



**Sarzamin Khan**

**Photoluminescent semiconductors nanoparticles as  
optical probes for the determination of captopril,  
histamine, aminoglycosides and thyroxine.**

**TESE DE DOUTORADO**

Thesis presented to the Programa de Pós-Graduação em Química  
of the Departamento de Química do Centro Técnico Científico da  
PUC-Rio, as partial fulfilment of the requirements for the degree  
of Doutor em Ciências- Química.

Advisor: Prof. Ricardo Queiroz Aucélio

Rio de Janeiro

April, 2013



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### Ficha Catalográfica

Khan, Sarzamin

Photoluminescent semiconductors nanoparticles as optical probes for the determination of captopril, histamine, aminoglycosides and thyroxine / Sarzamin Khan; orientador: Ricardo Queiróz Aucélio. – 2013.

180 f.: il. (color.) ; 30 cm

Tese (doutorado) - Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, 2013.

Inclui bibliografia

1. Química – Teses. 2. Semiconductor nanocrystals. 3. Quantum dots. 4. Stern-Volmer model. 5. Langmuir model for enhanced photoluminescence. 6. Captopril. 7. Histamine. 8. Aminoglycosides. 9. Thyroxine. I. Aucélio, Ricardo Queiróz. II. Pontifícia Universidade Católica do Rio de Janeiro. Departamento de Química. III. Título.

CDD:540

## Acknowledgments

I feel great delight and happiness in expressing, heart felt gratitude to my research advisor Prof. Dr. Ricardo Queiroz Aucélio, for his motivating and stirring guidance, devotion of time, valuable suggestions and courteous behaviour in completing this work.

I would like to thank everyone in our research group for your cooperation and kindness.

The time I spent with you will be remembered for ever.

I would like to express my gratitude to TWAS-CNPq for scholarship.

In last but not the least I wish to thanks my father and all family members for their love and endless support, none of this thesis would have even existed without the continual encouragement and support my family gives for everything I do.

I also thank FAPERJ, CNPq and FINEP for funding this research.

## Abstract

Khan, Sarzamin; Aucélio, Ricardo Queiroz (Advisor). **Photoluminescent semiconductors nanoparticles as optical probes for the determination of captopril, histamine, aminoglycosides and thyroxine.** Rio de Janeiro, 2013. 180p. Doctoral thesis- Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro.

Recently, semiconductor nanocrystals, also known as quantum dots, have become very attractive for photoluminescence based sensing approaches due to their unique optical properties like intense photoluminescence with narrow profile, maximum wavelength adjustable by the control of particle size and higher photostability in comparison of conventional organic dyes. Different synthesized nanoparticles were evaluated as photoluminescent probes (as aqueous dispersions) for the determination of captopril, histamine, kanamycin and thyroxine (non-photoluminescent analytes at room-temperature) avoiding the use of complex chemical derivatization procedures and enabling simple and sensitive quantifications. Thioglycolic acid (TGA) and 2-mercapopropionic acid (2MPA) modified CdTe nanoparticles and L-cysteine modified ZnS nanoparticles were synthesized via the colloid aqueous phase route. Their characterization was made using proper microscopic and spectroscopic methods.

The emission intensity of 2MPA-CdTe is greatly enhanced in the presence of captopril. Under optimum conditions, the calibration model (Langmuir binding isotherm) was linear up to  $4.8 \times 10^{-4} \text{ mol L}^{-1}$  with equilibrium binding constant of  $3.2 \times 10^4 \text{ L mol}^{-1}$  and limit of detection (LOD) of  $6.2 \times 10^{-6} \text{ mol L}^{-1}$  ( $1.3 \text{ } \mu\text{g mL}^{-1}$ ). Applications in captopril fortified human serum and in pharmaceutical formulations were demonstrated. The photoluminescence of TGA-CdTe nanoparticles was quenched by histamine in a concentration dependent manner (Stern-Volmer model). The linear response covered the concentration range up to  $5.7 \times 10^{-4} \text{ mol L}^{-1}$  with LOD of  $9.6 \times 10^{-6} \text{ mol L}^{-1}$  ( $1.1 \text{ } \mu\text{g mL}^{-1}$ ). The proposed method was used for the analysis of tuna fish. The presence of aminoglycosides enhanced the photoluminescence of the TGA-CdTe nanoparticles (following a Langmuir binding isotherm model). Kanamycin was used as a model aminoglycoside in order to study its effect on the photoluminescence enhancement of TGA-CdTe quantum dots dispersed in aqueous solution. The linear range

extended up to  $8.2 \times 10^{-7} \text{ mol L}^{-1}$  with LOD of  $2.5 \times 10^{-8} \text{ mol L}^{-1}$  ( $14.2 \text{ ng mL}^{-1}$ ). Binding constants were calculated for several aminoglycosides indicating that there is a relationship between the number of available primary amino groups and the increasing in photoluminescence. This approach was successfully applied for determination of kanamycin fortified milk and in stream water samples after solid phase extraction using a molecular imprinted polymer produced using a kanamycin template. The photoluminescence intensity of cysteine-ZnS in solution containing cetyltrimethyl ammonium bromide (CTAB) was quenched by thyroxine. The overall quenching followed a Stern-Volmer model with linear response covering an analyte concentration range up to  $4.0 \times 10^{-6} \text{ mol L}^{-1}$ . LOD was  $6.2 \times 10^{-8} \text{ mol L}^{-1}$  ( $48.3 \text{ ng mL}^{-1}$ ). The aqueous dispersion of cysteine-ZnS was used as optical probe for the determination of thyroxine in pharmaceutical formulations and in analyte fortified human saliva.

