mortazavi, Rapid and clean amine functionalization of carbon nanotubes in a dielectric barrier discharge reactor for biosensor development, *Electrochim. Acta.* 115 (2014) 378–385, <https://doi.org/10.1016/j.electacta.2013.10.039>.
- [11] G.V. Bianco, A. Sacchetti, C. Ingrosso, M.M. Giangregorio, M. Losurdo, P. Capezzuto, G. Bruno, Engineering graphene properties by modulated plasma treatments, *Carbon N. Y.* 129 (2018) 869–877, <https://doi.org/10.1016/j.carbon.2017.11.015>.
- [12] Luca Valentini, Debora Puglia, Fabio Carniato, Enrico Boccaleri, Leonardo Marchese, José M. Kenny, Use of plasma fluorinated single-walled carbon nanotubes for the preparation of nanocomposites with epoxy matrix, *Compos. Sci. Technol.* 68 (3–4) (2008) 1008–1014, <https://doi.org/10.1016/j.compscitech.2007.07.011>.
- [13] Silvia Bittolo Bon, Luca Valentini, Raquel Verdejo, Jose L. Garcia, Laura Peponi Fierro, Miguel A. Lopez-Manchado, Jose M. Kenny, Plasma fluorination of chemically derived graphene sheets and subsequent modification with butylamine, *Chem. Mater.* 21 (14) (2009) 3433–3438, <https://doi.org/10.1021/cm901039j>.
- [14] Li Tao, Qiang Wang, Shuo Dou, Zhaoling Ma, Jia Huo, Shuangyin Wang, Liming Dai, Edge-rich and dopant-free graphene as a highly efficient metal-free electrocatalyst for the oxygen reduction reaction, *Chem. Commun.* 52 (13) (2016) 2764–2767.