## Keywords

Semiconductor nanocrystals; quantum dots; Stern-Volmer model; Langmuir model for enhanced photoluminescence; captopril; histamine; aminoglycosides; thyroxine

## Resumo

Khan, Sarzamin; Aucélio, Ricardo Queiroz. **Nanopartículas semicondutores fotoluminescentes como sondas ópticas para determinação de captopril, histamina, aminoglicosídeos e tiroxina.** Rio de Janeiro, 2013. 180p. Tese de Doutorado - Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro.

Recentemente, os nanocristais semicondutores, também conhecidos como pontos quânticos, tornaram-se muito atrativos em abordagens de detecção por fotoluminescência devido as suas propriedades ópticas peculiares, tais como fluorescência intensa e com perfil estreito, comprimento de onda máximo ajustável através do controle do tamanho das partículas e maior fotoestabilidade em comparação com os corantes orgânicos convencionais. As nanopartículas sintetizadas foram avaliadas como sondas fotoluminescentes (na forma de dispersão aquosa) para a determinação de captopril, histamina, canamicina e tiroxina (analitos não fotoluminescentes na temperatura ambiente) evitando o uso de procedimentos complexos de derivatização química e permitindo quantificações de forma simples e com sensibilidade. Nanopartículas de CdTe modificadas com o ácido tioglicólico (TGA) e com o ácido 2-mercaptopropiônico (2MPA) e também nanopartículas de ZnS modificadas com L-cisteína foram sintetizadas pela abordagem em fase aquosa coloidal. Estas foram caracterizadas usando métodos microscópicos e espectroscópicos adequados.

A fotoluminescência da nanopartícula 2MPA-CdTe foi consideravelmente mais intensa quando na presença de captopril. Sob condições ótimas, o modelo de calibração (isoterma de ligação de Langmuir) foi linear até  $4,8 \times 10^{-4} \text{ mol L}^{-1}$  com constante de equilíbrio de ligação de  $3,2 \times 10^4 \text{ L mol}^{-1}$  e limite de detecção (LOD) de  $6,2 \times 10^{-6} \text{ mol L}^{-1}$  ( $1,3 \text{ } \mu\text{g mL}^{-1}$ ). Aplicações em soro sanguíneo humano fortificado com captopril e em formulações farmacêuticas foram demonstradas. A fotoluminescência das nanopartículas de TGA-CdTe foi reduzida (supressão) após adição de diferentes concentrações de histamina seguindo o modelo de Stern-Volmer. A resposta linear cobriu uma faixa de concentração até  $5,7 \times 10^{-4} \text{ mol L}^{-1}$ , com LOD de  $9,6 \times 10^{-6} \text{ mol L}^{-1}$  ( $1,1 \text{ } \mu\text{g mL}^{-1}$ ). A abordagem proposta foi utilizada para determinação de histamina em carne de atum. Já a presença de aminoglicosídeos aumentou a fluorescência das nanopartículas de TGA-CdTe

(seguindo o modelo da isoterma da adsorção de Langmuir). A kanamicina foi o aminoglicosídeo escolhido para estudar o efeito do aumento da intensidade da fotoluminescência das nanopartículas de TGA-CdTe disperso em solução aquosa. A faixa linear estendeu-se até  $8,2 \times 10^{-7} \text{ mol L}^{-1}$  com LOD de  $2,5 \times 10^{-8} \text{ mol L}^{-1}$  ( $14,2 \text{ ng mL}^{-1}$ ). As constantes de ligação entre diversos aminoglicosídeos e TGA-CdTe foram calculadas e indicou que existe uma relação entre o número de grupos amino primários disponíveis e o aumento da luminescência. Essa abordagem foi aplicada com sucesso para a análise de amostras de leite e água de riacho, ambos fortificados com kanamicina, usando procedimento de extração em fase sólida com um polímero impresso molecularmente (MIP). A intensidade da fotoluminescência da nanopartícula cisteína-ZnS em solução contendo brometo de cetiltrimetilamônio (CTAB) foi reduzida (quenched) após adição de tiroxina. A redução total do sinal (quenching) seguiu o modelo de Stern-Volmer com resposta linear até  $4,0 \times 10^{-6} \text{ mol L}^{-1}$  de concentração do analito, o LOD foi  $6,2 \times 10^{-8} \text{ mol L}^{-1}$  ( $48,3 \text{ ng mL}^{-1}$ ). A dispersão aquosa da cisteína-ZnS foi usada como sonda óptica para a determinação de tiroxina em formulações farmacêuticas e em saliva humana fortificada com analito.

## Palavras-chave

Nanocristais semicondutores; quantum dots; modelo de Stern-Volmer; modelo Langmuir para aumento da fotoluminescência; captopril; histamina; aminoglicosídeos; tiroxina.



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